# Geometric and Optical Stereospecificity Exhibited by Cobalt(III) Complexes Derived from *dl*-4-Methyl-1,8-diamino-3,6-dithiaoctane[1,2]

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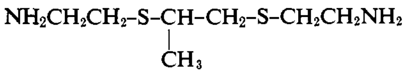
**Abstract:** The preparation and enantiomorphic resolution is given for *s-cis*-dichloro(*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) chloride, $[Co(epe)Cl_2]Cl$. Specific rotations at 546 mμ for the D and L complexes are +1885 and −1885 ± 25°, respectively. A unique stereoselectivity is exhibited by *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane (epe) upon coordination to cobalt(III). Optically pure $(+)_{589}$-epe and $(-)_{589}$-epe were recovered from the optically pure complexes D-*s-cis*-$(+)_{546}$-$[Co(epe)Cl_2]Cl$ and L-*s-cis*-$(-)_{546}$-$[Co(epe)Cl_2]Cl$, respectively. Absolute configurations of both the complex and the coordinated ligand are discussed on the basis of optical rotatory dispersion and circular dichroism data in conjunction with chelate ring strain and conformational considerations. The complex undergoes substitution reactions in aqueous acidic and basic solutions with retention of both geometry and absolute configuration.

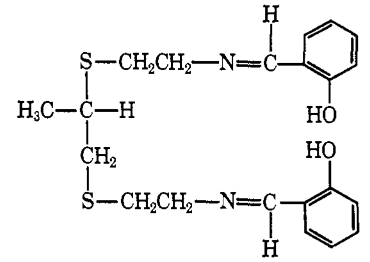
In previous communications the preparation, reactions,[4] optical resolution, geometry, and absolute configurations[5] have been presented and discussed for a number of cobalt(III) complexes derived from the flexible linear quadridentate 1,8-diamino-3,6-dithiaoctane, $NH_2CH_2CH_2\text{-}S\text{-}CH_2CH_2\text{-}S\text{-}CH_2CH_2NH_2$. We wish now to report the preparation and stereochemistries for a series of cobalt(III) complex ions derived from *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane having the skeletal arrangement



$$NH_2CH_2CH_2\text{-}S\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_2\text{-}S\text{-}CH_2CH_2NH_2$$

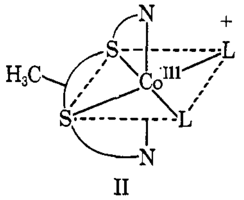
In their investigation of stereospecific multidentate ligands, Dwyer and Garvan[6] showed that only one isomer, L-$(+)_{546}$-$[Co(D\text{-}PDTA)]^-$ occurred when the *levo* isomer of propylenediaminetetracetic acid coordinates to cobalt(III). Absolute confirmation of the proposed stereospecificity was provided by Im and Busch, who showed that no mutarotation occurs when the complex is labilized.[7] The 100% stereospecificity for the ligand D-PDTA is indeed remarkable and suggests that the conformational requirements of the equatorially positioned methyl group as well as the nonbonded atomic interactions of the fused chelate ring system are responsible for the observed specificity.

In a similar investigation, Dwyer and MacDermott[8] extended this specificity to an asymmetric sexadentate ligand containing sulfur donors. The racemic ligand *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane (epe) was resolved into its optical antipodes and condensed with salicyaldehyde to form $(+)_{589}$- and $(-)_{589}$-4-methyl-1,8-bis(salicylideneamimo)-3,6-dithiaoctane (EPE) as illustrated in structure I. These authors found that upon coordination to cobalt(III), the *levo* EPE coordinated stereospecifically, giving 85% of the D-$[Co(-)DEPE]^+$ and 15% L-$[Co(-)DEPE]^+$.



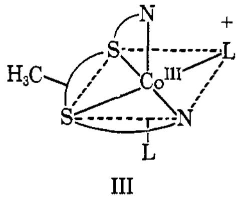
I

Since the compound of immediate interest, *s-cis*-$[Co(epe)Cl_2]Cl$, contains the same source of stereoselectivity, namely an equatorially positioned methyl group on the backbone of the fused chelate ring system, it would not be surprising if it also had a limited isomer distribution, exhibiting a definite preference for certain geometrical and optical configurations. In the study of quadridentate ligand stereochemistries, one must consider the possibility of three geometrically unique arrangements. These include the symmetrical *cis* (II), unsymmetrical *cis* (III), and the *trans* (IV) geometries.



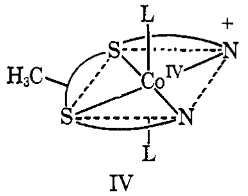
II

*s-cis*



III

*μ-cis*



IV

*trans*

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[1] Abstracted in part from the Ph.D. thesis of Jay H. Worrell, The Ohio State University, 1966; *Diss. Abstr. B*, 27 [7], 2287 (1967).

[2] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Tallahassee, Fla., Dec 1968.

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[4] J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969).

[5] J. H. Worrell and D. H. Busch, *ibid.*, **8**, 1572 (1969).

[6] F. P. Dwyer and F. C. Garvan, *J. Amer. Chem. Soc.*, **81**, 2955 (1959).

[7] Y. A. Im and D. H. Busch, *ibid.*, **83**, 3357 (1961).

[8] F. P. Dwyer and T. E. MacDermott, *ibid.*, **85**, 2916 (1963).

Recognizing the spatial distribution of donor atoms in structures II and III and the fact that the ligand *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane contains an asymmetric carbon atom on the center chelate ring, a number of optical isomers are immediately discernible. These include D-complex–D-ligand, D-complex–L-ligand, L-complex–D-ligand, and L-complex–L-ligand. We now report the results of this investigation.

## Experimental Section

**Optical Rotations.** Optical rotations were determined with a Rudolph high precision photoelectric polarimeter equipped with a mercury arc lamp and a Beckman monochrometer. The instrument zero was determined before and after each measurement using the same 10-cm cell and solvent as employed for the sample. All specific rotations are an average of at least six sets of readings and are accurate to 1% unless otherwise indicated.

Samples of 4–30 mg were accurately weighed to 0.001 mg using a Sartorius MPRS electromicrobalance.

**Optical Rotatory Dispersion Curves.** ORD data were obtained using a Bendix Model 460-C Polarmatic recording spectropolarimeter.

**Circular Dichroism Spectra.** The CD measurements were made using a Roussel-Jouan dichrographe equipped with cells of 2 and 5 cm in length. A base line was recorded for each spectrum using the same cell and solvent as for the sample. The formula for relating the measured data to circular dichroism is given by

$$(\epsilon_l - \epsilon_d) = \frac{d(\text{sensitivity} \times 10^{-4})MW}{cl}$$

where $d$ is the distance between the measured curve and the base line in mm, $MW$ is the molecular weight of the complex, $c$ is the concentration of solute in g/l., and $l$ is the length of the cell in cm. Spectra were recorded at a scan speeed of 4 sec/mμ.

**Infrared Spectra.** High-resolution infrared spectra were obtained using a Beckman IR-9 double beam, prism-grating instrument. Absorptions listed are accurate to ±1 $\text{cm}^{-1}$. Both potassium bromide pellet and Nujol mull techniques were employed. The following spectra were taken in KBr.

**$[Co(epe)Cl_2]Cl$:** 3304 (s), 3242 (s), 3172 (s), 3145 (sh), 3070 (s), 2972 (m), 2958 (m), 2905 (s), 1586 (m), 1580 (m), 1569 (m), 1479 (sh), 1463 (s), 1442 (s), 1432 (s), 1420 (sh), 1411 (s), 1399 (m), 1388 (w), 1372 (m), 1360 (w), 1311 (m), 1294 (m), 1270 (m), 1265 (sh), 1250 (s), 1170 (sh), 1164 (sh), 1154 (s), 1140 (s), 1120 (sh), 1111 (s), 1100 (w), 1075 (w), 1068 (w), 1054 (s), 1010 (s), 993 (sh), 988 (sh), 982 (s), 930 (m), 883 (w), 868 (m), 858 (m), 842 (m), 820 (m).

