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Complexes with Asymmetric Tetraamine Ligands. IV.* Cobalt(III) Complexes Containing Two Chiral Ligands. Structure of Λ-*cis*-β_2-(*SS*)-[*S*-alaninato-2*S*, 5*R*, 9*S*-trimethyltriencobalt(III)] Perchlorate Hydrate

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Abstract

Complexes of cobalt(III) with two optically active ligands have been prepared and characterized. One of the ligands was an amino acid (*S*-alanine or *S*-isoleucine) and the other was a methyl-substituted derivative of triethylenetetramine (trien), either 2*S*,5*R*,9*S*-Me$_3$trien or 2*S*,5*S*,9*S*-Me$_3$trien. The amino acid complexes were prepared from the *cis*-α or *cis*-β dichloro complexes of Co(III) with the appropriate trien derivative. The crystal and molecular structure of one of these complexes, with *S*-alanine and 2*S*,5*R*, 9*S*-Me$_3$trien, is reported.

Since the cobalt(III) complex contains two chiral ligands of known absolute configuration, the overall configuration of the complex could be assigned unambiguously as the Λ isomer. Although one of the three chelate rings of the chiral tetraamine deviates from ideal symmetric skew geometry, all three methyl groups are in equatorial positions. Both secondary nitrogen atoms have S configuration, and the methyl group on the central chelate ring of the tetraamine is adjacent to the 'flat' rather than the 'apical' secondary N. The alanine anion is coordinated with its nitrogen *trans* to a secondary nitrogen and its oxygen *trans* to a primary nitrogen of the tetraamine, to give the β_2 geometric isomer. Both perchlorate anions are disordered.

Crystallographic data for the title complex are as follows: $C_{12}H_{30}O_{11}N_5Cl_2Co$, $M_r = 550.23$, tetragonal, $P4_32_12$, $Z = 8$, $a = 9.166(5)$, $c = 53.51(4)$ Å, $V = 4495.4$ Å^3, $D_m = 1.63(1)$, $D_c = 1.657$ g cm^{-3}, Cu Kα, $\lambda = 1.54178$ Å, μ(Cu Kα) = 90.89 cm^{-1}, $F(000) = 2288$, room temperature, final $R = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|] = 0.089$ for 2620 unique, observed reflections.

Introduction

The chiral tetraamines 2*S*,5*R*,9*S*- and 2*S*,5*S*,9*S*-Me$_3$trien, (2*S*,9*S*)-2,9-diamino-(5*R* or 5*S*)-5-methyl-4,7-diazadecane, have the formula $H_2N-CH(CH_3)-CH_2-NH-CH(CH_3)-CH_2-NH-CH_2-CH(CH_3)-NH_2$. The presence of methyl substituents on the carbon atoms in the trien chain makes the ligand highly stereoselective in its coordination to a metal ion [3–9]. Only two of the possible isomers of [Co(2*S*,5*S*,9*S*-Me$_3$trien)Cl$_2$]$^+$ and three of the possible isomers of [Co(2*S*,5*R*,9*S*-Me$_3$trien)Cl$_2$]$^+$ could be isolated [8].

The assignments of configuration for those isomers were based on comparison of ORD and UV–Vis spectra with complexes of known configuration, since no suitable crystals of the dichloro complexes were obtained. There were two main goals for this work: to compare the reactions of these optically active complexes with optically-active, chelating ligands, and to prepare derivatives suitable for X-ray structural determination.

Experimental

Materials

The tetraamine ligands and their dichloro complexes were prepared as described previously [8]. All other materials were reagent grade and used without purification. *S*-Alanine and *S*-isoleucine were obtained from Aldrich Chem. Co.

Preparation of Complexes

The method of Job and Bruice [7] was followed for all the complexes. The conditions were controlled to give the *cis*-β_2 isomer for all cases. In one preparation in which the pH was permitted to exceed 9.0, a mixture of substances, the major component of wich was probably the *cis*-β_1 isomer, was obtained. Purification of the mixture was difficult and that preparation is not included here.

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*For Part III, see ref. 1; presented in part previously, see ref. 2.

