Stereochemistry of Complexes of Multidentate Ligands. Part VI. Stereoselective Cobalt(III) Complexes of (3*R*)3-Methyl-1,6-bis[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane and (3*S*)3-Methyl-1,6-bis[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane

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The compounds (3*R*)3-methyl-1,6-bis[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane (L^1) and (3*S*)3-methyl-1,6-bis[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane (L^2) have been synthesized, together with their cobalt(III) complexes, *cis*- and *trans*-$[CoCl_2L]^+$ and *cis*-$[CoL(NO_2)_2]^+$ and *cis*-$[CoL(C_2O_4)]^+$. The optically active quadridentate ligands co-ordinate stereospecifically in both the *cis* and *trans* complexes: in the *cis* geometry, L^1 and L^2 give stereospecifically the Λ-*cis*-β and Δ-*cis*-β configurations, respectively; in the *trans* geometry, both ligands give optically active *trans* configurations. Electronic-absorption, circular-dichroism, and optical-rotatory-dispersion spectra are reported and used, together with chemical data, to assign the absolute configurations of the complexes.

We have already described the synthesis and absolute configurations of some cobalt(III) complexes of 1,6-bis[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane,[1] 1,7-bis[(2*S*)-pyrrolidin-2-yl]-2,6-diazaheptane,[2] and *NN'*-bis[(2*S*)-pyrrolidin-2-ylmethyl]-*trans*-*R*-cyclohexane-1,2-diamine.[3] In all cases the co-ordination of these ligands to Co^{III} showed marked stereospecificity, and the optically active pyrrolidine ring played a significant role. As part of our continuing study of the stereospecific co-ordination of quadridentate ligands, we have synthesized the linear flexible tetra-amines (3*R*)3-methyl-1,6-bis[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane (L^1) and (3*S*)3-methyl-1,6-bis-[(2*S*)-pyrrolidin-2-yl]-2,5-diazahexane (L^2). These ligands are also expected to possess the ability of stereospecific co-ordination because they each contain two optically active pyrrolidine rings. In addition, they each contain one additional optically active centre in their central ethylenediamine backbone, but the absolute configurations in each ligand are opposite to each other: *R* in L^1 and *S* in L^2. Therefore, it was interesting to study the stereochemistry of the complexes formed with these ligands where the central chelate ring involves ligands having opposite configurations and the terminal chelate rings have the same absolute configuration. The ligands were prepared according to the Scheme.

EXPERIMENTAL

Reagents.—*S*-Proline and benzyloxycarbonyl chloride were purchased from Nutritional Biochemical Corp., Cleveland, Ohio. Isobutyl chloroformate was obtained from J. T. Baker Chemical Co., Philipsberg, New Jersey, and lithium tetrahydridoaluminate(III) from Ventron Corp., Berverly, Massachusetts. Propylenediamine was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. All other chemicals used were commercial reagent grade.

Physical Measurements.—Infrared spectra of the solid samples were recorded using potassium bromide discs on a Perkin-Elmer model 337 grating spectrophotometer. The spectra of liquid samples were obtained for neat smears on KBr plates. Electronic-absorption spectra were recorded on a Unicam SP 800A u.v. spectrophotometer. Optical-rotatory-dispersion (o.r.d.) and circular-dichroism (c.d.) curves were measured on a Jasco ORD/CD-5 spectrophotometer using 1-cm cells and water as the solvent. Hydrogen-1 n.m.r. spectra were recorded on a Varian A-60 spectrometer using 2,2-dimethyl-2-silapentane-5-sulphonate (dss) as the internal standard. The solvent was D_2O. Elemental analyses were by Spang Microanalytical Laboratories, Ann Arbor, Michigan, and by Micro-Tech Laboratories, Stokie, Illinois.

Resolution of Propylenediamine.—Optically inactive propylenediamine was resolved according to the method of Dwyer *et al.*[4] using D-tartaric acid. The least-soluble diastereoisomer contained *R*-propylenediamine. After 12 recrystallizations the diastereoisomer was converted into the dihydrochloride by the method of Bailar *et al.*[5] Each optically active propylenediamine base was obtained by