**$[Co(epe)Br_2]Br$.** Band positions and intensities are almost identical with those found for $[Co(epe)Cl_2]Cl$.

**$[Co(epe)(NO_2)_2]Cl$:** 3480 (b), 3285 (sh), 3228 (w), 3165 (s), 3050 (s), 2995 (w), 2950 (w), 1585 (m), 1464 (s), 1445 (sh), 1430 (s), 1405 (s), 1380 (sh), 1332 (s), 1315 (sg), 1302 (s), 1287 (s), 1270 (w), 1255 (s), 1240 (sh), 1165 (s), 1142 (m), 1120 (m), 1100 (m), 1070 (sh), 1060 (m), 1016 (m), 1000 (sh), 995 (s), 929 (m), 872 (m), 850 (w), 828 (s), 818 (s).

**$[Co(epe)CO_3]Cl$:** 3440 (b), 3235 (s), 3197 (s), 3103 (s), 3000 (w), 2979 (m), 2962 (m), 2934 (s), 2920 (sh), 2905 (s), 2870 (w), 2830 (m), 1760 (w), 1666 (s), 1643 (s), 1635 (sh), 1608 (s), 1455 (sh), 1448 (sh), 1442 (m), 1421 (m), 1418 (sh), 1381 (m), 1330 (w), 1311 (sh), 1309 (m), 1281 (s), 1265 (sh), 1255 (m), 1221 (s), 1195 (w), 1178 (s), 1160 (w), 1140 (s), 1110 (m), 1102 (m), 1070 (w), 1042 (s), 1009 (m), 1000 (m), 990 (m), 929 (m), 880 (w), 852 (m), 847 (m), 827 (s), 748 (s), 735 (sh), 772 (sh), 669 (s).

**$[Co(epe)gly](ClO_4)_2$:** 3440 (b), 3304 (s), 3255 (s), 3160 (b), 3090 (s), 2379 (m) 2020 (w), 1669 (w), 1325 (sh), 1315 (s), 1289 (m), 1272 (m), 1255 (s), 1229 (m), 1120 (s), 1019 (m), 1000 (sh), 960 (w), 943 (sh), 934 (s), 921 (s), 872 (m), 859 (m), 838 (m), 800 (w), 748 (m), 710 (w), 678 (w), 670 (w), 655 (sh), 639 (sh), 628 (s), 583 (m).

**Electronic Absorption Spectra.** Electronic spectra were recorded at 25° by a Cary-14 recording spectrophotometer using aqueous solutions of the complexes in 1.0-cm matched cells.

**Analyses.** Nitrogen analyses were obtained in these laboratories using a Coleman nitrogen analyzer. All other microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

**Preparation of Ligand.** *dl*-4-Methyl-1,8-diamino-3,6-dithiaoctane was prepared from 1,2-propanedithiol (Aldrich Chemical Co.) and N-β-bromoethylphthalimide (K and K Laboratories, Inc.) as described by Dwyer and Lions.[9] *Anal.* Calcd for the dihydrochloride, $C_7H_{20}N_2S_2Cl_2$: C, 31.48; H, 7.49; N, 10.49; S, 23.98. Found: C, 31.35; H, 7.42; N, 10.42; S, 24.12.

### Preparation of Complexes

**(a) *s-cis*-Dichloro(*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.** Cobalt(II) chloride hexahydrate (3.2 g, 2.24 × $10^{-2}$ mol) and *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane dihydrochloride (6.0 g, 2.24 × $10^{-2}$ mol) are dissolved in the smallest possible volume of absolute methanol at room temperature. The mixture is aerated in a 500-ml erlenmeyer flask for 30 min; then lithium hydroxide (0.51 g, 10 × $10^{-2}$ mol) dissolved in hot methanol is added slowly over a 15-min period. The solution is constantly stirred and air-oxidized for several hours at 35-40°. Periodically, more absolute methanol is added to compensate for that lost by evaporation. The deep blue product will crystallize out of solution as it is formed owing to its limited solubility in methanol. At the end of 7 hr, the product is collected by filtration. An additional 0.50 g is obtained by reducing the filtrate to half its original volume giving a total yield of 5.50 g, 68%. The yield is always 60–75% irrespective of the preparative scale employed. A solution of ligand monohydrochloride can also be used in place of the ligand dihydrochloride. The product is recrystallized by dissolving it in concentrated hydrochloric acid (10 ml/g) and adding ethanol (10 ml/g) followed by cooling for several hours. *Anal.* Calcd for $[Co(C_7H_{18}N_2S_2)Cl_2]Cl$: C, 23.39; H, 5.01; N, 7.79; S, 29.51. Found: C, 23.53; H, 5.11; N, 7.64; S, 29.73.

**(b) $(+)_{546}$-*s-cis*-Dichloro[$(+)_{546}$-4-methyl-1,8-diamino-3,6-dithiaoctane]cobalt(III) Chloride.** Once-recrystallized *s-cis*-dichloro(*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) chloride (6.00 g, 1.67 × $10^{-2}$ mol) is dissolved in 100 ml of water at 40° and filtered quickly. To this solution is added potassium antimonyl-*d*-tartrate (2.79 g, 8.35 × $10^{-3}$ mol) dissolved in 15 ml of water at 75°. The mixture is stirred and quickly cooled to −4° in an ice bath for 8 min, then filtered. The fine purple-blue needles are collected by filtration and washed with 20 ml of absolute ethanol in 5-ml portions, the washings being added to the filtrate. The filtrate (135 ml) is set aside for the recovery of the $(-)_{546}$ isomer.

The precipitate of diastereoisomer $(+)_{546}$-$[Co(epe)Cl_2]\cdot[SbO\text{-}d\text{-tartrate}]$ with $[\alpha]_{546}$ +975 ± 20° is washed with acetone and air-dried, yielding 5.02 g. Two recrystallizations from hot 7 *M* acetic acid yields 3.5 g of product with $[\alpha]_{546}$ +1154 ± 20° (2.47 × $10^{-2}$ g/100 ml; $\alpha$ +0.285). This may be used without further purification since three additional recrystallizations will not improve the rotation $[\alpha]_{546}$ beyond +1175 ± 15°. *Anal.* Calcd for $[Co(C_7H_{18}N_2S_2)Cl_2]\cdot[SbO\text{–}C_4H_4O_6]$: C, 21.66; H, 3.61; N, 4.59. Found: C, 21.43; H, 3.82; N, 4.41.

The diastereoisomer (3.0 g, $[\alpha]_{546}$ +1154 ± 20°) is dissolved in 200 ml of 3 *N* hydrochloric acid and stirred for 45 min. The yellow-green antimonyl oxychloride is filtered off and washed with a little 3 *N* HCl to remove any blue complex which may be present. Absolute ethanol (2000 ml), followed by ether (500 ml), is added slowly with stirring to the filtrate in a 4-l. beaker. The clear blue solution is cooled overnight in the refrigerator. The first fraction (0.43 g) is collected by filtration and has $[\alpha]_{546}$ +1856 ± 30° (18.16 mg/100 ml; $\alpha$ +0.337). By careful addition of ether to the filtrate followed by cooling overnight, three additional fractions totaling 0.86 g are collected with $[\alpha]_{546}$ +1875 ± 30°; total yield 1.29 g, 76%. Two additional recrystallizations from concentrated hydrochloric acid and ethanol give deep blue-green plates which are washed with acetone and air-dried. A 0.01 *N* hydrochloric acid solution of the complex (15.99 mg/100 ml) gives $\alpha$ +0.300, whence $[\alpha]_{546}$ +1875 ± 25°. *Anal.* Calcd for $[Co(C_7H_{18}N_2S_2)Cl_2]Cl$: C, 23.39; H, 5.01; N, 7.79; Cl, 29.51. Found: C, 23.10; H, 4.99; N, 7.73; Cl, 29.60.

**(c) $(-)_{546}$-*s-cis*-Dichloro[$(-)_{546}$-4-methyl-1,8-diamino-3,6-dithiaoctane]cobalt(III) Chloride.** The filtrate from above containing the $(-)_{546}$ isomer is poured into 500 ml of absolute ethanol at 0° causing potassium chloride to precipitate. The solution is filtered and ether (400 ml) is added to the filtrate, which is cooled in the refrigerator overnight. The deep blue-green rosette plates (0.15 g) with $[\alpha]_{546}$ −1845 ± 16° are collected by filtration. Acetone (900 ml) is added to the filtrate and the solution is cooled overnight yielding 2.50 g of blue solid with $[\alpha]_{546}$ −1642 ± 12°. These two fractions are combined and exhaustively recrystallized (six times) from concentrated hydrochloric acid and ethanol until the maximum rotation of $[\alpha]_{546}$ −1885 ± 25° (15.65 mg/100 ml;

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[9] F. P. Dwyer and F. Lions, *J. Amer. Chem. Soc.*, 69, 2917 (1947).