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cis-β₂-(S-alaninato)(2S,5R,9S-trimethyltrien)-cobalt(III) perchlorate monohydrate, cis-β₂-[Co(2S,5R,9S-Me₃trien)(S-ala)](ClO₄)₂·H₂O

(a) *cis*-β-[Co(2*S*,5*R*,9*S*-Me$_3$trien)Cl$_2$]Cl (0.157 g, 0.44 mmol) and *S*-alanine (0.039 g, 0.44 mmol) were dissolved in 4 ml hot water with magnetic stirring. The pH of the red–purple solution was adjusted to 7.5 by dropwise addition of 5 M NaOH. The solution was stirred at 70 °C on a steam bath overnight. The resulting red–orange solution was then brought to pH 8.0 and the solution stirred at 70 °C for another two hours. An excess of NaClO$_4$ (1.0 g) was added and the volume of the solution was reduced nearly to dryness under an air stream at room temperature. The product was recrystallized by dissolving it in a minimum of warm 1 M NaClO$_4$. When the solution cooled to room temperature it was placed in a refrigerator. Red–orange crystals formed, to give 0.165 g, 68% yield.

(b) *cis*-α-[Co(2*S*,5*R*,9*S*-Me$_3$trien)Cl$_2$]Cl (0.152 g, 0.43 mmol) and *S*-alanine (0.038 g, 0.43 mmol) were dissolved in 4 ml of hot water. The procedure described above was followed, and an identical product, 0.102 g, 43%, was obtained.

cis-β₂-(S-isoleucinato)(2S,5R,9S-trimethyltrien)-cobalt(III) perchlorate monohydrate, cis-β₂-[Co(2S,5R,9S-Me₃trien)(S-ile)](ClO₄)₂·H₂O

(a) *cis*-β-[Co(2*S*,5*R*,9*S*-Me$_3$trien)Cl$_2$]Cl (0.257 g, 0.727 mmol) and *S*-isoleucine (0.095 g, 0.727 mmol) were dissolved in 8 ml hot water with magnetic stirring. The procedure described above was followed, to give 0.237 g, 55% yield.

(b) *cis*-α-[Co(2*S*,5*R*,9*S*-Me$_3$trien)Cl$_2$]Cl (0.354 g, 1.0 mmol) and *S*-isoleucine (0.131 g, 1.0 mmol) were dissolved in 8 ml of hot water. The procedure described above was followed, to give 0.386 g, 65% yield.

cis-β₂-(S-alaninato)(2S,5S,9S-trimethyltrien)-cobalt(III) perchlorate, cis-β₂-[Co(2S,5S,9S-Me₃trien)(S-ala)](ClO₄)₂

cis-β-[Co(2*S*,5*S*,9*S*-Me$_3$trien)Cl$_2$]Cl (0.152 g, 0.43 mmol) and *S*-alanine (0.038 g, 0.43 mmol) were dissolved in 4 ml hot water with magnetic stirring. The procedure described above was followed, to give 0.089 g, 39% yield.

cis-β₂-(S-isoleucinato)(2S,5S,9S-trimethyltrien)-cobalt(III) perchlorate, cis-β₂-[Co(2S,5S,9S-Me₃trien)(S-ile)](ClO₄)₂

cis-β-[Co(2*S*,5*S*,9*S*-Me$_3$trien)Cl$_2$]Cl (0.135 g, 0.38 mmol) and *S*-isoleucine (0.0498 g, 0.38 mmol) were dissolved in 4 ml hot water with magnetic stirring. The procedure described above was followed, to give 0.122 g, 56% yield.

Characterization of the Complexes

Visible–ultraviolet spectra of the complexes were obtained for 1.00 × 10^{-3} M aqueous solutions using a Perkin-Elmer model 200 or an Hitachi–Perkin-Elmer model 139 spectrophotometer. Values of optical rotation were obtained for the same aqueous solutions with a Perkin-Elmer model 141 polarimeter equipped with a Bausch and Lomb grating monochromator and xenon source, to permit readings at any wavelength in the visible region.