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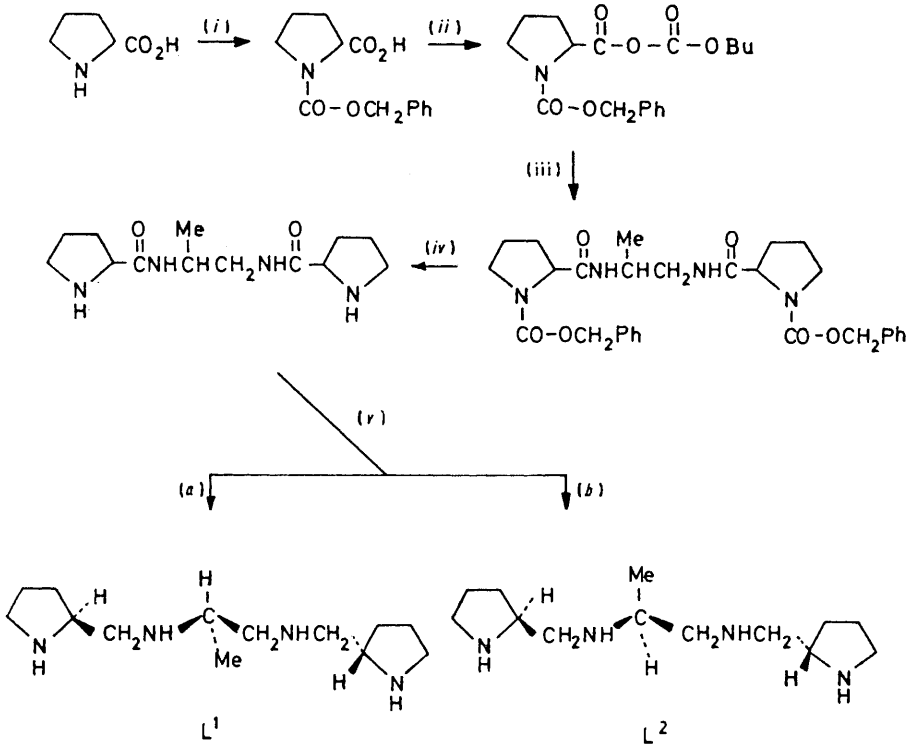
[1] Moo-Jin Jun and Chui Fan Liu, *Inorg. Chem.*, 1975, **14**, 2310.
[2] Moo-Jin Jun and Chui Fan Liu, *J. Co-ord Chem.*, 1975, **5**, 1.
[3] Moo-Jin Jun and Chui Fan Liu, *Inorg. Chim. Acta*, 1975, **15**, 111.
[4] F. P. Dwyer, F. L. Garven, and A. Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290.
[5] J. C. Bailar, H. B. Johnson, and A. D. Gott, *J. Amer. Chem. Soc.*, 1952, **74**, 3131.

cautious distillation of the hydrochloride mixed with an excess of sodium hydroxide.

Preparations.— NN′-*Bis*(*benzyloxycarbonyl*-S-*propyl*)-R-*propylene*-1,2-*diamine*. A solution of *N*-benzyloxycarbonyl-*S*-proline (17.9 g, 0.072 mol) and triethylamine (12 cm^3) in toluene (200 cm^3) was chilled to −5 °C and treated with isobutyl chloroformate (9.7 cm^3, 0.072 mol). After standing for 1 h, a cold solution of *R*-propylenediamine and NEt_3 (12 cm^3) in chloroform (150 cm^3) was added, and the mixture was allowed to stand overnight at room temperature. It was then washed successively with water, 3% sodium hydrogencarbonate solution, and water, and finally dried over anhydrous sodium sulphate. After evaporation under reduced pressure, a pale yellow oil was obtained. The oil crystallized slowly to give white crystals, which were recrystallized from hot acetone and diethyl ether, yield 14.7 g (76%) (Found: C, 64.8; H, 7.00; N, 9.90. Calc. for $C_{28}H_{36}N_4O_6$: C, 64.9; H, 6.90; N, 10.44%).

NN′-*Bis*(S-*propyl*)-R-*propylene*-1,2-*diamine*. *NN*′-Bis-(benzyloxycarbonyl-*S*-prolyl)-*R*-propylene-1,2-diamine (14.1 g) and methanol (230 cm^3) were placed in a 500-cm^3 Paar low-pressure hydrogenation bottle. To this mixture, 0.5 g of palladium on charcoal (10%) catalyst was added. The resulting mixture was shaken for 3 h, the catalyst was filtered off, and the filtrate was concentrated under reduced pressure to give a pale yellow oil.