Table I. Analytical Data for the New Compounds

| Complexes | Color | % C | | % H | | % N | | % X | |
|---|---|---|---|---|---|---|---|---|---|
| | | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| $[Co(epe)(NO_2)_2]Cl$ | Orange | 22.08 | 22.05 | 4.73 | 4.89 | 14.72 | 14.61 | 9.20 | 9.22 |
| $[Co(epe)Br_2]Br$ | Green | 17.05 | 17.16 | 3.65 | 3.45 | 5.68 | 5.84 | 48.66 | 48.40 |
| $[Co(epe)CO_3]Cl$ | Red | 27.56 | 27.73 | 5.16 | 5.13 | 8.04 | 7.81 | 10.16 | 9.98 |
| $[Co(epe)NH_2CH_2COO](ClO_4)_2 \cdot H_2O$ | Red | 19.86 | 19.63 | 4.41 | 4.21 | 7.72 | 7.60 | | |

$\alpha$ −0.295) is attained. The fraction giving this maximum rotation was recrystallized two additional times without an increase in rotation. The total yield of optically pure $(-)_{546}$ isomer is proportional to one's patience and recrystallization scheme, varying from 1.0 to 1.95 g (30–65%) of the theoretical yield. The product is washed with acetone and air-dried. *Anal.* Calcd for $[Co(C_7H_{18}N_2S_2)Cl_2]Cl$: C, 23.39; H, 5.01; N, 7.79; Cl, 29.51. Found: C, 23.65; H, 5.14; N, 7.83; Cl, 29.59.

**(d) Recovery of Optically Pure Ligand from $(+)_{546}$-*s*-*cis*-$[Co(epe)Cl_2]Cl$ and $(-)_{546}$-*s*-*cis*-$[Co(epe)Cl_2]Cl$.** The method used to determine whether or not *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane coordinated stereospecifically is outlined below. A sample of optically pure *s*-*cis*-$[Co(epe)Cl_2]Cl$ is weighed into a 25-ml volumetric flask. To this are added 0.15 g of KCN and 4 drops of 1.0 *N* NaOH. The sample is diluted to the mark with water and allowed to stand at room temperature for 3 hr before measuring the rotation of the amber colored solution in a 2-dm polarimeter tube. The rotation is measured at 546 and 589 m$\mu$ using a mercury arc lamp and a Beckman monochrometer with a slit width of 0.60 mm at both wavelengths.

The first sample contained 46.64 mg of $(+)_{546}$-*s*-*cis*-$[Co(epe)Cl_2]Cl$ with $[\alpha]_{546}$ +1885 ± 10°. This gives a free ligand concentration of 0.10084 g/100 ml. The rotation in a 2-dm tube gives $\alpha$ +0.069 ± 0.003° at 546 m$\mu$ and $\alpha$ +0.096 ± 0.004° at 589 m$\mu$, whence $[\alpha]_{546}$ +34.2 ± 2° and $[\alpha]_{589}$ +47.6 ± 2°. Optically pure $(+)_{589}$-epe has $[\alpha]_{589}$ +50 ± 2°.

The second sample contained 49.32 mg of $(-)_{546}$-*s*-*cis*-$[Co(epe)Cl_2]Cl$ with $[\alpha]_{546}$ −1885 ± 10°. This gives a free ligand concentration of 0.1066 g/100 ml. The rotation in a 2-dm tube gives $\alpha$ −0.065 ± 0.004° at 546 m$\mu$ and $\alpha$ −0.096 ± 0.004° at 589 m$\mu$, whence $[\alpha]_{546}$ −30.6 ± 2° and $[\alpha]_{589}$ −45.2 ± 2°. Optically pure $(-)_{589}$-epe has $[\alpha]_{589}$ −50° ± 2°.

In each case a blank using optically pure D- and L-*s*-*cis*-$[Co(eee)Cl_2]Cl$ having $[\alpha]_{546}$ + and −2300 ± 20°, respectively, was employed. At the completion of reaction the blank has zero observable optical activity.[6]

## Results and Discussion

**Synthetic Studies.** A very general synthetic route to the cobalt(III) complexes of *dl*-4-methyl-1,8-diamino-3,6-dithiaoctane involves the air oxidation of an appropriate cobalt(II) salt and ligand monohydrohalide in methanol and/or methanol–water mixtures. Octahedral complexes of the general type $[Co(epe)L_2]^{n+}$, where the monodentate L is $Cl^-$, $Br^-$, or $NO_2^-$ or the bidentate $L_2$ is $CO_3^{2-}$, $C_2O_4^{2-}$, or $NH_2CH_2COO^-$, can be prepared by metathetical interaction of *s*-*cis*-$[Co(epe)Cl_2]Cl$ with the appropriate salt NaL or $Na_2L$.

Unlike *s*-*cis*-$[Co(eee)Cl_2]Cl$, the epe analog can be prepared directly by air oxidation of cobalt(II) chloride in the presence of ligand monohydrochloride in water or methanol. This distinct contrast in ease of preparation suggests that the methyl group present on the backbone of the linear quadridentate ligand epe exerts a pronounced effect, facilitating the exact sequence of events which finally results in the formation of *s*-*cis*-$[Co(epe)Cl_2]Cl$. The complex produced by this method gives infrared and visible absorption spectra identical with those found for *s*-*cis*-$[Co(epe)Cl_2]Cl$ prepared *via* several other reactions.

In the course of this investigation several other diacidocobalt(III) complexes were prepared from the ligand epe. The methods of preparation are exactly analogous to those described in a previous publication.[4] Analytical data exhibited by these compounds are presented in Table I.

Optical isomers of racemic *s*-*cis*-$[Co(epe)Cl_2]Cl$, prepared from a racemic ligand, were separated using potassium antimonyl-*d*-tartrate as the resolving agent. Optically pure $(+)_{546}$-*s*-*cis*-$[Co(epe)Cl_2]Cl$ with $[\alpha]_{546}$ + 1885 ± 25° was obtained from the diastereoisomer, while the $(-)_{546}$ isomer was obtained from the original mother liquor.

The optical resolution and close similarity to $[Co(eee)Cl_2]Cl$[4,5] argue strongly for the *cis* configuration for the $[Co(epe)Cl_2]Cl$ complex. It is now appropriate to present evidence in support of the symmetrical *cis* arrangement as opposed to the unsymmetrical *cis* geometry.

The four basic compounds, *s*-*cis*-$[Co(epe)(NO_2)_2]Cl$, *s*-*cis*-$[Co(epe)Cl_2]Cl$, *s*-*cis*-$[Co(epe)Br_2]Br$, and *s*-*cis*-$[Co(epe)CO_3]Cl$, were synthesized and each was converted completely into the other three without the production of additional geometric isomers, as evidenced by careful fractional crystallization of each complex followed by quantitative examination of visible absorption spectra for each fraction. In addition, infrared spectra of each fraction also failed to show differences in peak intensities and/or peak positions from fraction to fraction. This strongly suggests that all four compounds have a common configuration. The chemical interconversions are summarized in Figure 1.

**Electronic Absorption Spectra.** It should be possible to assign the *s*-*cis* or *u*-*cis* geometric configuration to the $[Co(epe)L_2]^{n+}$ complexes on the basis of the parent octahedron. For the symmetrical *cis* arrangement, characteristic tetragonal splitting of the $^1T_{1g}$ state is expected. This will occur because the average in-plane ($xy$) ligand field will not be the same as the axial field along the $z$ axis. In contrast to this, the $^1T_{1g}$ band would *not* be expected to split in the unsymmetrical *cis* structure because then the donor atoms of the quadridentate ligand and two acido groups are positioned so as to result in three unique axial fields of comparable magnitude.