X-ray Crystallography. Data Collection for [Co(2S,5R,9S-Me₃trien)(S-alanine)](ClO₄)₂·H₂O, C₁₂H₃₀N₅O₁₁CoCl₂

An octahedral prismatic crystal, 0.25 × 0.25 × 0.25 mm, was mounted on a Nicolet R3m diffractometer with graphite monochromated Cu Kα radiation (due to the extremely long lattice parameter). The density was determined by flotation in chloroform/1,2-dibromoethane. A θ–2θ scan was used, with scan rates 3.91°–29.30° 2θ/min, to make background time = scan time. Room temperature lattice parameters were obtained from least-squares for 15 reflections in the range of $30° < 2\theta < 35°$, and absorption corrections were made from psi scans, with transmission factors 0.25 to 0.32, $2\theta_{\max} = 115°$, $\pm h + k + l$ with $h \leqslant 6$, $0 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 48$. Standard reflections 220 and 00.32 were checked every 50 reflections, and intensities were constant within experimental error, with no decay. Total reflections were 3604, with 3088 unique reflections, $R_{\text{int}} = 0.03$, 2620 reflections with $F > 3\sigma(F)$.

Structural Solution and Refinement

The structure was solved with SHELXTL [10], using heavy-atom and difference-Fourier methods. Isotropic then anisotropic refinement on F was carried out for all non-hydrogen atoms except the oxygens on perchlorate ions and the water molecule. The hydrogen atoms were located via a riding model (C–H 0.96 Å, U(H) = 0.06), and the perchlorate ions were included as nearly rigid tetrahedra (Cl–O = 1.419(7) Å). The perchlorate centered on Cl(1) includes one oxygen atom at full occupancy, with three at one set of positions with fractional occupancy 0.745(7) and three at complementary positions with fractional occupancy 0.255(7). The perchlorate centered on Cl(2) includes four oxygen atoms at 0.54(7) fractional occupancy, and four at complementary positions with 0.46(7) fractional occupancy. For 263 parameters refined, $w^{-1} = \sigma^2(F) + 0.0036\ F^2$, and $S = 1.46$. The final difference synthesis showed a maximum density of 1.70 e Å^{-3} near a disordered perchlorate ion and a minimum density of −1.6 e Å^{-3}, final $R = 0.089$, $R_w = 0.098$, mean $\Delta/\sigma = 0.20$, max. $\Delta/\sigma = 0.78$ for a disordered

TABLE I. Wavelength and Molar Absorptivity Values for $[Co(L)(aa)]^+$

L	aa	λ (nm)	ε ($l\ mol^{-1}\ cm^{-1}$)
2*S*,5*R*,9*S*-Me_3trien	*S*-alanine	483 345	100[a] 148
2*S*,5*R*,9*S*-Me_3trien	*S*-alanine	485 346	120 167
2*S*,5*R*,9*S*-Me_3trien	*S*-isoleucine	485 348	119 168
2*S*,5*S*,9*S*-Me_3trien	*S*-alanine	488 348	138 183
2*S*,5*S*,9*S*-Me_3trien	*S*-isoleucine	483 350	164 189
trien	*S*-alanine	479 346	125 148

[a] This complex was prepared from the *cis*-α dichloro complex.

perchlorate oxygen positional parameter. Scattering factors were from the International Tables for X-ray Crystallography [11]. No correction was made for secondary extinction.

Results and Discussion

Although a linear tetraamine such as these trien derivatives can wrap around the metal ion to give three different geometrical isomers (*cis*-α, *cis*-β, and *trans*), the coordination of a bidentate ligand such as alanine or isoleucine in the same complex restricts the possibilities to *cis*-α or *cis*-β. Under the conditions used in these syntheses, only *cis*-β isomers were expected [7, 12]. Variation of the preparative conditions failed to yield any product identifiable as the *cis*-α isomer. Since the amino acid is an unsymmetrical bidentate ligand, there are two possible *cis*-β isomers: *cis*-β_1, with the amino acid N *trans* to a primary N of the tetraamine, and *cis*-β_2, with the amino acid N *trans* to a secondary N of the tetraamine. These can sometimes be distinguished by comparing the molar absorptivities of the two absorption bands in the visible region [12]. Representative spectral data for the new complexes are given in Table I. Some *cis*-β_1 isomer was obtained from a reaction mixture during which the pH was accidentally permitted to rise above 9.0, but the procedure described above gave *cis*-β_2 in all other cases. Yields were relatively high, so that no steric effects from the methyl substituents were evident in the yields. Variations in the yields seemed to depend more on the amount of material used, rather than the particular starting compounds.