(3R)3-*Methyl*-1,6-*bis*[(2S)-*pyrrolidin*-2-*yl*]-2,5-*diazahexane tetrakis*(*hydrochloride*)(L^1·4HCl). Anhydrous tetrahydrofuran (thf) (250 cm^3) and *NN*′-bis(*S*-prolyl)-*R*-propylene-1,2-diamine (6.0 g, 0.044 mol) were placed in a 500 cm^3 three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. The mixture was cooled in an ice-bath and $Li[AlH_4]$ (9.0 g) was carefully added with vigorous stirring at ice temperature. After warming slowly to room temperature, the reaction mixture was heated under reflux and stirred for 2 d. It was then cooled and transferred to a 1-l three-necked round-bottomed flask, equipped with a mechanical stirrer, and placed in an ice-bath. A solution of water (20 g) in thf (200 cm^3) was carefully added with vigorous stirring. The mixture was filtered off and the filter-cake was extracted twice with boiling thf. The combined filtrate and washings were concentrated under reduced pressure to give a pale yellow oil. The product was dissolved in absolute ethanol. Concentrated hydrochloric acid was then added and the solution was stored in a refrigerator overnight. White crystals were precipitated on adding diethyl ether. The product was washed with absolute ethanol and diethyl ether, and dried in the air, yield 5.6 g (Found: C, 40.35; H, 8.40; Cl, 36.95; N, 14.05. Calc. for $C_{13}H_{28}N_4$·4HCl: C, 40.45; H, 8.35; Cl, 36.7; N, 14.5%). The specific rotation for this ligand was −7.6 (c = 0.0079 g per 3 cm^3 of water) at 589 nm.



SCHEME (*i*), $PhCH_2OCOCl$; (*ii*), $ClCO_2Bu^i$; (*iii*), *R*- (*a*) or *S*-propylenediamine (*b*); (*iv*), H_2–Pd; (*v*), $Li[AlH_4]$

NN′-*Bis*(*benzyloxycarbonyl*-S-*prolyl*)-S-*propylene*-1,2-*diamine*. A solution of *N*-benzyloxycarbonyl-*S*-proline (24.92 g, 0.1 mol) and NEt_3 (15.5 cm^3) in toluene (300 cm^3) was chilled to −5 °C and treated with isobutyl chloroformate (13.1 cm^3) with stirring. After standing for 1 h, a cold solution of *S*-propylenediamine (3.7 g, 0.05 mol) and NEt_3 (15 cm^3) in chloroform (200 cm^3) was added, and the mixture was allowed to stand overnight at room temperature. The mixture was then filtered, washed successively with water, 3% sodium hydrogencarbonate solution, and water, and finally dried over anhydrous $Na_2[SO_4]$. After evaporation under reduced pressure, a pale yellow oil resulted. The oil crystallized slowly overnight to give a white crystalline residue, which was recrystallized from hot acetone and diethyl ether, yield 21.5 g, $\alpha_{589} = -7.08$

(c = 0.0195 g per 2.5 cm³ of water) (Found: C, 64.6; H, 6.90; N, 10.4. Calc. for $C_{29}H_{36}N_4O_6$: C, 64.9; H, 6.75; N, 10.45%).

NN'-Bis(S-*prolyl*)-S-*propylene*-1,2-*diamine*. This compound was prepared by the same method as that used for *NN'*-bis(*S*-prolyl)-*R*-propylene-1,2-diamine.

(3S)3-*Methyl*-1,6-*bis*[(2S)-*pyrrolidin*-2-*yl*]-2,5-*diazahexane tetrakis*(*hydrochloride*)(L^2·4HCl). This ligand was prepared by the same method as that used for L^1·4HCl using *NN'*-bis(*S*-prolyl)-*S*-propylene-1,2-diamine (9.5 g) and $Li[AlH_4]$ (15.2 g), yield 8.6 g (Found: C, 40.2; H, 8.35; Cl, 36.6; N, 14.25. Calc. for $C_{13}H_{28}N_4$·4HCl: C, 40.45; H, 8.35; Cl, 36.7; N, 14.5%). The specific rotation for this ligand was $\alpha_{589} = -2.7$ (c = 0.0585 g per cm³ of water).

trans-*Dichloro*[(3R)3-*methyl*-1,6-*bis*{(2S)-*pyrrolidin*-2-*yl*}-2,5-*diazahexane*]*cobalt*(III) *perchlorate–water* (2/1), *trans*-$[CoCl_2L^1][ClO_4]$·0.5H_2O. To a solution of L^1·4HCl (3.8 g) and $CoCl_2$·6H_2O (2.34 g) dissolved in water (60 cm³) was added Li[OH]·H_2O (1.65 g). The brown solution was aerated with carbon-dioxide–free air for 36 h. It was then reduced in volume to 30 cm³ under a stream of air at room temperature and concentrated hydrochloric acid (10 cm³) was added. Evaporation was continued until the volume reached 20 cm³. On addition of $Li[ClO_4]$·3H_2O, a green compound precipitated. This was filtered off and washed with acetone and diethyl ether. More of the green compound was obtained from the filtrate by evaporating the solution and filtering off the precipitates formed. The final filtrate was kept for the isolation of the *cis* isomer (Found: C, 31.4; H, 6.00; Cl, 21.3; N, 10.85. Calc. for $C_{13}H_{28}Cl_2CoN_4$·0.5H_2O: C, 31.4; H, 6.30; Cl, 21.4; N, 11.3%).

