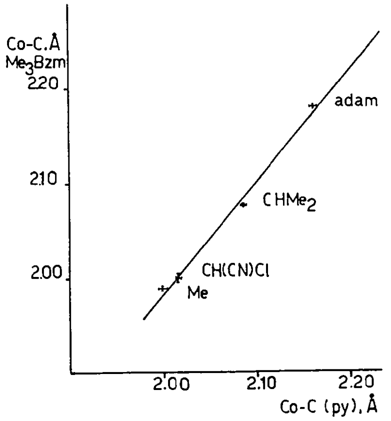

Fig. 3. Co—C bond lengths in Me_3Bzm complexes against the corresponding distances in py analogues for different R groups. The equation is $y = -0{\cdot}378 + 1{\cdot}181x$ for a correlation factor of 0·9965.

The values of the Co—C distances, reported in Table 2, illustrate the effect of the R bulk on the Co—C bond length which varies about 0·2 Å from (I) to (II). It should be observed that the Co—C distances in Me_3Bzm linearly correlate with those in py derivatives (Fig. 3). The slope of 1·181 derived for the least-squares line of Fig. 3 indicates that the Co—C distance is scarcely affected by the type of neutral N-ligand.

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Structure of a Cobalt(III) Complex with Two Optically Active Ligands*

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Abstract. Δ-*cis*-β_2-(RR)-[(S)-Alaninato][($2S$,$5S$,$9S$)-5-methyl-4,7-diazadecane-2,9-diamine]ocbalt(III) perchlorate, $[Co(C_3H_6NO_2)(C_9H_{24}N_4)](ClO_4)_2$, $M_r = 534{\cdot}24$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}668\ (4)$, $b = 14{\cdot}236\ (5)$, $c = 17{\cdot}439\ (5)$ Å, $V = 2151{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}65\ (1)$, $D_x = 1{\cdot}649$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, μ(Cu $K\alpha$) = 9·44 mm^{-1}, $F(000) = 1112$, room temperature, final $R = 0{\cdot}086$ for 1603 unique observed reflections. The cationic six-coordinate cobalt(III) complex contains two chiral ligands of known absolute configuration, so the overall configuration of the complex could be assigned unambiguously as the Δ isomer. The chiral tetraamine, which forms three chelate rings with the Co ion, has one methyl in an axial position, with the other two methyl groups in equatorial positions. Both secondary N atoms have R configuration. The alanine anion is coordinated with its

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* This work was presented in part at the American Crystallographic Association Meeting, Snowmass, Colorado, 1983, at which time the space group was incorrectly reported as $P2_12_12$ and two waters of hydration were incorrectly included.

N *trans* to a secondary N and its O *trans* to a primary N of the tetraamine, to give the β_2 geometric isomer. Both perchlorate anions are disordered.

Introduction. The chiral tetraamine (2*S*,5*S*,9*S*)-Me$_3$trien, formula $H_2N-CH(CH_3)-CH_2-NH-CH(CH_3)-CH_2-NH-CH_2-CH(CH_3)-NH_2$, can be considered as a C-methyl-substituted derivative of triethylenetetramine (trien). The presence of methyl groups on trien makes the ligand highly stereoselective in its coordination to a metal ion (Muir, Rechani & Diaz, 1981; Muir & Diaz, 1981; Saburi, Sawai & Yoshikawa, 1972; Asperger & Liu, 1965; Job & Bruice, 1974; Goto, Saburi & Yoshikawa, 1969). Only two of the possible isomers of [Co{(2*S*,5*S*,9*S*)-Me$_3$trien}Cl$_2$]$^+$ could be isolated (Muir *et al.*, 1981). The assignments of configuration for these isomers as *Δ-cis-β-RS* and *trans-SS* were based on comparison of optical rotatory dispersion (ORD) and UV–visible spectra with complexes of known configuration, since no suitable crystals of the dichloro complexes were obtained. However, upon replacement of the two chloride ligands in the *cis-β* isomer with the alaninate anion, crystals of the perchlorate salt were obtained. Determination of the structure of the title complex provides a basis for assignment of other related complexes whose ORD curves are similar.

