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## Absolute Structure of (–)<sub>546</sub>-*cis*-β-Carbonato(triethylenetetramine)cobalt(III) Perchlorate Monohydrate

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**Abstract.** [Co(CO<sub>3</sub>)(C<sub>7</sub>H<sub>16</sub>N<sub>4</sub>)]ClO<sub>4</sub>·H<sub>2</sub>O, *M*<sub>r</sub> = 382·6, monoclinic, *P*2<sub>1</sub>, *a* = 7·418 (1), *b* = 12·365 (3), *c* = 8·690 (2) Å, β = 108·8 (3)°, *V* = 755 (2) Å<sup>3</sup>, *Z* = 2, *D*<sub>m</sub>(floatation) = 1·69 (1), *D*<sub>x</sub> = 1·68 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0·71069 Å, μ = 1·31 mm<sup>-1</sup>, *F*(000) = 396, *T* = 298 (1) K, final *R* = 0·031 for 3322 observed reflections. The Co<sup>III</sup> ion is in a distorted octahedral environment surrounded by the four N atoms of the tetradentate trien ligand coordinated in the *cis*-β configuration. The remaining two sites are occupied by the O atoms of the chelating carbonate group. The water molecule is hydrogen bonded to the complex *via* intermolecular links with the carbonate group and the perchlorate anion.

**Introduction.** There has been considerable interest in the *cis*-β complexes of the triethylenetetramine ligand, H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (trien), and its derivatives. For these compounds the stereochemistry about the 'planar' secondary N atom dictates the conformations of the rings (Buckingham, Marzilli & Sargeson, 1967). Kinetic and structural studies have shown that the more stable configuration at this N atom is one in which the attached proton is directed toward the apical ring (Buckingham, Marzilli & Sargeson, 1967; Sargeson & Searle, 1967; Freeman, Marzilli & Maxwell, 1970). In this conformation the two secondary N atoms adopt the same absolute configuration (Freeman, Marzilli & Maxwell, 1970; Dellaca, Janson, Robinson, Buckingham, Marzilli, Maxwell, Turnbull &

Sargeson, 1972). Exceptions are known amongst the configurational isomers of *cis*-β<sub>1</sub>- and *cis*-β<sub>2</sub>-[Co(trien)(gly)]<sup>2+</sup> (Dellaca *et al.*, 1972; Buckingham, Dwyer, Gainsford, Janson, Marzilli, Robinson, Sargeson & Turnbull, 1975). For these complexes it has been suggested that the apical ring is sufficiently flexible to adopt either the δ or the λ conformation. The present work was undertaken to establish the stereochemistry and absolute configuration of (–)<sub>546</sub>-*cis*-β-[Co(trien)(CO<sub>3</sub>)]ClO<sub>4</sub>·H<sub>2</sub>O, and to obtain an unambiguous description of the configuration of the 'planar' and trigonal secondary N atoms. Hitherto, the absolute configuration of the title compound has been inferred from comparative optical rotatory dispersion and circular dichroism studies, in conjunction with the results of rearrangement reactions known to occur with retention of configuration (Sargeson & Searle, 1965).

**Experimental.** Single crystals grown from aqueous solution. Crystal system and space group determined from oscillation and Weissenberg photographs. Structure solved by the Patterson/Fourier method with intensity data visually estimated from Weissenberg photographs, 0 to 16 layers about [0 1 0] and 0 to 4 layers about [1 0 0] with Co *K*α and Cu *K*α radiation, respectively. The absolute configuration from Friedel pairs selected from the Cu *K*α set, later confirmed by diffractometer (Siemens) measurements. Because of difficulties with refinement of thermal parameters of the perchlorate anion, data remeasured using counter methods. A crystal of *ca* (100) 0·095, (010) 0·261, (001) 0·101, (–101) 0·095 mm was mounted in a general orientation on an Enraf–Nonius CAD-4F diffractometer; Mo *K*α