Λ-*cis*-β-$[CoCl_2L^1][ClO_4]$. The solution, after isolation of the *trans* complex as described above, was evaporated to dryness under a stream of air at room temperature. The residue was washed with acetone several times and then dissolved in the minimum of hot methanol. A red product was precipitated on cooling in an ice-bath and on slowly adding acetone. The product was recrystallized from the minimum of hot methanol (Found: C, 33.0; H, 5.90; N, 11.8. Calc. for $C_{13}H_{28}CoCl_3N_4O_4$: C, 33.25; H, 6.00; N, 11.95%).

Λ-*cis*-β-$[CoL^1(C_2O_4)]$. A solution of *trans*-$[CoCl_2L^1][ClO_4]$·0.5H_2O (0.028 g) and potassium oxalate hydrate (0.033 g) in water (10 cm³) was warmed on a steam-bath for 2 h. The solution was evaporated under a stream of air on a steam-bath until crystals separated. The pinkish red product was filtered off and recrystallized from hot water (Found: C, 37.0; H, 6.00; N, 11.55. Calc. for $C_{15}H_{28}ClCoN_4O_8$: C, 37.0; H, 5.80; N, 11.5%).

trans-*Dichloro*[(3S)3-*methyl*-1,6-*bis*{(2S)-*pyrrolidin*-2-*yl*}-2,5-*diazahexane*]*cobalt*(III) *perchlorate*, *trans*-$[CoCl_2L^2][ClO_4]$. The ligand L^2·4HCl (5.7 g, 0.01 mol) and $CoCl_2$·6H_2O (3.51 g, 0.0148 mol) were dissolved in water (60 cm³). To this solution, Li[OH]·H_2O (2.52 g) was added, and the dark brown solution was aerated with carbon-dioxide-free air for 36 h. The solution was reduced to half its original volume under a stream of air at room temperature. Concentrated hydrochloric acid (15 cm³) was then added and the evaporation continued to near dryness. The residue was washed several times with acetone, dissolved in water, and $Li[ClO_4]$·3H_2O (2.38 g) was added. The solution was evaporated until a green compound precipitated. The green product was filtered off, washed with acetone, a little ethanol, and diethyl ether, and dried in air. More of the green compound was isolated by further evaporation of the solution. The final filtrate was kept for the isolation of the *cis* isomer (Found: C, 33.5; H, 6.15; N, 11.75. Calc. for $C_{13}H_{28}Cl_3CoN_4O_4$: C, 33.25; H, 6.00; N, 11.95%).

Δ-*cis*-β-$[CoCl_2L^2][ClO_4]$·0.5H_2O. The solution remaining after the isolation of the *trans* complex as described above was evaporated to dryness. The residue was washed twice with acetone and dissolved in the minimum of hot methanol. A red product was precipitated on cooling to room temperature and on evaporating part of the solvent. The product was recrystallized from methanol (Found: C, 32.6; H, 5.90; N, 11.75. Calc. for $C_{13}H_{28}Cl_2CoN_4$·0.5H_2O: C, 32.6; H, 5.90; N, 11.7%).

Δ-*cis*-β-$[CoClL^2(OH_2)]^{2+}$ in situ. When Δ-*cis*-β-$[CoCl_2L^2][ClO_4]$·0.5H_2O was dissolved in water it quickly began to aquate, and after 24 h the rotation was constant. The c.d. spectrum of this solution was then measured.

Δ-*cis*-β-$[CoL^2(C_2O_4)][ClO_4]$. Potassium oxalate hydrate (0.06 g) was dissolved in water and *trans*-$[CoCl_2L^2][ClO_4]$ (0.14 g) was added. The resulting solution was heated on a steam-bath for 1.5 h and then evaporated to dryness under a stream of air. The red residue was washed with acetone and recrystallized from hot water (Found: C, 37.1; H, 5.80; N, 11.45. Calc. for $C_{15}H_{28}ClCoN_4O_8$: C, 37.0; H, 5.80; N, 11.5%).