The assignment of overall configuration of the complexes was based on comparison of the ORD curves, shown in Figs. 1 and 2, with those for related complexes in the literature. All of the complexes were assigned the Δ-*cis*-β_2 configuration, except one, the complex with 2*S*,5*R*,9*S*-Me_3trien and *S*-alanine, which differed completely in its ORD curve (Fig. 2a) from the other complexes, and was assigned the Λ-*cis*-β_2 configuration. These assignments have now been confirmed for both of the alanine complexes by single crystal X-ray diffraction studies. The complex with 2*S*,5*S*,9*S*-Me_3 trien and *S*-alanine was confirmed to have the Δ-*cis*-β_2-(*RR*) configuration [13], and the structure of the complex with 2*S*,5*R*,9*S*-Me_3trien and *S*-alanine was also confirmed to be correctly assigned, as reported below.

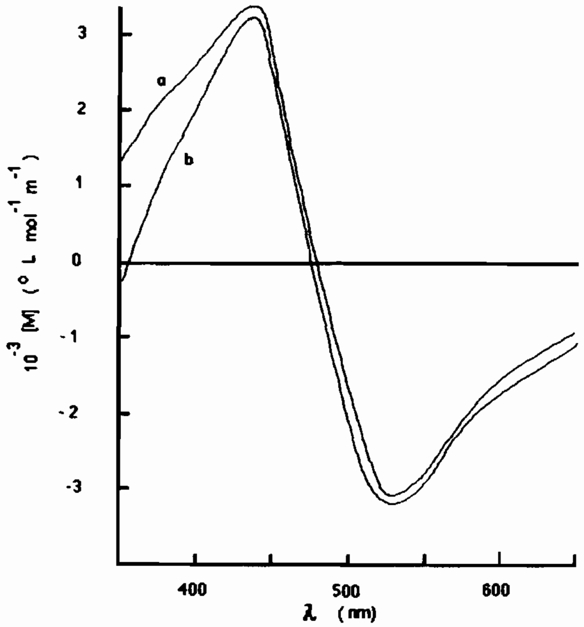

Fig. 1. ORD curves for $[Co(2S,5S,9S\text{-}Me_3trien)(aa)](ClO_4)_2$, 0.001 M aqueous solution. (a) aa = *S*-alanine, (b) aa = *S*-isoleucine.

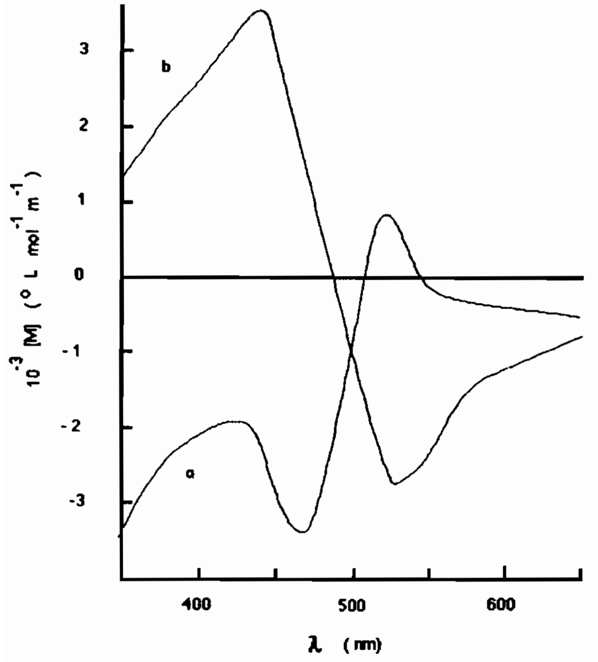

Fig. 2. ORD curves for [Co(2*S*,5*R*,9*S*-Me$_3$trien)(aa)](ClO$_4$)$_2$, 0.001 M aqueous solution. (a) aa = *S*-alanine, (b) aa = *S*-isoleucine.