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radiation, recorded with an  $\omega$ - $2\theta$  scan. Cell parameters determined by least squares from  $2\theta$  values ( $19 \leq 2\theta < 30^\circ$ ) for 25 strong reflections. Four standard reflections monitored every 3000 s of X-ray exposure time, no significant intensity variation. Intensity measurements  $1 < 2\theta < 27.5^\circ$ .  $h$  -11 to 11,  $k$  -1 to 16,  $l$  -1 to 9, gave 3436 unique data,  $R_{\text{int}} = 0.012$ , 3322 data [ $I > 3\sigma(I)$ ] for refinement; corrections for Lorentz and polarization factors and for absorption (transmission factors 0.7925 to 0.7188). Full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976); anisotropic temperature factors for Co, Cl, C, N and O atoms; H atoms attached to C atoms included at idealized positions and given a common isotropic temperature factor [ $U_{\text{iso}} = 0.062$  (3)  $\text{\AA}^2$ ]; protons bonded to N atoms included at located sites, their positional parameters not varied and given a common isotropic temperature factor [ $U_{\text{iso}} = 0.054$  (4)  $\text{\AA}^2$ ]; refinement converged at  $R = 0.031$  and  $wR = 0.034$ ; function minimized  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1.0/[\sigma(F_o)^2 + 0.003|F|^2]$ . Refinement with coordinates for the enantiomeric configuration converged with  $R$  and  $wR$  values of 0.053 and 0.062 respectively. On the basis of the Hamilton  $R$ -factor test, ratios are significantly greater than those for the absolute configuration derived from the photographic data and confirm the original assignment to be correct at convergence.  $(\Delta/\sigma)_{\text{max}} = 0.005$ ;  $(\Delta\rho)_{\text{max}}$ ,  $(\Delta\rho)_{\text{min}}$  0.9 and  $-1.0 \text{ e \AA}^{-3}$  respectively in the vicinity of the Co atom. Atomic scattering factors and anomalous-dispersion corrections for C, Cl, N, O and Co from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). Figs. 1 and 2 were prepared from the output of *ORTEPII* (Johnson, 1976). Calculations performed on a CYBER computer.

**Discussion.** Final atomic coordinates for the non-H atoms are given in Table 1.\* A perspective view of the complex cation  $(-)_546\text{-cis-}\beta\text{-[Co(trien)(CO}_3\text{)]}^+$  and the numbering scheme are shown in Fig. 1. Fig. 2 shows a stereoview of the crystal packing. Bond lengths and angles together with their estimated standard deviations are given in Table 2 along with short intermolecular contacts.

The structure contains discrete  $[\text{Co(trien)(CO}_3\text{)]}^+$  cations, perchlorate anions and waters of hydration held together by electrostatic interactions and hydrogen bonding (Figs. 1 and 2). The absolute configuration of the complex is described as a skew chelate pair,  $\Delta$ . The conformation of the apical ring (I) is  $\delta$

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54217 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_i a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{\text{eq}}(\text{\AA}^2)$
Co	3429 (3)	0	-4886 (3)	2.299 (4)
Cl	6391 (1)	-2085 (1)	3987 (1)	3.528 (9)
C(1)	-882 (4)	1744 (2)	-2682 (3)	3.72 (4)
C(2)	-1473 (5)	704 (2)	-3631 (3)	3.83 (4)
C(3)	-3620 (3)	9 (3)	-2173 (4)	4.01 (4)
C(4)	-3287 (4)	-253 (2)	-399 (4)	3.93 (4)
C(5)	-735 (4)	6 (3)	2244 (3)	4.40 (5)
C(6)	1249 (5)	488 (3)	2843 (4)	4.62 (6)
C(7)	1666 (4)	-1629 (2)	-911 (3)	3.11 (4)
N(1)	685 (3)	1468 (2)	-1160 (3)	3.03 (3)
N(2)	-1763 (3)	-120 (2)	-2508 (3)	3.11 (3)
N(3)	-1546 (3)	337 (2)	522 (3)	3.09 (3)
N(4)	2234 (3)	170 (2)	1673 (3)	3.31 (3)
O(1)	2096 (2)	-688 (1)	-1388 (2)	3.23 (3)
O(2)	362 (3)	-1535 (2)	-188 (2)	3.22 (3)
O(3)	2366 (3)	-2503 (2)	-1091 (3)	4.50 (4)
O(4)	5607 (8)	-1066 (5)	3504 (12)	15.1 (2)
O(5)	8287 (4)	-1889 (3)	5068 (4)	6.19 (6)
O(6)	5252 (6)	-2576 (6)	4790 (5)	11.0 (1)
O(7)	6440 (8)	-2717 (6)	2722 (8)	14.7 (2)
O(w)	4452 (4)	-7911 (3)	1890 (4)	5.90 (5)

Table 2. Molecular geometry ( $\text{\AA}$ ,  $^\circ$ ) with e.s.d.'s in parentheses