Λ-*cis*-β-$[CoL^1(NO_2)_2][ClO_4]$. To a solution of L^1·4HCl (0.87 g, 0.0228 mol) and Li[OH]·H_2O (0.38 g) in water (30 cm³) were added successively $CoCl_2$·6H_2O (0.53 g, 0.0228 mol) and $Na[NO_2]$ (0.32 g). The resulting solution was aerated with carbon-dioxide-free air for 24 h at room temperature, and then reduced in volume to 20 cm³ under a stream of air at room temperature. An excess of $Li[ClO_4]$·3H_2O was added and evaporation was continued until the volume of the solution was *ca.* 12 cm³. The solution was then allowed to stand overnight in a refrigerator. The precipitated crystals were filtered off, washed with acetone and diethyl ether, and recrystallized from hot water (Found: C, 31.7; H, 5.70; N, 17.2. Calc. for $C_{13}H_{28}ClCoN_6O_8$: C, 31.8; H, 5.75; N, 17.1%).

Δ-*cis*-β-$[CoL^2(NO_2)_2][ClO_4]$. This complex was prepared by the same method as that used for *cis*-$[CoL^1(NO_2)_2][ClO_4]$ using L^2·4HCl in place of L^1·4HCl (Found: C, 31.7; H, 5.70; N, 17.2. Calc. for $C_{13}H_{28}ClCoN_6O_8$: C, 31.8; H, 5.75; N, 17.1%).

RESULTS AND DISCUSSION

Preparations.—The ligands were prepared following the synthetic route shown in the Scheme. In the ^1H n.m.r. spectra doublets occurred at δ 1.5 p.p.m. due to the methyl protons. The pyrrolidinyl protons resonated between δ 1.80 and 3.50 p.p.m. and the methylene protons between δ 3.5 and 3.8 p.p.m. The chemical shift patterns are consistent with the structural assignments.

Dichloro- and dinitro-cobalt(III) complexes containing L^1 or L^2 were prepared by the usual technique of air oxidation. *cis*-Dichloro-complexes of L^1 and L^2 were obtained as pinkish red crystals and *trans*-dichloro-complexes of these ligands as green crystals. In both $[CoCl_2L^1][ClO_4]$ and $[CoCl_2L^2][ClO_4]$ the *trans* isomers were present as more than 95% of the total product. Oxalatocobalt(III) complexes were prepared by heating

dichloro-complexes with either potassium oxalate or oxalic acid and were obtained as pink crystals.

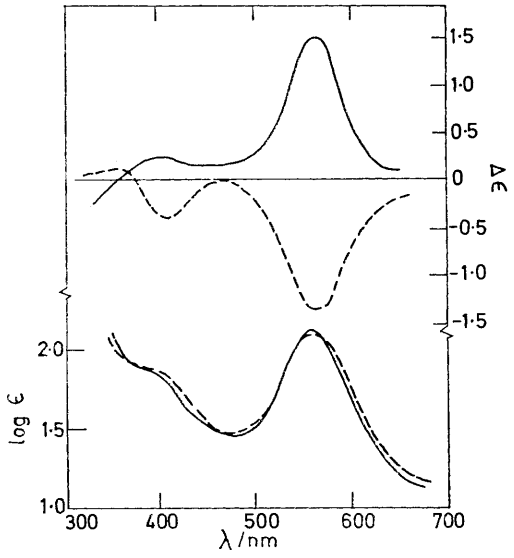


FIGURE 1 C.d. and electronic-absorption spectra of Λ-*cis*-β-$[CoCl_2L^1]^+$ (——) and Δ-*cis*-β-$[CoCl_2L^2]^+$ (– – – –)

Electronic-absorption Spectra.—Electronic-absorption spectra of *cis*- and *trans*-dichlorocobalt(III) complexes containing L^1 or L^2 ligands are shown in Figures 1 and 4. The first absorption band of the *cis* isomers was generally observed at *ca.* 550 nm and did not show a shoulder to longer wavelengths. Thus, the *cis* isomers are assigned the β geometric configuration. For these *cis*-β isomers the band at *ca.* 550 nm is assigned as $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$, and that at *ca.* 400 nm as $^1A_{1g}\rightarrow{}^1T_{2g}(O_h)$, electronic transitions of cobalt(III) ion.