The atomic coordinates and equivalent isotropic temperature factors are listed in Table II, and bond lengths and angles in Table III. The conformation of the complex with 2*S*,5*R*,9*S*-Me$_3$trien and *S*-alanine and the numbering scheme for the atoms are shown in the ORTEP plot [14] in Fig. 3, and a packing

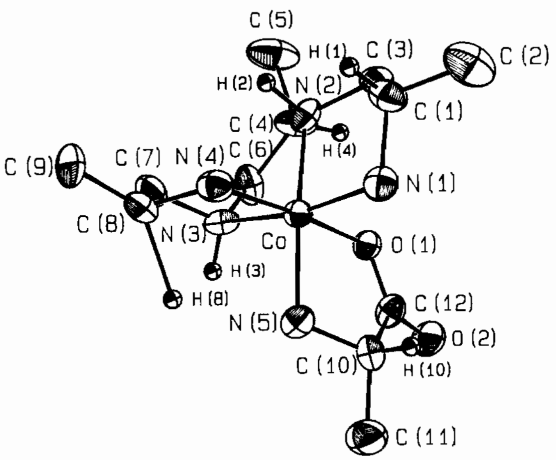

Fig. 3. Atom numbering for the Λ-*cis*-β$_2$-(*SS*)-[Co(2*S*,5*R*,9*S*-Me$_3$trien)(*S*-alanine)]$^{2+}$ cation, including H atoms on chiral atoms.

TABLE II. Atom Coordinates and Equivalent Isotropic Temperature Factors for Λ-*cis*-β$_2$-(*SS*)-[Co(2*S*,5*R*,9*S*-Me$_3$trien)(*S*-alanine)](ClO$_4$)$_2$·H$_2$O

Atom	*x*	*y*	*z*	Occupancy	*U*[a]
Co	0.9152(2)	0.3040(2)	0.9219(1)	1.000	0.025(1)*
N(1)	0.1113(8)	0.3890(9)	0.9227(1)	1.000	0.034(3)*
C(1)	0.1279(12)	0.4637(12)	0.9477(2)	1.000	0.038(4)*
C(2)	0.2594(13)	0.5712(15)	0.9476(3)	1.000	0.060(5)*
C(3)	0.9867(12)	0.5372(11)	0.9530(2)	1.000	0.037(4)*
N(2)	0.8704(9)	0.4248(9)	0.9507(1)	1.000	0.032(3)*
C(4)	0.7182(10)	0.4793(12)	0.9486(2)	1.000	0.036(4)*
C(5)	0.6577(15)	0.5216(16)	0.9741(2)	1.000	0.068(5)*
C(6)	0.6257(11)	0.3716(11)	0.9341(2)	1.000	0.039(4)*
N(3)	0.7137(9)	0.2400(9)	0.9269(1)	1.000	0.031(3)*
C(7)	0.7105(12)	0.1236(11)	0.9464(2)	1.000	0.037(4)*
C(8)	0.8465(14)	0.0335(12)	0.9437(2)	1.000	0.045(4)*
C(9)	0.8643(19)	−0.0738(13)	0.9649(2)	1.000	0.068(6)*
N(4)	0.9723(9)	0.1362(9)	0.9417(2)	1.000	0.036(3)*
N(5)	0.9507(9)	0.1995(9)	0.8902(1)	1.000	0.031(3)*
C(10)	0.9642(13)	0.3137(12)	0.8705(2)	1.000	0.042(4)*
C(11)	0.9340(16)	0.2519(13)	0.8447(2)	1.000	0.056(5)*
C(12)	0.8686(11)	0.4406(11)	0.8774(2)	1.000	0.032(3)*
O(1)	0.8480(7)	0.4576(7)	0.9010(1)	1.000	0.030(2)*
O(2)	0.8215(8)	0.5240(8)	0.8613(1)	1.000	0.043(3)*
Cl(1)	0.0852(3)	0.8202(3)	0.8879(1)	1.000	0.043(1)*
O(11)	0.0852(8)	0.8602(7)	0.9135(1)	0.745(7)	0.060
O(12)	0.1683(7)	0.9229(6)	0.8740(1)	0.745(7)	0.060
O(13)	0.1478(7)	0.6794(4)	0.8852(1)	1.000	0.060
O(14)	−0.0603(5)	0.8183(8)	0.8788(1)	0.745(7)	0.060
O(15)	0.1953(8)	0.9214(7)	0.8948(4)	0.255(7)	0.060