Experimental. The tetraamine ligand and its dichloro complex were prepared as described previously (Muir *et al.*, 1981). *cis-β*-[Co{(2*S*,5*S*,9*S*)-Me$_3$trien}Cl$_2$]Cl and (*S*)-alanine (Aldrich Chem. Co.) in a 1:1 molar ratio were dissolved in hot water. The pH of the solution was adjusted to 7·5 by addition of 5 *M* NaOH. The solution was stirred at 343 K overnight. Then the pH was brought to 8·0 and the solution stirred at 343 K for another 2 h. An excess of $NaClO_4$ was added and the solution was left to evaporate at room temperature. The product was recrystallized by dissolving it in a minimum of warm 1 *M* $NaClO_4$. Red-orange crystals formed upon slow evaporation at room temperature. The yeild was 40%. The ORD curve for a 1·01 m*M* aqueous solution gave a minimum at 530 nm and a maximum at 435 nm (molar optical rotatory power $M = -3139$ and +3338° L mol^{-1} m^{-1}, respectively), and the absorption spectrum gave maxima at 488 nm and at 350 nm (molar absorption coefficient $\varepsilon = 145$ and 158 L mol^{-2} cm^{-1}, respectively).

Rectangular crystal, 0·25 × 0·40 × 0·20 mm, D_m by flotation in chloroform/1,2-dibromoethane, Nicolet *R*3*m* diffractometer, graphite-monochromated Cu *Kα*, $2\theta_{max} = 116°$, room-temperature lattice parameters from least squares for 18 reflections in the range $25 < 2\theta < 30°$. $+h+k+l$ with $0 \le h \le 9$, $0 \le k \le 15$, $0 \le l \le 19$; standard reflections 040 and 115 checked every 50 reflections, intensities constant within experimental error; total reflections 1803, 1701 unique reflections, 1603 with $F > 2{\cdot}5\sigma(F)$. $\sigma(F_o)^2 = [(I_{raw})^2 + (0{\cdot}03\, I_{raw})^2]^{1/2}/(Lp)$. Absorption corrections from ψ scans, transmission factors 0·06–0·33. Structure was solved with *SHELXTL* (Sheldrick, 1981), heavy-atom and difference-Fourier methods; isotropic then anisotropic refinement on *F* for all non-hydrogen atoms except oxygens on perchlorate ions, H atoms *via* a riding model [C—H 0·96 Å, $U(H) = 0{\cdot}06$ Å^2]; perchlorate ions initially showed disorder and could only be refined by constraining them to be nearly rigid tetrahedra using the *SHELXTL* DFIX instruction [averages: Cl—O = 1·404 (9) Å, O—Cl—O = 109·5 (6)°]; 232 parameters refined, $w^{-1} = \sigma^2(F) + 0{\cdot}001F^2$; $S = 2{\cdot}84$, difference syntheses showed a maximum density of 1·24 e Å^{-3} near a disordered perchlorate ion; min. density −0·83 e Å^{-3}; final $R = 0{\cdot}086$, $wR = 0{\cdot}092$, mean $\Delta/\sigma = 0{\cdot}008$, max. $\Delta/\sigma = 0{\cdot}047$ for an anisotropic temperature factor; neutral scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, and bond lengths and angles in Table 2.*

The conformation of the title compound and the numbering scheme for the atoms are shown in the *ORTEP* plot (Johnson, 1976) of Fig. 1, and a packing diagram (Motherwell, 1976) is given as Fig. 2. The Co atom is coordinated to one O and five N atoms in approximately octahedral geometry. The geometric isomer is designated β_2, since the O atom of the alanine anion is *trans* to a primary N of the Me$_3$trien, while the alanine N atom is *trans* to a secondary N atom of the Me$_3$trien. This confirms the assignment of β_2 geometry made by comparison of spectral data with literature values (Lin & Douglas, 1970; Marzilli & Buckingham, 1967).

The (*S*)-alanine used was of known configuration, and the tetraamine ligand was prepared by coupling (*S*)-alanine and (*S*)-1,2-propanediamine followed by reduction of the amides, as described elsewhere (Muir *et al.*, 1981). Thus, the absolute configuration of the complex could be assigned unambiguously as *Δ*, simply by selecting the isomer with correct configurations for the two chiral ligands. The two secondary N atoms of the tetraamine both have *R* configuration in the complex.