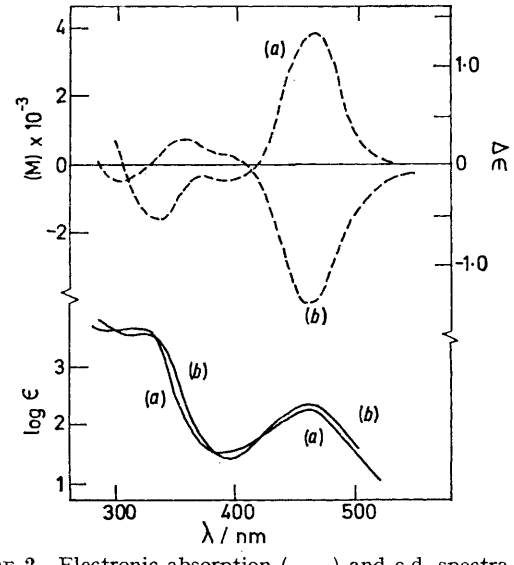


FIGURE 2 Electronic absorption (——) and c.d. spectra (– – –) of (*a*) Λ-*cis*-β-$[CoL^1(NO_2)_2]^+$ and (*b*) Δ-*cis*-β-$[CoL^2(NO_2)_2]^+$ ions

As expected for *trans*-dichloro-complexes of Co^{III}, splitting of the lower-energy band was observed for the complexes shown in Figure 4. The *trans* complexes had, in general, a band at *ca.* 620 nm and a band at 480 nm, which are assigned to the spin-allowed $^1A_{1g}\rightarrow{}^1E_g(D_4)$ and $^1A_{1g}\rightarrow{}^1A_{2g}(D_4)$ electronic transitions, respectively. Electronic spectra of the dinitro- and oxalato-complexes are shown in Figures 2 and 3, respectively. The first absorption band (at *ca.* 460 nm for the dinitro-complexes and at *ca.* 510 nm for the oxalato-complexes) is assigned

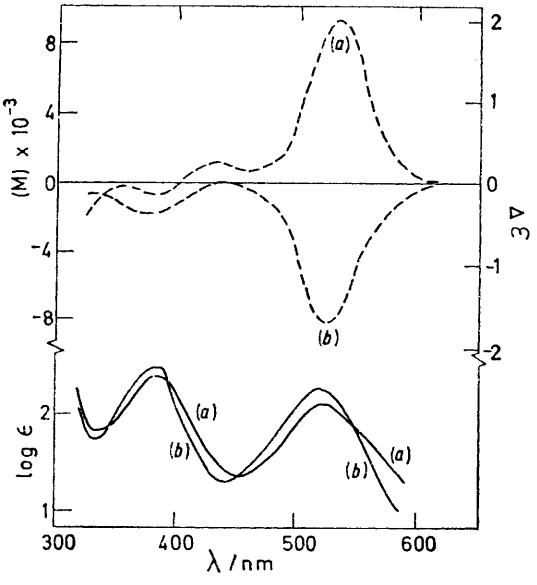


FIGURE 3 Electronic absorption (——) and c.d. spectra (– – –) of (*a*) Λ-*cis*-β-$[CoL^1(C_2O_4)]^+$ and (*b*) Δ-*cis*-β-$[CoL^2(C_2O_4)]^+$ ions

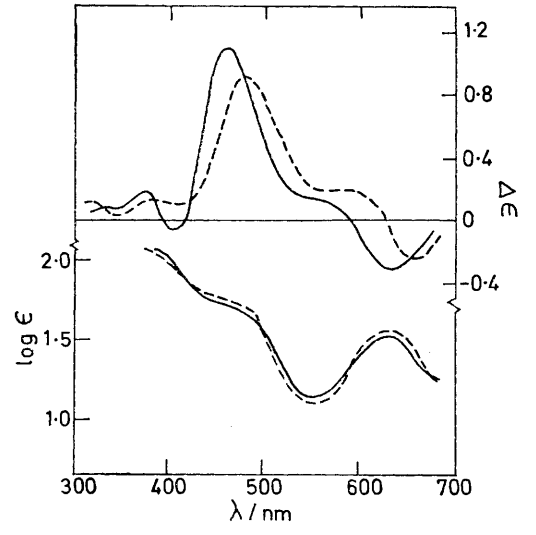


FIGURE 4 C.d. and electronic-absorption of *trans*-$[CoCl_2L^1]^+$ (– – –) and *trans*-$[CoCl_2L^2]^+$ (——)

to the $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ electronic transition. The second absorption band (at *ca.* 330 nm for the dinitro-complexes and at *ca.* 380 nm for the oxalato-complexes) is assigned to the $^1A_{1g}\rightarrow{}^1T_{2g}(O_h)$ electronic transition. Assignment of the *cis*-β geometry is made to all the dinitro- and oxalato-complexes, since their c.d. and o.r.d. spectra also closely resemble those of known *cis*-β complexes.