(continued)

TABLE II. *(continued)*

Atom	x	y	z	Occupancy	U^a
O(16)	0.0217(19)	0.8638(11)	0.8649(1)	0.255(7)	0.060
O(17)	−0.0239(15)	0.8161(9)	0.9067(3)	0.255(7)	0.060
Cl(2)	0.3365(3)	−0.0117(3)	0.9822(1)	1.000	0.072(1)*
O(21)	0.2569(9)	−0.0553(10)	0.0037(1)	0.541(7)	0.060
O(22)	0.2396(6)	0.0039(11)	0.9616(1)	0.541(7)	0.060
O(23)	0.4430(8)	−0.1190(7)	0.9764(1)	0.541(7)	0.060
O(24)	0.4065(10)	0.1236(7)	0.9869(1)	0.541(7)	0.060
O(25)	0.4757(7)	0.0276(11)	0.9916(1)	0.459(7)	0.060
O(26)	0.3537(12)	−0.0887(6)	0.9593(1)	0.459(7)	0.060
O(27)	0.2529(8)	0.1163(7)	0.9779(2)	0.459(7)	0.060
O(28)	0.2636(11)	−0.1019(10)	0.9998(2)	0.459(7)	0.060
O(H)	0.3249(14)	0.1511(11)	0.9197(2)	1.000	0.078(4)*
H(A)	0.303(12)	0.061(5)	0.925(2)	1.000	0.060
H(B)	0.311(14)	0.140(14)	0.903(1)	1.000	0.060

[a] Starred items: equivalent isotropic U calculated from anisotropic U. $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

TABLE III. Bond Lengths (A) and Angles (°) For Λ-*cis*-β_2-(*SS*)-[Co(2*S*,5*R*,9*S*-Me_3trien)(*S*-alanine)]$(ClO_4)_2 \cdot H_2O$