The three chelate rings of the Me$_3$trien show significant deviations from the ideal symmetric skew geometry. The central ring, coordinated through N(2)

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* Lists of H-atom coordinates, anisotropic thermal factors, mean planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43849 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates and equivalent isotropic temperature factors*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	*y*	*z*	U_{eq}(Å^2)
Co	0·0444 (2)	0·1219 (1)	0·7060 (1)	0·016 (1)
N(1)	0·2574 (11)	0·1176 (7)	0·7412 (5)	0·026 (3)
C(1)	0·2667 (15)	0·1308 (9)	0·8274 (7)	0·025 (4)
C(2)	0·3194 (18)	0·2307 (10)	0·8438 (9)	0·044 (5)
C(3)	0·1146 (15)	0·1081 (9)	0·8604 (6)	0·025 (4)
N(2)	−0·0071 (12)	0·1511 (6)	0·8113 (5)	0·019 (3)
C(4)	−0·1674 (14)	0·1205 (10)	0·8251 (7)	0·027 (4)
C(5)	−0·2337 (18)	0·1540 (12)	0·9014 (8)	0·048 (6)
C(6)	−0·2534 (15)	0·1567 (10)	0·7577 (8)	0·035 (5)
N(3)	−0·1744 (12)	0·1303 (7)	0·6847 (5)	0·026 (3)
C(7)	−0·2000 (15)	0·2021 (9)	0·6224 (7)	0·028 (4)
C(8)	−0·1010 (17)	0·2852 (8)	0·6392 (7)	0·030 (4)
C(9)	−0·0703 (19)	0·3451 (10)	0·5674 (8)	0·043 (5)
N(4)	0·0525 (12)	0·2536 (7)	0·6741 (6)	0·027 (3)
N(5)	0·1009 (12)	0·0752 (7)	0·6037 (5)	0·022 (3)
C(10)	0·0261 (19)	−0·0215 (9)	0·5931 (8)	0·040 (5)
C(11)	0·0887 (22)	−0·0769 (12)	0·5332 (8)	0·058 (6)
C(12)	0·0220 (15)	−0·0656 (9)	0·6732 (7)	0·025 (4)
O(1)	0·0269 (10)	−0·0077 (5)	0·7292 (4)	0·024 (3)
O(2)	0·0121 (12)	−0·1492 (5)	0·6803 (5)	0·034 (3)
Cl(1)	−0·0707 (4)	0·1339 (3)	0·3857 (2)	0·052 (1)
O(11)	−0·0926 (15)	0·2180 (6)	0·3452 (6)	0·099 (5)*
O(12)	0·0187 (14)	0·1514 (8)	0·4513 (5)	0·096 (5)*
O(13)	0·0057 (16)	0·0687 (9)	0·3387 (6)	0·288 (17)*
O(14)	−0·2145 (10)	0·0973 (10)	0·4077 (8)	0·220 (12)*
Cl(2)	0·5035 (4)	−0·0341 (2)	0·6172 (2)	0·039 (2)
O(21)	0·4684 (10)	0·0603 (5)	0·6017 (5)	0·078 (4)*
O(22)	0·3936 (9)	−0·0710 (6)	0·6682 (5)	0·072 (4)*
O(23)	0·6508 (8)	−0·0399 (6)	0·6505 (5)	0·055 (3)*
O(24)	0·5012 (11)	−0·0857 (6)	0·5487 (4)	0·109 (5)*

* Isotropic *U*.