In support of this premise, no splitting is observed for the $^1T_{1g}$ band in *u*-*cis*-$[Co(trien)L_2]^+$- or *u*-*cis*-$[Co(EDDA)en]^+$-type complexes. Splitting of the $^1T_{1g}$ band is observed, however, for the corresponding *s*-*cis* isomers.[10–12]

Typical electronic spectra for various diacido (*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) complexes are summarized in Table II. The *s*-*cis*-$[Co(epe)Cl_2]^+$ and *s*-*cis*-$[Co(epe)Br_2]^+$ ions exhibit spectra in which a definite splitting of the low-energy $^1T_{1g}$ band

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(10) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965)

(11) J. I. Legg and D. W. Cooke, *ibid.*, **4**, 1576 (1965).

(12) M. Goto, M. Saburi, and S. Yoshikawa, *ibid.*, **8**, 358 (1969).

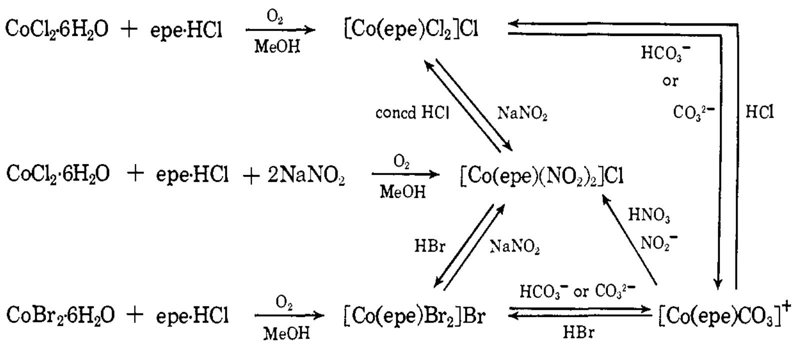

Figure 1. Chemical interconversions for *s-cis*-$[Co(epe)L_2]^{n+}$ complexes.

is observed. The wavelength of maximum absorption for the principle band of *s-cis*-$[Co(epe)Cl_2]Cl$ is 610 mμ (16,393 $cm^{-1}$) with a molar extinction coefficient of 313 ± 4. A shoulder occurs on the high-energy side of this principle band at approximately 550 mμ (18,181 $cm^{-1}$) and appears to be less intense than the major band. It is assumed that the axially positioned $NH_2$ groups provide a considerably stronger ligand field than do the in-plane chloride and thioether atoms. The intense low-energy component is therefore assigned to the $^1A_1 \rightarrow {}^1A_2$ $(^1T_1)$ transition and the higher energy, although less intense, shoulder component as the $^1A_1 \rightarrow E_a(^1T_1)$ transition. Comparable assignments can be made for the other complexes. The results are entirely consistent with the structures assigned.

**Table II.** Wavelength of Maximum Absorption and Molar Extinction Coefficients for Various Diacido(epe)cobalt(III) Complexes

| *s-cis* compound | $\lambda_{max}$, mμ[a] | ε (molar) |
|---|---|---|
| $[Co(epe)(NO_2)_2]Cl$ | 463 | 587 ± 4 |
| | 347 | 11,800 |
| | 273 | 17,000 |
| | 240 | 12,700 |
| $[Co(epe)Cl_2]Cl$ | 610 | 313 ± 4 |
| | 550 (sh) | |
| $(+)_{546}$-$[Co(epe)Cl_2]Cl$ | 610 | 309 ± 4 |
| and | 545 (sh) | |
| $(-)_{546}$-$[Co(epe)Cl_2]Cl$ | 280 | 13,700 |
| | 226 | 14,000 |
| $[Co(epe)Br_2]Br$ | 628 | 375 ± 5 |
| | 575 (sh) | |
| $[Co(epe)CO_3]Cl$ | 520 | 228 ± 8 |
| | 390 (sh) | |
| $[Co(epe)CO_3]ClO_4 \cdot H_2O$ | 520 | 223 ± 8 |
| | 390 (sh) | |
| | 303 | 13,200 |
| | 242 | 11,200 |

[a] sh = shoulder.

The visible spectra for the *s-cis*-$[Co(epe)L_2]^{n+}$ and *s-cis*-$[Co(eee)L_2]^{n+}$ ions are identical except for the intensities of the charge-transfer bands.[4] The epe compounds always exhibit higher extinction coefficients for the bands occurring in the ultraviolet region. That a particular compound exhibits the same visible electronic spectrum regardless of whether it has eee or epe as the quadridentate ligand, supports the premise that both series of compounds have the same geometry, *s-cis*.

**Relative and Absolute Configuration for Diacido(*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) Complexes.** The relative and absolute configurations of the diacido(*dl*-4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) complexes have been assessed using chemical interconversion methods in conjunction with optical rotatory dispersion and circular dichroism spectra.

**Transformation Reactions for epe Complexes.** Optically pure $(+)_{546}$-*s-cis*-$[Co(epe)Cl_2]Cl$ with $[\alpha]_{546}$ +1885 ± 15° was allowed to aquate for 96 hr in dilute acid solution, at which time the predominant species in solution is the $(+)_{546}$-*s-cis*-$[Co(epe)ClH_2O]^{2+}$ ion. The epe aquochloro ion has a specific rotation of +4550 ± 50° at 546 mμ, as determined from its optical rotatory dispersion curve. The $(+)_{546}$-*s-cis*-$[Co(epe)ClH_2O]^{2+}$ ion was converted quantitatively, as evidenced spectrophotometrically, into the optically pure $(+)_{546}$-*s-cis*-$[Co(epe)CO_3]^+$ ion by treating the solution with lithium carbonate. The carbonato complex has a specific rotation ($[\alpha]_{546}$) of +225 ± 50°. Acidification of $(+)_{546}$-*s-cis*-$[Co(epe)CO_3]^+$ ion gave the corresponding $(+)_{546}$-*s-cis*-$[Co(epe)(H_2O)_2]^{3+}$ ion also with retention of configuration. The diaquo complex so produced was reconverted to the $(+)_{546}$-*s-cis*-$[Co(epe)CO_3]^+$ species, by adding lithium carbonate to the solution, without any loss of optical activity as evidenced by both ORD and CD spectra. The specific rotation, $[\alpha]_{546}$, for the $(+)_{546}$-*s-cis*-$[Co(epe)(H_2O)_2]^{+3}$ ion is +4775 ± 50°. By treating this complex with excess sodium nitrite, it was transformed into the optically active $(-)_{546}$-*s-cis*-$[Co(epe)(NO_2)_2]^+$ ion which exhibited a specific rotation ($[\alpha]_{546}$) of −475 ± 30°. The complete transformation series for the epe complexes is given in Figure 2. The relative configurations of all the products are thus determined independently of ORD and CD measurements. The specific rotation for each ion in the sequence was calculated on the basis of the initial weight of D-*s-cis*-$[Co(epe)Cl_2]Cl$ employed, in mg/100 ml. The error in rotation introduced by this assumption is well within the ±10% limits of average deviation inherent in the measurement of ORD curves.

This particular reaction sequence was specially selected because available mechanistic studies support the contention that each substitution step shown in Figure 2 should occur with complete retention of configuration. This aspect has been discussed previously.[10]

Several other reactions which do not mechanistically require retention of configuration were investigated. The diacido(epe)cobalt(III) complexes were found to undergo the same type reactions as previously reported for the eee series.[4,5]

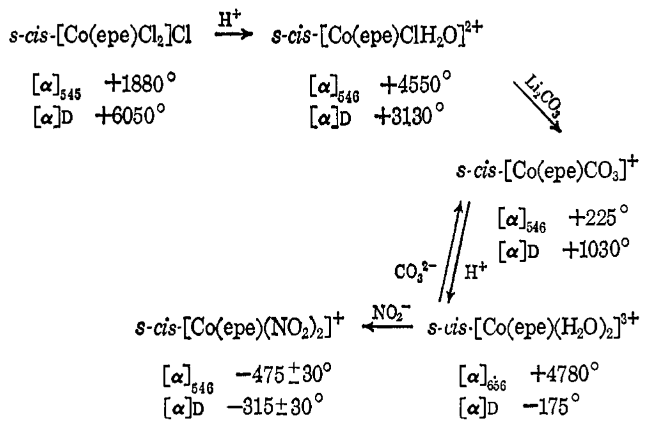

Figure 2. Transformation reactions for the epe series.