Co–N(1)	1.960(8)	N(1)–Co–N(2)	87.1(3)	C(3)–N(2)–C(4)	116.5(8)
Co–N(2)	1.939(8)	N(1)–Co–N(3)	169.2(3)	N(2)–C(4)–C(5)	111.2(8)
Co–N(3)	1.956(8)	N(1)–Co–N(4)	93.2(4)	N(2)–C(4)–C(6)	110.1(8)
Co–N(4)	1.939(8)	N(1)–Co–N(5)	93.5(3)	C(5)–C(4)–C(6)	115.0(9)
Co–N(5)	1.974(8)	N(1)–Co–O(1)	90.9(3)	C(4)–C(6)–N(3)	110.7(8)
Co–O(1)	1.901(6)	N(2)–Co–N(3)	82.2(3)	Co–N(5)–C(10)	106.3(6)
N(1)–C(1)	1.512(13)	N(2)–Co–N(4)	94.4(3)	C(10)–C(12)–O(1)	114.8(8)
C(1)–C(2)	1.557(17)	N(2)–Co–N(5)	173.3(3)	C(10)–C(12)–O(2)	121.9(9)
C(1)–C(3)	1.486(15)	N(2)–Co–O(1)	88.6(3)	Co–O(1)–C(12)	116.2(6)
C(3)–N(2)	1.488(13)	N(3)–Co–N(4)	86.7(3)	C(11)–C(10)–C(12)	113.9(9)
C(4)–N(2)	1.487(13)	N(3)–Co–N(5)	97.3(3)	Co–N(3)–C(6)	107.5(6)
C(4)–C(6)	1.517(15)	N(3)–Co–O(1)	89.8(3)	Co–N(3)–C(7)	109.2(6)
C(4)–C(5)	1.521(15)	N(4)–Co–N(5)	92.2(3)	C(6)–N(3)–C(7)	112.5(7)
N(3)–C(6)	1.502(13)	N(4)–Co–O(1)	175.0(3)	N(3)–C(7)–C(8)	107.9(8)
N(3)–C(7)	1.494(13)	N(5)–Co–O(1)	84.7(3)	C(7)–C(8)–C(9)	111.9(10)
C(7)–C(8)	1.502(16)	N(1)–C(1)–C(2)	111.1(9)	C(7)–C(8)–N(4)	107.6(8)
C(8)–C(9)	1.513(16)	N(1)–C(1)–C(3)	106.7(8)	C(9)–C(8)–N(4)	112.3(10)
C(8)–N(4)	1.492(15)	C(2)–C(1)–C(3)	112.8(9)	Co–N(4)–C(8)	109.3(6)
C(10)–N(5)	1.493(13)	C(1)–C(3)–N(2)	107.0(8)	N(5)–C(10)–C(11)	111.6(9)
C(10)–C(11)	1.518(15)	Co–N(2)–C(3)	108.2(6)	N(5)–C(10)–C(12)	108.7(8)
C(10)–C(12)	1.502(15)	Co–N(2)–C(4)	109.4(6)		
O(1)–C(12)	1.288(11)				
O(2)–C(12)	1.227(12)				
O–H(A)	0.90(6)				
O–H(B)	0.90(8)				

diagram in the PLUTO plot [15] in Fig. 4. The complex has approximately octahedral geometry, with the Co coordinated to one O and five N atoms. The O of the alanine anion is *trans* to a primary N of the Me_3trien, while the alanine N is *trans* to a secondary N of the Me_3trien, which confirms the assignment of β_2 geometry made by comparison of spectral data with literature values [7, 16].

Since the *S*-alanine and the tetraamine used were of known configuration, the absolute configuration of the complex could be assigned unambiguously as Λ, simply by selecting the isomer with correct configurations for the two chiral ligands. The two secondary N atoms of the tetraamine both have S configuration in the complex. (In making this assignment, the methyl substituents on the chain were ignored for determination of the priority, so that the configurations can be compared to those for trien.) The Λ-*cis*-β-(*SS*) isomer of the chloroaquo complex of Co(III) with the 2*S*,5*R*,9*S*-Me_3trien ligand was