Table 2. *Bond lengths* (Å) *and angles* (°) *for the cation Δ-cis-β_2-(RR)*-[Co{(2*S*,5*S*,9*S*)-Me$_3$trien}{(*S*)-*alanine*}]$^{2+}$

Co—N(1)	1·947 (10)	C(4)—C(5)	1·526 (19)
Co—N(2)	1·936 (9)	N(3)—C(6)	1·494 (16)
Co—N(3)	1·935 (11)	N(3)—C(7)	1·508 (16)
Co—N(4)	1·956 (10)	C(7)—C(8)	1·491 (18)
Co—N(5)	1·965 (9)	C(8)—C(9)	1·538 (18)
Co—O(1)	1·896 (7)	C(8)—N(4)	1·531 (17)
N(1)—C(1)	1·516 (15)	C(10)—N(5)	1·532 (16)
C(1)—C(2)	1·522 (19)	C(10)—C(11)	1·417 (20)
C(1)—C(3)	1·473 (18)	C(10)—C(12)	1·532 (18)
C(3)—N(2)	1·490 (15)	O(1)—C(12)	1·278 (14)
C(4)—N(2)	1·475 (16)	O(2)—C(12)	1·200 (15)
C(4)—C(6)	1·483 (18)		

N(1)—Co—N(2)	85·7 (4)	C(3)—N(2)—C(4)	116·9 (9)
N(1)—Co—N(3)	172·4 (4)	N(2)—C(4)—C(5)	113·8 (11)
N(1)—Co—N(4)	94·9 (4)	N(2)—C(4)—C(6)	104·0 (10)
N(1)—Co—N(5)	92·2 (4)	C(5)—C(4)—C(6)	113·1 (11)
N(1)—Co—O(1)	88·7 (4)	C(4)—C(6)—N(3)	110·9 (11)
N(2)—Co—N(3)	86·7 (4)	Co—N(5)—C(10)	107·9 (7)
N(2)—Co—N(4)	94·2 (4)	C(10)—C(12)—O(1)	115·5 (10)
N(2)—Co—N(5)	172·4 (4)	C(10)—C(12)—O(2)	120·2 (11)
N(2)—Co—O(1)	89·3 (4)	Co—O(1)—C(12)	117·9 (7)
N(3)—Co—N(4)	85·5 (4)	C(11)—C(10)—C(12)	116·9 (12)
N(3)—Co—N(5)	95·3 (4)	Co—N(3)—C(6)	107·6 (7)
N(3)—Co—O(1)	91·3 (4)	Co—N(3)—C(7)	108·9 (8)
N(4)—Co—N(5)	93·3 (4)	C(6)—N(3)—C(7)	112·1 (10)
N(4)—Co—O(1)	175·2 (4)	N(3)—C(7)—C(8)	108·2 (10)
N(5)—Co—O(1)	83·3 (4)	C(7)—C(8)—C(9)	112·4 (11)
N(1)—C(1)—C(2)	108·5 (10)	C(7)—C(8)—N(4)	110·2 (10)
N(1)—C(1)—C(3)	108·2 (10)	C(9)—C(8)—N(4)	109·6 (11)
C(2)—C(1)—C(3)	113·5 (11)	Co—N(4)—C(8)	111·3 (7)
C(1)—C(3)—N(2)	108·6 (9)	N(5)—C(10)—C(11)	115·3 (13)
Co—N(2)—C(3)	107·1 (7)	N(5)—C(10)—C(12)	105·5 (10)
Co—N(2)—C(4)	107·9 (7)		

and N(3), has a somewhat asymmetric δ conformation with the C(5) methyl in a nearly equatorial position. Both outer rings have a distorted envelope or boat conformation. The ring coordinated through N(1) and N(2) has the C(2) methyl group in essentially an axial position, while the C(9) methyl group on the N(3)—N(4) ring is closer to equatorial. The plane defined by Co, N(1) and N(2) is essentially coplanar with the plane defined by Co, N(2) and N(3) of the central ring, with a dihedral angle of less than a degree. The plane defined by Co, N(3) and N(4) has a dihedral angle of 85·6° with the central plane.