The optically active epe carbonato and dinitro derivatives were prepared by treating an aqueous solution of the optically pure $(+)_{546}$-*s-cis*-[Co(epe)-$Cl_2$]Cl with lithium carbonate and sodium nitrite, respectively. The observed rotations were within 10% of the values obtained from the transformation reactions. When treated with sodium hydroxide, the optically pure $(+)_{546}$-*s-cis*-[Co(epe)$Cl_2$]Cl complex gave optically active $(+)_{546}$-*s-cis*[Co(epe)$(OH)_2$]$^+$, which was then converted to both the corresponding $(+)_{546}$-*s-cis*-[Co(epe)$CO_3$]$^+$ and $(+)_{546}$-*s-cis*-[Co(epe)$(H_2O)_2$]$^{3+}$ ions with complete retention of configuration. The rotational values for both ions were within 10% of the values obtained from the transformation sequence. Like the eee complexes, negligible loss of activity was observed for the $(+)_{546}$-*s-cis*-[Co(epe)$(OH)_2$]$^+$ ion at pH 8 for several hours; however, prolonged contact with strong alkali results in the slow decomposition of ligand and/or complex.

**Absolute Configuration Based on CD and ORD Measurements.** Mason[13,14] has developed several criteria for assigning the electronic circular dichroism transitions and the absolute configuration for the *cis*-[Co-$(en)_2L_2$]$^{n+}$ ions of $C_2$ symmetry. The absolute stereochemistries for *s-cis*- and *u-cis* isomers of the [Co(trien)-$L_2$]$^{n+}$ ions have also been established using CD measurements.[10]

Circular dichroism spectra are illustrated in Figure 3 for the $(+)_{546}$-*s-cis*-[Co(epe)$Cl_2$]$^+$, $(+)_{546}$-*s-cis*-[Co(epe)-$ClH_2O$]$^{2+}$, and $(+)_{546}$-*s-cis*-[Co(epe)$(H_2O)_2$]$^{3+}$ ions. Using the formalism suggested by Mason and the energy level scheme presented in Figure 4, the low-energy band exhibiting a negative Cotton effect is assigned in each case to the $^1A_1 \rightarrow B_1(A_2)$ transition and the higher energy component showing a positive Cotton effect is considered as the composite transition, $^1A_1 \rightarrow A_2(E_a) + B_2(E_a)$.

The lowest energy CD component for the $(+)_{546}$-*s-cis*-[Co(epe)$(H_2O)_2$]$^{3+}$ ion is of greater intensity than the second band exhibiting a positive Cotton effect. This suggests that this low energy band may represent the composite transition (illustrated in Figure 4) $^1A_1 \rightarrow {}^1B_1(A_2) + {}^1B_2(E_a)$. Accordingly, the positive Cotton effect observed for this ion may then be due to the $^1A_1 \rightarrow {}^1A_2(E_a)$ transition.

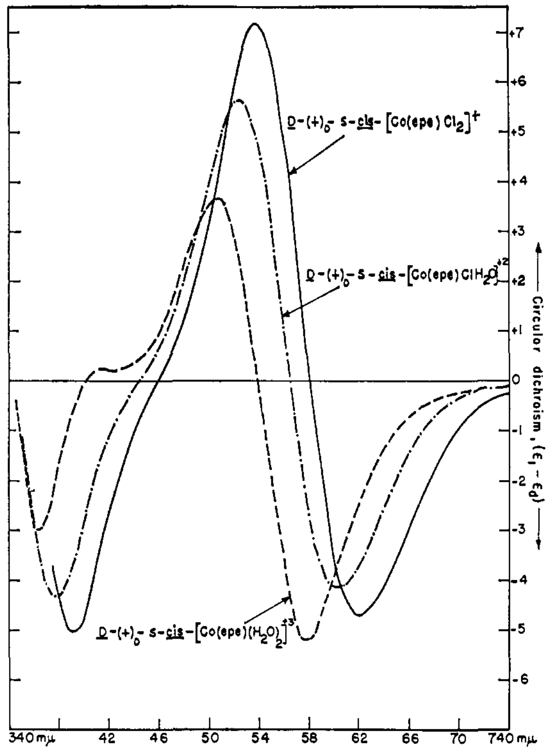

Figure 3. CD spectra for the epe dichloro, aquochloro, and diaquo cobalt(III) ions.

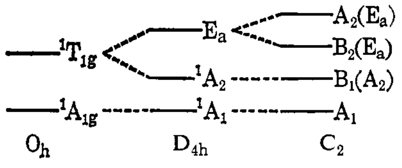

Figure 4. Energy levels for electronic circular dichroism transitions.

Only two electronic CD components are evident in the lowest energy d–d visible absorption band and both components simultaneously shift to higher energy in accord with the normal spectrochemical series, $(+)_{546}$-*s-cis*-[Co(epe)$Cl_2$]$^+$, $(+)_{546}$-*s-cis*-[Co(epe)$ClH_2O$]$^{2+}$, $(+)_{546}$-*s-cis*-[Co(epe)$(H_2O)_2$]$^{3+}$. In all three cases, the second CD component is positive and lies closest to the reference $^1A_1 \rightarrow E_a$ transition positioned at 493 mμ for D-[Co$(en)_3$]$^{3+}$. Similarly the sign pattern observed for the Cotton effect for these three $(+)_{546}$ ions is −,+ and is in agreement with the sign patterns exhibited by the corresponding cobalt(III) complexes of ethylenediamine and triethylenetetramine which are of the D absolute configuration. Thus $(+)_{546}$-*s-cis*-[Co(epe)$Cl_2$]$^+$, $(+)_{546}$-*s-cis*-[Co(epe)$ClH_2O$]$^{2+}$, and $(+)_{546}$-*s-cis*-[Co(epe)-$(H_2O)_2$]$^{3+}$ ions appear also to possess the D absolute configuration.

The circular dichroism spectra characteristic of the $(+)_{546}$-*s-cis*-[Co(epe)$(OH)_2$]$^+$, $(+)_{546}$-*s-cis*-[Co(epe)-$CO_3$]$^+$, and $(-)_{546}$-*s-cis*-[Co(epe)$(NO_2)_2$]$^+$ ions are presented in Figure 5. The $(+)_{546}$-*s-cis*-[Co(epe)-$(OH)_2$]$^+$ ion exhibits a spectrum consisting of three components with a sign sequence −,+,−. It should be noted that the lowest energy transition showing a negative Cotton effect, for both this ion and the $(+)_{546}$-*s-cis*-[Co(epe)$(H_2O)_2$]$^{3+}$ ion, is more intense than the second band. This suggests that the two lowest energy

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[13] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

[14] S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

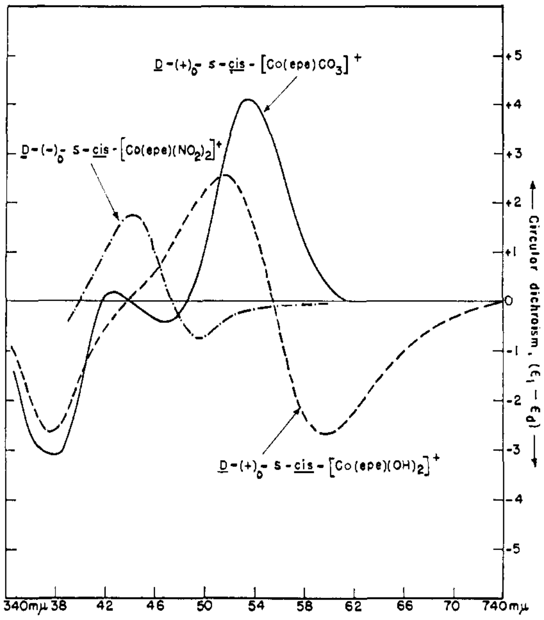

Figure 5. CD spectra for the epe dihydroxo, carbonato, and dinitro cobalt(III) ions.

B states are mixed, thus resulting in the composite transition $^1A_1 \rightarrow B_1(A_2) + B_2(E_a)$. The second component showing a positive Cotton effect is assigned the $^1A_1 \rightarrow A_2(E_a)$ transition and is used to deduce the absolute configuration. Since this latter band is positive, the (+)$_{546}$-*s-cis*-[Co(epe)(OH)$_2$]$^+$ ion is assigned the D absolute configuration. Addition of acid to a solution containing this ion converts it to the D-*s-cis*-[Co(epe)(H$_2$O)$_2$]$^{3+}$ ion.