Optical Activity and Absolute Configuration.—C.d. and

o.r.d. spectra of *cis*-β-dichloro-complexes are shown in Figure 1. The c.d. and o.r.d. curves of *cis*-β-$[CoCl_2L^1]^+$ have only one dominant positive Cotton effect in the first absorption region, and those of *cis*-β-$[CoCl_2L^2]^+$ have only one dominant negative Cotton effect in this region. In applying Mason's and MacDermott's formalisms [6,7] to these complexes, the dominant $^1A_1 \rightarrow {}^1A_2$ low-energy Cotton effect, assuming these complexes approximate to C_2 symmetry, is assigned to the major c.d. and o.r.d. components centred between 520 and 620 nm. For *cis*-β-$[CoCl_2L^1]^+$ the major c.d. and o.r.d. bands are positive and therefore the Λ absolute configuration is assigned. The same assignment can also be made based on the similarity of the c.d. and o.r.d. curves of this isomer with those of Λ-*cis*-β-$[CoCl_2L]^+$ [L = 3,6-diazaoctane-1,8-diamine,[8] *N*,*N*′-bis(β-aminoethyl)-*R*-1,2-diaminocyclohexane,[9] (4*R*)4-methyl-3,6-diazaoctane-1,8-diamine,[9] and *NN*′-bis[(2*S*)-pyrrolidin-2-ylmethyl]-*trans*-*R*-cyclohexane-1,2-diamine [3]]. For the *cis*-β-$[CoCl_2L^2]^+$ the major c.d. and o.r.d. bands showed negative Cotton effects and the Δ absolute configuration is assigned. The same assignment can also be made from the similarity of the c.d. and o.r.d. curves of this isomer with those of Δ-*cis*-β-$[CoCl_2L]^+$ [L = (2*S*,7*S*)2,7-, (1*S*,8*S*)1,8-, and (4*S*,5*S*)4,5-dimethyl-3,6-diazaoctane-1,8-diamine [9]].

Further support for these assignments of absolute configurations is obtained from the o.r.d. and c.d. curves of the dinitro- and the oxalato-complexes shown in Figures 2 and 3. The dinitro- and the oxalato-complexes of L^1 have dominant positive o.r.d. and c.d. curves in the first absorption region and are therefore each assigned the Λ absolute configuration. The corresponding complexes of L^2 have dominant negative o.r.d. and c.d. curves in the same region and therefore are assigned the Δ absolute configuration.

The c.d. curve for *trans*-$[CoCl_2L^1]^+$ (Figure 4) shows a dominant negative band at *ca.* 650 nm and a smaller positive band at *ca.* 600 nm in its first absorption region. Like *trans* complexes of 1,7-bis[(2*S*)-pyrrolidin-2-yl]-2,6-diazaheptane [2] and *NN*′-bis[(2*S*)-pyrrolidin-2-ylmethyl]-*trans*-*R*-cyclohexane-1,2-diamine,[3] the *trans* complex of L^1 has a dominant positive c.d. band at *ca.* 480 nm whose sign is opposite to that of *trans*-$[CoCl_2L]^+$ (L = *N*,*N*′,2,7-tetramethyl-3,6-diazaoctane-1,8-diamine).[10] This pattern of c.d. spectrum is familiar among the *trans* complexes studied in this series of our work whose ligand backbones (ethylenediamine bridges) have *R* asymmetric centres and therefore adopt the λ conformation in the central chelate ring. The two bands of opposite sign in the first absorption region are, as were those of the complexes in the previous studies,[2,3] assigned to the two components of the $E(D_4)$ transition, and the two outside chelate rings then each have the δ conformation. The two terminal nitrogen atoms have *S* absolute configurations as deduced previously.[2,3]

Once again the presence of the pyrrolidine ring has exercised a profound influence, as discussed in the previous papers.[1-3] The pyrrolidine rings force the terminal nitrogen atoms to adopt the *S* absolute configuration. The preferred conformation of the central chelate ring of the L^1 is λ. Since asymmetrically substituted methyl groups (or asymmetric C-methylene groups with the pyrrolidine ring) are expected to assume an equatorial position, the ligand L^1 requires the conformation of the two outside ethylenediamine linkages to be δ. Therefore, the *trans*-$[CoCl_2L^1]^+$ complex has the λ conformation in its central chelate ring and the δ conformation in its two outside chelate rings.