The bond distances and angles given in Table 2 are all within the expected ranges. The C—C distances to the three methyl groups on the trien are all somewhat longer [1·529 (19) Å average] than the C—C distances in the trien chain [1·482 (18) Å average]. The average C—N distance is slightly longer for the primary N atoms [1·526 (16) Å] than for the secondary N atoms [1·492 (16) Å]. The three Me$_3$trien chelate rings all have N—Co—N angles less than 90° (85·7, 86·7 and 85·5°), and the alanine N(5)—Co—O angle is only 83·3°. The average Co—N distance for the four tetraamine N atoms is 1·943 (10) Å, which is shorter than the average of 1·972 Å for a *cis-β* isomer of a dichloro complex with the ligand Me$_2$trien (Ito,

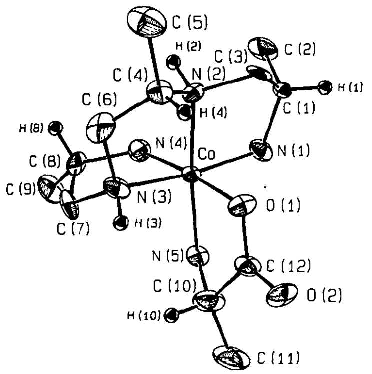

Fig. 1. Atom numbering for the complex cation (H atoms omitted except on chiral atoms).

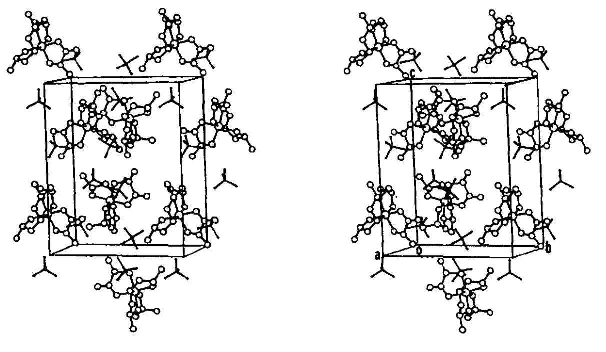

Fig. 2. Packing diagram for the title compound.

Marumo & Saito, 1970), for which the N—Co—N angles were 85·0, 86·7 and 86·0°. With the exception of these rather small angles and the axial methyl group, there was little evidence of significant steric problems in the complex.

The two perchlorates were somewhat disordered and could only be refined satisfactorily by imposing geometrical constraints. This disorder, commonly encountered for this anion, presumably contributed to the unusually high value of R. Another contributing factor was the use of Cu radiation, which was convenient for comparing this Co complex with another which had a lattice parameter in excess of 53 Å. The high R value in no way limits the value of the structure, since the major question, the chirality of the complex, is clearly established.

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Structure of Chlorotris(triphenylphosphine)copper(I)–Tetrahydrofuran (1/3)

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Abstract. $[CuCl(C_{18}H_{15}P)_3].3C_4H_8O$, $M_r = 1102·2$, hexagonal, $P6_3$, $a = 18·444\ (7)$, $c = 9·817\ (2)$ Å, $V = 2891·4$ Å^3, $Z = 2$, $D_x = 1·27$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 5·49$ cm^{-1}, $F(000) = 1160$, $T = 115$ K, $R = 0·035$ based on 1264 observed $[F > 3\sigma(F)]$ reflections. The pseudo-tetrahedral CuP_3Cl geometry (with tetrahydrofuran in the lattice) shows altered structural parameters from those in a previously studied material lacking lattice solvent.

Introduction. The influence of coordination number on Cu^I—PPh_3 bond length has been described (Gill *et al.*, 1976). Distances can range from 2·01 (1) (Abu Salah, Bruce & Redhouse, 1974) to 2·605 (11) Å (Engelhardt, Pakawatchai, White & Healy, 1985). We report here the results of a structural study of $CuCl(PPh_3)_3.3THF$ (THF = tetrahydrofuran), (1), which shows significantly different structural parameters from the previously studied crystalline material $CuCl(PPh_3)_3$, (2) (Gill *et al.*, 1976).

Experimental. The compound was synthesized by the method of Jardine, Rule & Vohra (1970) and was recrystallized from THF/pentane. A small crystal (0·40 × 0·40 × 0·40 mm) was selected and transferred to the goniostat where it was cooled to 115 K for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited $6/m$ symmetry; the only observed extinction was that of $00l$ for $l = 2n+1$. The possible space groups were $P6_3/m$ or $P6_3$. The choice of the non-centrosymmetric space group $P6_3$ was confirmed by the successful solution and refinement of the structure. Data collection ($6 \leq 2\theta \leq 45°$) and processing methods, as well as programs

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