The (+)$_{546}$-*s-cis*-[Co(epe)CO$_3$]$^+$ ion exhibits a CD curve characteristic of complexes containing a bidentate conjugated ligand. One and three circular dichroism bands are associated, respectively, with the longer and shorter wavelength d–d absorption spectral bands. That the (+)$_{546}$-*s-cis*-[Co(epe)CO$_3$]$^+$ ion exhibits an intense low-energy circular dichroism band showing a positive Cotton effect, as do the D-[Co(en)$_2$CO$_3$]$^+$, D-[CO(trien)CO$_3$]$^+$, D-[Co(en)$_2$ox]$^+$, D-[Co(trien)ox]$^+$, and D-[Co(pn)$_2$CO$_3$]$^+$ ions,[10,13] strongly suggests that the (+)$_{546}$-*s-cis*-[Co(epe)CO$_3$]$^+$ ion also possesses the D absolute configuration. In accord wih Mason's formalism,[13] the composite transition assigned to this positive Cotton effect is $^1A_1 \rightarrow B_1(A_2) + B_2(E_a) + A_2(E_a)$. In addition, this ion could be converted quantitatively and reversibly to the D-(+)$_{546}$-*s-cis*-[Co(epe)(H$_2$O)$_2$]$^{3+}$ ion. Treatment of D-(+)$_{546}$-*s-cis*-[Co(epe)Cl$_2$]$^+$ with sodium hydroxide to give the D-(+)$_{546}$-*s-cis*-[Co(epe)(OH)$_2$]$^+$ ion followed by addition of lithium carbonate, resulted in the quantitative production of (+)$_{546}$-*s-cis*-[Co(epe)CO$_3$]$^+$. The CD spectrum of the solution obtained by treating D-(+)$_{546}$-*s-cis*-[Co(epe)Cl$_2$]Cl directly with lithium carbonate also is the same as obtained for the (+)$_{546}$-*s-cis*-[Co(epe)-CO$_3$]$^+$ ion prepared by these other methods.

The (−)$_{546}$-*s-cis*-[Co(epe)(NO$_2$)$_2$]$^+$ ion exhibits a CD spectrum quite different from the corresponding bis-(ethylenediamine)– and trien–cobalt(III) complexes. In these latter two complexes, substitution of nitrite ion into the coordination sphere, causes the in-plane electrostatic field to become considerably greater than the axial field. As a result, the electronic levels derived from the $T_{1g}$ manifold are inverted, the lowest energy transition being $^1A_1 \rightarrow B_1(A_2)$. In contrast to this, the electric field caused by the in-plane thioether groups of *s-cis*-[Co(epe)(NO$_2$)$_2$]$^+$, is so weak that even with the substitution of two nitrite groups into the in-plane positions, the axial field remains greater than the in-plane field. Thus, the energy levels are *not* inverted for this complex. The negative low-energy CD component is therefore assigned the $^1A_1 \rightarrow B_1(A_2)$ transition and the positive higher energy component is assigned the composite transition $^1A_1 \rightarrow A_2(E_a) + B_2(E_a)$. This latter transition is diagnostic of absolute configuration as related to the $^1A_1 \rightarrow E_a$ component for the trigonal ion D-[Co(en)$_3$]$^{3+}$. It is positive for the (−)$_{546}$ isomer of *s-cis*-[Co(epe)(NO$_2$)$_2$]$^+$ and therefore this ion must also be of the D absolute configuration. Table III tabulates the wavelength of maximum ellipticity, ellipticity, and the corresponding electronic assignment for the particular CD components for the diacido cobalt(III) complexes of epe.

**Table III.** Circular Dichroism Data for [Co(epe)L$_2$]$^{n+}$ Ions

| D-*s-cis* ions | $\lambda_{max}$, Å | $(\epsilon_l - \epsilon_d)_{max}$ | Transition |
|---|---|---|---|
| (+)$_{546}$-[Co(epe)Cl$_2$]$^+$ | 6200 | −4.70 | $B_1$ |
| | 5380 | +7.15 | $A_2 + B_2$ |
| | 3930 | −5.05 | $B_2$ |
| (+)$_{546}$-[Co(epe)ClH$_2$O]$^{2+}$ | 6020 | −4.15 | $B_1$ |
| | 5250 | +5.65 | $A_2 + B_2$ |
| | 3780 | −4.35 | $B_2$ |
| (+)$_{546}$-[Co(epe)(H$_2$O)$_2$]$^{3+}$ | 5980 | −5.20 | $B_1 + B_2$ |
| | 5080 | +3.67 | $A_2$ |
| | 4150 | +0.25 | |
| | 3630 | −3.00 | |
| (+)$_{546}$-[Co(epe)(OH)$_2$]$^+$ | 5960 | −2.68 | $B_1 + B_2$ |
| | 5160 | +2.58 | $A_2$ |
| | 3760 | −2.65 | |
| (+)$_{546}$-[Co(epe)CO$_3$]$^+$ | 5350 | +4.10 | $B_1 + A_2 + B_2$ |
| | 4700 | −0.40 | |
| | 4250 | +0.20 | |
| | 3800 | −3.10 | |
| (−)$_{546}$-[Co(epe)(NO$_2$)$_2$]$^+$ | 4950 | −0.75 | $B_1$ |
| | 4420 | +1.77 | $A_2 + B_2$ |

From the CD curves and the retention of activity involved in the transformation of the optically pure dichloro complex to the dinitro compound, it is evident that negligible geometrical isomerization occurs. Since the transformation sequence takes place with retention of configuration, the absolute configuration for the D-*s-cis*-[Co(epe)Cl$_2$]$^+$, D-*s-cis*-[Co(epe)ClH$_2$O]$^{2+}$, D-*s-cis*-[Co(epe)(NO$_2$)$_2$]$^+$, and D-*s-cis*-[Co(epe)CO$_3$]$^+$ ions have been established by both CD and chemical interconversion methods.

The optical rotatory dispersion curves for the (+)$_{546}$-*s-cis*-[Co(epe)Cl$_2$]$^+$, (+)$_{546}$-*s-cis*-[Co(epe)Cl-H$_2$O]$^{2+}$, (+)$_{546}$-*s-cis*-[Co(epe)(H$_2$O)$_2$]$^{3+}$, (+)$_{546}$-*s-cis*-[Co(epe)(OH)$_2$]$^+$, (+)$_{546}$-*s-cis*-[Co(epe)CO$_3$]$^+$, and (−)$_{546}$-*s-cis*-[Co(epe)(NO$_2$)$_2$]$^+$ ions are presented in Figures 6 and 7.

Examination of optical rotatory dispersion spectra in conjunction with the CD spectra and transformation reaction sequences already discussed, further reinforces our assignment of absolute configurations for these ions.

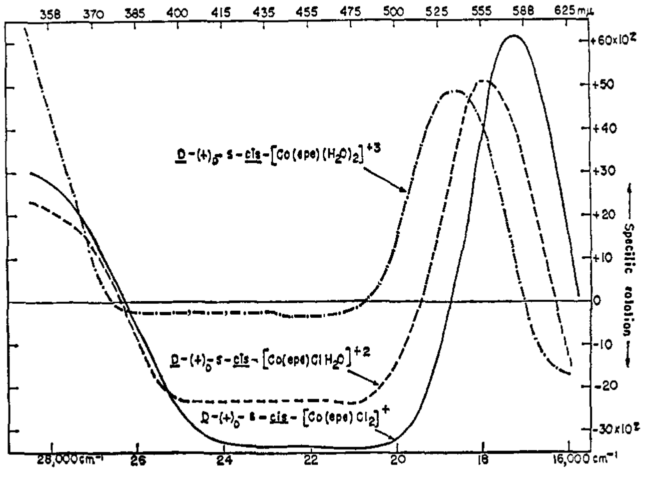

Figure 6. ORD curves for the epe dichloro, aquochloro, and diaquo cobalt(III) ions.

Table IV presents the wavelength of maximum positive, zero, and maximum negative specific rotation for these ions.