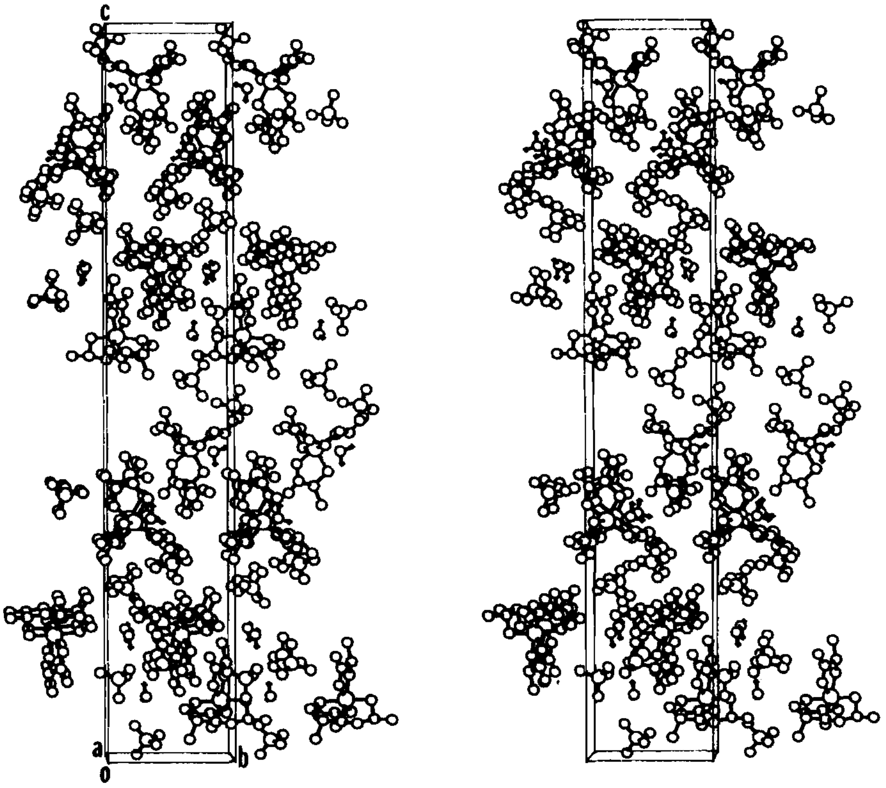

Fig. 4. Packing diagram for the title compound.

observed in solution during a kinetic study of aquation and isomerization reactions [9], but could not be isolated, which was consistent with predictions based on models that the Δ-*cis*-β-(*RS*) isomer should be more stable than the *SS* isomer. The two outer chelate rings of the Me_3trien both have nearly symmetrical skew δ conformations with equatorial methyl groups. The central ring (coordinated through N2 and N3) has an envelope (ϵ) conformation with the methyl group nearly equatorial. That methyl group on the central ring is on C4, adjacent to the 'flat' secondary nitrogen, as has been observed in other complexes with one methyl substituent on the central ring [13, 17].

The bond distances and angles given in Table III are all within the expected ranges. The average C—C distance is 1.52(2) Å, and the average C—N distance is 1.496(16) Å. The average Co—N distance for the four tetraamine N atoms is 1.948(9) Å, which is consistent with the 1.943(10) Å found for Δ-*cis*-β_2-$[Co(2S,5S,9S\text{-}Me_3trien)(S\text{-}ala)]^{2+}$ [13]. The three Me_3trien chelate rings all have N—Co—N angles less than 90° (87.1°, 82.2°, and 86.7°), and the alanine N5—Co—O1 angle is 84.7°. Comparable N—Co—N angles for *cis*-β Co(III) complexes of trien derivatives have been reported [5, 13].

Both perchlorate anions showed evidence of disorder, and could be refined satisfactorily only by assuming two sets of O atoms with partial occupancies. Such disorder is not unusual for the perchlorate anion and presumably contributes to the rather large value for *R*. However, the use of Cu radiation, as a result of the long lattice parameter, would certainly contribute to a high *R* value for a Co complex. Nevertheless, the major objectives of the structure determination, the chirality of the complex and of the secondary nitrogen atoms, were clearly achieved.

Several observations on the structures and syntheses of these complexes should be noted. For 2*S*,5*R*,9*S*-Me_3trien, the syntheses used gave identical products whether the starting dichloro complexes were the *cis*-α or the *cis*-β isomers. Thus, changes in configuration of the secondary N atoms of the tetraamine occurred in at least some of the reactions. Since no *cis*-α isomers have been isolated for the dichloro complexes of the 2*S*,5*S*,9*S*-Me_3trien ligand, only *cis*-β isomers were used in those syntheses. However, the secondary N atoms also showed changes of configuration, since both the *S*-ala and *S*-ile complexes were assigned *RR* configurations, and for either of these tetraamine ligands, only *cis*-β-*RS* or *cis*-β-*SS* isomers are known. Finally, no obvious reason has been found for the difference between the complexes of 2*S*,5*R*,9*S*-Me_3trien when *S*-alanine and *S*-isoleucine were used. The structure reported here for the *S*-ala complex has no unusual steric problems.

Attempts to determine the structure of the isoleucine complex have not been successful, due to poor quality crystals. However, the ORD curve (Fig. 2b) is so similar to the curves in Fig. 1, that there is little doubt as to the assignment of configuration for the complex. Neither the *S*-ala nor the *S*-ile complex has the structure predicted, based on ideal symmetric skew conformations for the chelate rings.

Supplementary Material

Lists of structure factors, anisotropic thermal factors and H-coordintes are available from author M. M. Muir on request.

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