The c.d. curve for *trans*-$[CoCl_2L^2]^+$ shows the same pattern as that of the *trans*-$[CoCl_2L^1]^+$ complex. Therefore it is concluded that *trans*-$[CoCl_2L^2]^+$ has essentially the same configuration as the *trans*-$[CoCl_2L^1]^+$ ion. The conformation of the outside chelate rings should then be δ and that of the central chelate ring λ. Thus, the overall configuration is *trans*-(*SS*)-(δλδ), where *S* indicates the absolute configuration of each of the two nitrogen atoms in the central chelate ring. The position of the substituted methyl group in the central chelate ring is then axial. There are two other alternative structures: *trans*-(*RR*)-(λδλ), the enantiomer of *trans*-(*SS*)-(δλδ); and *trans*-(*RS*)-(λεδ), in which the central chelate ring has an envelope shape.[11] However, these alternative structures are ruled out because, if the *trans* complex of L^2 had adopted one of them, an entirely different c.d. curve would have been obtained.

Chelate-ring Conformation and Stereospecificity.—In a five-membered chelate ring a substituted methyl group prefers the equatorial position. The ligands L^1 and L^2 have a substituted methyl group at the central ethylenediamine bridge. Therefore, the ligands will prefer λ and δ conformations, respectively, of the central chelate ring.

It was observed in this study that ligand L^1 coordinated to Co^{III} stereospecifically to give the Λ-*cis*-β-(*SS*) configuration. The conformation of the outside chelate ring coplanar with the central chelate ring is δ, in which an asymmetric C-methylene group in the pyrrolidine ring adopts an equatorial position, (A). The conformation of the other chelate ring above the plane containing the two coplanar chelate rings should also be δ, for the asymmetric C-methylene group in the pyrrolidine ring adopts an equatorial position in this conformation and the non-bonded interaction between the pyrrolidine ring and the central chelate ring is minimized. Therefore, structure (A) rather than (B) is the most probable for the Λ-*cis*-β-$[CoCl_2L^1]^+$ ion. For this Λ-*cis*-β(*SS*) isomer, two isomers are possible arising

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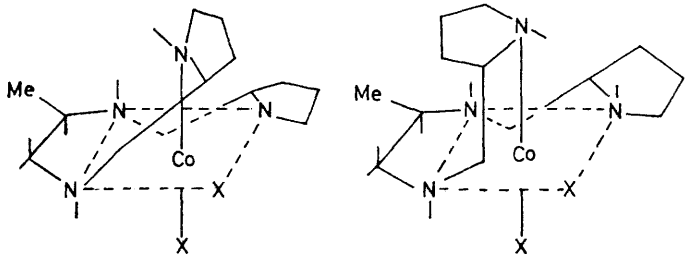
from the different positions [two carbon atoms in the central chelate ring in (A)] of the substituted methyl group in the central chelate ring. Although the ^1H n.m.r. spectrum of this dichloro-complex shows only one doublet at *ca.* δ 1.64 p.p.m., it was not possible to determine which one of the two isomers were present.



(A) (B)

It was mentioned earlier that ligand L^2 should prefer the δ conformation in the central chelate ring. In this work we observed that L^2 co-ordinated to Co^{III} stereospecifically to give the Δ-*cis*-β(*RR*) configuration. The conformation of the outside chelate ring coplanar with the central chelate ring should be δ because of the reason used to explain the conformation of the corresponding ring of the complex of L^1. The conformation of the outside chelate ring above the plane containing the two coplanar chelate rings becomes δ, which is the preferred conformation.

In conclusion, the ligands L^1 and L^2 show remarkable stereospecificity in their co-ordination to Co^{III} as expected. The cobalt(III) complexes with L^1 gave stereospecifically the Λ-*cis*-β(δλδ) configuration in the *cis* geometry, and the *trans*-(δλδ) configuration with the *S* absolute configuration at the terminal nitrogen atoms in the *trans* geometry. The cobalt(III) complexes with L^2 gave stereospecifically the Δ-*cis*-β(δδδ) configuration in the *cis* geometry, and the *trans*-(δλδ) configuration in the *trans* geometry, with the methyl group of the central chelate ring adopting an axial position. In all cases no *cis* geometrical isomers were observed. The ligands L^1 and L^2 prefer to adopt λ and δ conformations, respectively, in the central chelate ring containing the asymmetrically substituted methyl group. Both ligands prefer to adopt the δ conformation in the outside chelate rings, since they have the same asymmetrically substituted pyrolidine rings. It is to be noted that, when the central chelate ring prefers the λ or δ conformation, the absolute configurations of the complexes are Λ or Δ, respectively; also, when the central chelate ring is forced to adopt a λ conformation,[3] the absolute configuration of the complexes has been shown to be Λ. Therefore, it is concluded that the chirality of the central chelate ring determines the overall absolute configurations of the complexes in the case of the *cis* geometry observed here. Both the chirality of the central chelate ring and the conformational preference of the outside chelate rings of the ligands are responsible for the stereospecificities shown by the ligands.

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