Table IV. Wavelength of Maximum Positive, Zero, and Maximum Negative Specific Rotation of the *s-cis*-$[Co(epe)L_2]^{n+}$ Ions

| *s-cis* compound | λ, mμ | cm⁻¹ | [α] |
|---|---|---|---|
| $[Co(epe)Cl_2]^+$ | 581 | 17,200 | +6150 |
| | 533 | 18,750 | 0 |
| | 488 | 20,500 | −3350 |
| $[Co(epe)ClH_2O]^{2+}$ | 613 | 16,300 | 0 |
| | 559 | 17,900 | +5100 |
| | 515 | 19,400 | 0 |
| | 478 | 20,900 | −2300 |
| $[Co(epe)(H_2O)_2]^{3+}$ | 587 | 17,050 | 0 |
| | 538 | 18,600 | +4900 |
| | 482 | 20,750 | 0 |
| | 465 | 21,500 | −250 |
| $[Co(epe)(OH)_2]^+$ | 608 | 16,450 | 0 |
| | 549 | 18,200 | +1900 |
| | 500 | 20,000 | 0 |
| | 426 | 23,500 | −900 |
| $[Co(epe)CO_3]^+$ | 571 | 17,500 | +1175 |
| | 543 | 18,400 | 0 |
| | 500 | 20,000 | −3200 |
| $[Co(epe)(NO_2)_2]^+$ | 533 | 18,750 | −600 |
| | 500 | 20,000 | 0 |
| | 474 | 21,100 | +1225 |
| | 451 | 22,150 | 0 |

**Attempted Preparation of *u-cis* and *trans* Isomers.** The experimental conditions which produce *u-cis* and *trans* isomers of $[Co(trien)X_2]^{n+}$ did not produce similar isomers of $[Co(epe)X_2]^{n+}$. Both $NaHCO_3$ and $Li_2CO_3$ in basic solution react with *s-cis*-$[Co(epe)Cl_2]^{n+}$ to produce the same $[Co(epe)CO_3]^+$ complex regardless of temperature, solvent, or how alkaline the reaction solution is. This is in striking contrast to the trien–Co(III) system. Attempts to detect isomerization in the presence of base and $HCO_3^-$ or $CO_3^{2-}$ using optically active *s-cis*-$[Co(epe)Cl_2]^+$ in conjunction with circular dichroism and optical rotatory dispersion techniques also failed to suggest the presence of *u-cis* or *trans* isomers.

Attempts to prepare *trans*-$[Co(epe)Br_2]Br$ and *trans*-$[Co(epe)Cl_2]Cl$ were not successful. The methods used included attempted isomerization by heating in the solid state and with water, ethanol, and methanol mixtures.

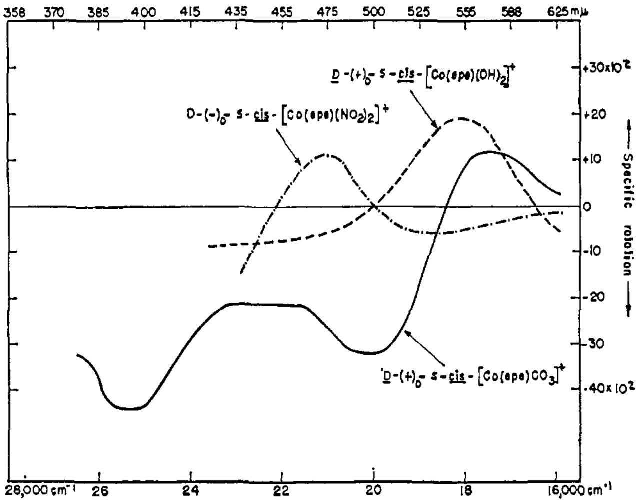

Figure 7. ORD curves for the epe dihydroxo, dinitro, and carbonato cobalt(III) ions.

In the present work, even after determined efforts, no evidence could be found suggesting the existence of either the *trans* or the unsymmetrical *cis* geometry.

**Stereospecificity of Dichloro(4-methyl-1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.** The preceding work establishes that the absolute configuration about the cobalt(III) atom is D for the $(+)_{546}$-*s-cis*-$[Co(epe)Cl_2]^+$ ion and L for the $(-)_{546}$-*s-cis*$[Co(epe)Cl_2]^+$ ion. As described in the Experimental Section, only two optically pure isomers were found for the *s-cis*-$[Co(epe)Cl_2]Cl$ complex when prepared from racemic ligand. This suggests an extreme geometric and optical stereospecificity.

Treatment of optically pure D- and L-*s-cis*-$[Co(epe)Cl_2]Cl$ with excess cyanide ion in alkali causes the ligand 4-methyl-1,8-diamino-3,6-dithiaoctane to be released from the trivalent cobalt atom. The observed rotation is then due only to the free ligand in solution and thus is indicative of the extent of stereospecificity exerted by the ligand epe. A similar control experiment using optically pure D-*s-cis*-$[Co(eee)Cl_2]Cl$ demonstrated that there was zero rotation after treatment of the complex with cyanide ion and alkali.[15] The ligand isolated from the D-*s-cis*-$[Co(epe)Cl_2]^+$ ion was dextrorotatory having a specific rotation of +47.6 ± 2° at 589 mμ.

The research of Dwyer and MacDermott[8] reports the optically active forms of the free diamine, 4-methyl-1,8-diamino-3,6-dithiaoctane, to have specific rotations of + and −50 ± 2° at 589 mμ. This information in conjunction with our work establishes that the D-*s-cis*-$[Co(epe)Cl_2]^+$ ion contains exclusively optically pure dextrorotatory ligand, whereas the L-*s-cis*-$[Co(epe)Cl_2]^+$ ion contains exclusively the optically pure *levorotatory* ligand. It would be instructive at this time to consider the configuration and ring conformations of the optically active ligand relative to the absolute configuration of the cobalt(III) ion.[16,17] Since extreme

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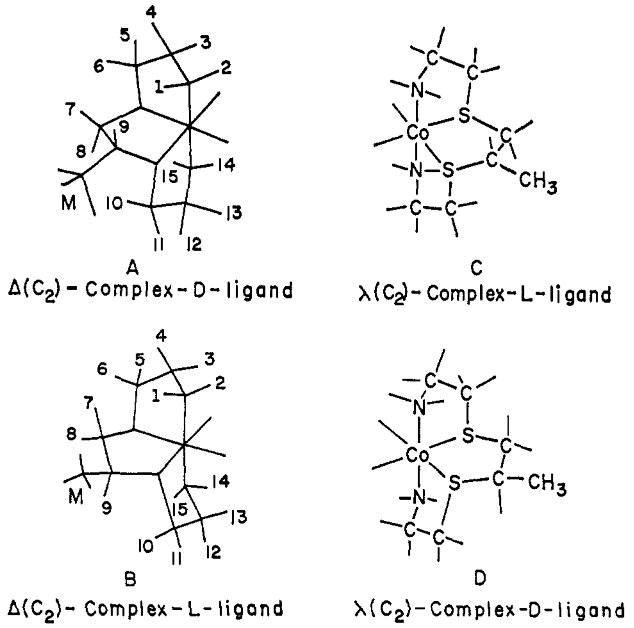
(15) The ligand eee does not have a methyl group present on the central chelate ring.

(16) The complexes discussed here have $C_2$ or pseudo-$C_2$ symmetry and the absolute configurations are related to the configurations of the $\Delta(C_2)$-$(+)_{589}$-$[Co(en)_3]^{3+}$ ion as viewed down a $C_2$ axis in the manner



A
Δ($C_2$) - Complex - D - ligand

C
λ($C_2$) - Complex - L - ligand

B
Δ($C_2$) - Complex - L - ligand

D
λ($C_2$) - Complex - D - ligand

Figure 8. Absolute configurations and ring conformations in which $CH_3$ of epe assumes an equatorial position.

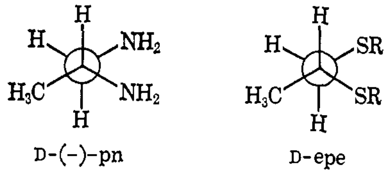
specificity exists, it should be possible to derive the absolute configuration of the coordinated epe by considering the steric requirements of the methyl group in addition to the nonbonded interatomic interactions first described by Corey and Bailar[18] and later substantiated by the researches of Dwyer and coworkers.[19-21]

For the complex with the absolute configuration D or Δ($C_2$), the methyl group positioned on the center ring of the fused chelate ring system can, theoretically, assume an axial or an equatorial position. In addition, the center chelate ring may also assume either a δ or λ conformation. Thus by considering only the central chelate ring, four conformational isomers may exist for each of the complexes D-*s*-*cis*-[Co(epe)$Cl_2$]Cl and L-*s*-*cis*-[Co(epe)$Cl_2$]Cl. These are presented in Table V where the absolute configuration of the complex and ligand are given, then the orientation of the methyl group followed by the ring conformational[22] designations. The energy difference between a conformation in which the methyl group is axial *vs.* the equatorial arrangement has been assessed at greater than 2 kcal/mol per ring in favor of the equatorial form for the propylenediamine chelate.[8] This strongly suggests that the methyl group must be positioned equatorially. This, in turn, fixes the five-membered ring conformation for a given set of ligand and octahedron configurations. The configurations associated with schemes 1, 3, 5, and 7 in Table V may thus be ruled out. Structures given in Figure 8 represent the four most reasonable combinations of absolute configuration and conformational arrangements for the metal, ligand, and center chelate ring.

**Table V.** Stereochemical Combinations

| Scheme | Absolute configurations Complex[17] | Ligand[23] | $CH_3$ position | Ring conformation[22] |
|---|---|---|---|---|
| 1. | Δ($C_2$) | D | Axial | δ |
| 2. (A)[a] | Δ($C_2$) | D | Equatorial | λ |
| 3. | Δ($C_2$) | L | Axial | λ |
| 4. (B)[a] | Δ($C_2$) | L | Equatorial | δ |
| 5. | λ($C_2$) | L | Axial | λ |
| 6. (C)[a] | λ($C_2$) | L | Equatorial | δ |
| 7. | λ($C_2$) | D | Axial | δ |
| 8. (D)[a] | λ($C_2$) | D | Equatorial | λ |

[a] Refers to the structure in Figure 8.



D-(-)-pn

D-epe

Figure 9. Absolute configurations of D-pn and D-epe.

The adjacent -$SCH_2CH_2NH_2$ rings can each assume two conformations.[22] The one shown in the structures of Figure 8 is preferred since the other causes the carbon atom adjacent to the nitrogen atom to move in toward the center chelate ring. This latter conformation is unlikely since severe H-H interactions occur between the adjacent ring protons, the shortest interatomic distances being approximately 1.5 to 1.8 Å, measured using Dreiding stereomodels.

Given these structures it is possible to relate the spatial distribution of atoms or groups of atoms about the asymmetric carbon atom on the central chelate ring of epe to the atom distribution about the asymmetric carbon in D- and L-propylenediamine. The absolute configuration for D-(−)$_{589}$-pn has been determined relative to D-alanine.[23] The relationship between D-propylenediamine and D-epe are shown in Figure 9. Using this model, the absolute configurations for epe in the structures of Figure 8 were deduced as summarized in Table V.

The question now arises: is the ligand (+)$_{589}$-epe, as isolated from Δ($C_2$)-*s*-*cis*-[Co(epe)$Cl_2$]Cl, of the D or L absolute configuration? The answer manifests itself in the stability of structure A *vs.* the stability of structure B in Figure 8. If structure A is correct for *s*-*cis*-[Co(epe)$Cl_2$]Cl, then (+)$_{589}$-epe has the D absolute configuration, whereas structure B requires (+)$_{589}$-epe to have the L configuration relative to D-alanine. Meticulous examination of Dreiding scale steromodels suggests that structures B and C experience the least severe hydrogen-hydrogen nonbonded interactions. In opposition to this, structures B and D seem to suffer

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described by J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2697 (1966).

(17) The letter designations D and L as used in this paper are equivalent to the absolute configurational designation Δ and Λ as discussed in ref 16.

(18) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(19) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963).

(20) F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

(21) T. E. MacDermott, *Chem. Commun.*, 223 (1968).

(22) According to an IUPAC recommendation (pending) the λ conformation is equivalent to Corey and Bailar's designation. This represents a C-C axis essentially parallel to a pseudo threefold axis in the octahedron. Such a convention fails in the present case. Here λ represents a left-handed helical relationship between the two C-N axes of the ring. Conversely, δ is associated with an absolute right-handed helix. See ref 25.

(23) S. Schnell and P. Karrer, *Helv. Chim. Acta*, **38**, 2036 (1955); Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jap.*, **35**, 1131 (1962).

the greatest ring strain in the backbone and two adjacent chelate rings. Consequently, the delicate balance between the subtle stereochemical features present in the molecule $\Delta(C_2)$-*s-cis*-[Co(epe)$Cl_2$]Cl dictates that there is not an obvious choice between structures A and B.

The absolute configuration of 4-methyl-1,8-bis-(salicylidineamino)-3,6-dithiaoctanecobalt(III) iodide (I), first studied by Dwyer and MacDermott[8] and more recently by Bosnich and Phillip,[24] has been established using circular dichroism techniques. In accord with the earlier work,[6] Bosnich and Phillip conclude that the absolute configuration of $(+)_{589}$-epe is D relative to D-alanine and D-propylenediamine.

Given that $(+)_{589}$-epe has the D absolute configuration and given that the configuration about the metal ion is $\Delta(C_2)$, then it follows that $\Delta(C_2)$-*s-cis*-[Co(epe)$Cl_2$]Cl has the geometry and ring conformations depicted in structure A of Figure 8.

The research of Goto and coworkers[25] using selectively methyl-substituted triethylenetetramine ligands of known absolute configuration concludes that the absolute configurations of the cobalt(III) complexes are determined by the conformations assumed by the central diamine bridges containing optically active sites. When the central ethylenediamine bridge adopts the $\lambda$ conformation with asymmetrically D-substituted alkyl groups present, the substituted trien coordinates stereospecifically to give only the $\Delta(C_2)$ unsymmetrical *cis* isomer.[26] Complexes which contain ligands of the L absolute configuration adopt the $\Lambda(C_2)$ unsymmetrical *cis* geometry.

In comparing the stereochemistries of cobalt(III) complexes having ligands with a donor atom sequence of NNNN with ligands of the type NSSN, two unique and important contrasts become apparent. First, *s-cis*-[Co(epe)$Cl_2$]$^+$ does not isomerize to the unsymmetrical *cis* or *trans* geometries in basic solution or in the presence of basic $Li_2CO_3$ solution as do the corresponding complexes derived from trien. Second, the relative stabilities of the possible geometric isomers are determined by somewhat different effects. While the work of Goto, *et al.*,[25] demonstrated that substitution of a methyl group on the central trien chelate ring results in the exclusive production of the unsymmetrical *cis* isomer, the studies of Hamilton and Alexander[27,28] and of Bosnich, *et al.*,[29] have shown that the chelate ring size, as controlled by varying the number of $CH_2$ groups between adjacent nitrogens, greatly affects the relative stabilities of the geometric isomers. As ring size increases *trans* isomers increase in stability. Our work with nitrogen–sulfur–sulfur–nitrogen ligands shows exclusive formation of the symmetrical *cis* geometry for the 2,2,2 case. This almost certainly suggests a ring size effect derived from the relatively long Co–S distance.

The significance of the absolute stereospecificity of this new ligand (epe) upon coordination to cobalt(III) extends well beyond its fundamental stereochemical importance. Cobalt(III) complexes containing four inert donors and two reactive sites have been instrumental in revealing the detailed mechanisms of the metal ion promotion of those crucial nucleophilic processes that involve the organic carbonyl function, *i.e.*, amino acid esters and amides and peptides.[30] To date, the studies have involved such familiar inert ligands as ethylenediamine and triethylenetetramine. Two limitations of these systems are the absence of stereospecificity and the fact that the manner of chelation of the so-called inert ligands may change during the course of the reaction of interest.[31] Ligands such as epe therefore hold much promise for future studies in this important area.

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(24) B. Bosnich and A. T. Phillip, *J. Amer. Chem. Soc.*, **90**, 6352 (1968).

(25) M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **8**, 358 (1969).

(26) The unsymmetrical *cis* geometry is analogous to the *β-cis* designation adopted by Sargeson for triethylenetetramine complexes.

(27) H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

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