Co—N(1)	1.948 (2)	C(4)—N(3)	1.475 (3)
Co—N(2)	1.943 (2)	N(3)—C(5)	1.480 (3)
Co—N(3)	1.924 (2)	C(5)—C(6)	1.516 (5)
Co—N(4)	1.960 (2)	C(6)—N(4)	1.484 (5)
Co—O(1)	1.919 (2)	C(7)—O(1)	1.308 (3)
Co—O(2)	1.915 (2)	C(7)—O(2)	1.317 (4)
N(1)—C(1)	1.492 (3)	C(7)—O(3)	1.231 (4)
C(1)—C(2)	1.514 (3)	Cl—O(4)	1.395 (6)
C(2)—N(2)	1.474 (4)	Cl—O(5)	1.437 (3)
N(2)—C(3)	1.505 (4)	Cl—O(6)	1.397 (6)
C(3)—C(4)	1.516 (5)	Cl—O(7)	1.359 (8)
O(1)—Co—N(4)	93.9 (1)	C(3)—C(4)—N(3)	105.9 (2)
O(1)—Co—N(2)	93.0 (1)	C(4)—N(3)—Co	106.5 (2)
N(1)—Co—N(2)	86.9 (1)	Co—N(3)—C(5)	106.4 (2)
N(2)—Co—N(3)	86.4 (1)	N(3)—C(5)—C(6)	105.8 (2)
N(3)—Co—N(4)	86.6 (1)	C(5)—C(6)—N(4)	107.3 (2)
O(1)—Co—O(2)	68.9 (1)	C(6)—N(4)—Co	109.1 (2)
N(1)—Co—O(1)	97.0 (1)	C(2)—N(2)—C(3)	113.1 (2)
N(1)—Co—N(3)	96.8 (1)	C(4)—N(3)—C(5)	114.3 (2)
N(1)—Co—N(4)	93.7 (1)	Co—O(1)—C(7)	89.9 (1)
O(2)—Co—N(1)	165.5 (1)	Co—O(2)—C(7)	89.8 (2)
O(2)—Co—N(2)	90.9 (1)	O(1)—C(7)—O(2)	111.4 (2)
O(2)—Co—N(3)	97.3 (1)	O(1)—C(7)—O(3)	125.8 (2)
O(2)—Co—N(4)	90.2 (1)	O(2)—C(7)—O(3)	122.9 (2)
Co—N(1)—C(1)	109.8 (2)	O(4)—Cl—O(5)	105.6 (3)
N(1)—C(1)—C(2)	107.1 (2)	O(4)—Cl—O(6)	106.3 (3)
C(1)—C(2)—N(2)	107.8 (2)	O(4)—Cl—O(7)	113.2 (4)
C(2)—N(2)—Co	107.4 (2)	O(5)—Cl—O(6)	111.6 (2)
Co—N(2)—C(3)	109.7 (2)	O(6)—Cl—O(7)	109.4 (3)
N(2)—C(3)—C(4)	108.3 (2)	O(7)—Cl—O(5)	110.5 (3)
	N...O	H...O	N—H—O
N(1)—H(N1a)...O(2) <sup>i</sup>	2.943 (4)	2.07	143
N(1)—H(N1b)...O(7) <sup>ii</sup>	3.045 (8)	2.15	146
N(2)—H(N2)...O(5) <sup>iii</sup>	3.045 (5)	2.12	152
N(3)—H(N3)...O(3) <sup>i</sup>	2.817 (4)	1.84	163
N(4)—H(N4a)...O(4)	2.926 (6)	2.10	138
N(4)—H(N4b)...O(w) <sup>v</sup>	2.859 (4)	1.89	
	O...O		
O(w)...O(3) <sup>v</sup>	2.714 (4)		
O(w)...O(6) <sup>vi</sup>	2.852 (6)		

Symmetry codes: (i)  $-x, \frac{1}{2} + y, -z$ ; (ii)  $1 - x, \frac{1}{2} + y, -z$ ; (iii)  $-1 + x, y, -1 + z$ ; (iv)  $x, -1 + y, z$ ; (v)  $1 - x, \frac{1}{2} + y, -z$ ; (vi)  $1 - x, \frac{1}{2} + y, 1 - z$ .

and the planar rings II and III adopt  $\delta$  and  $\lambda$  conformations respectively. Four N atoms supplied by the trien ligand in the *cis- $\beta$*  coordination and two O atoms from the carbonate group surround the Co atom at the apices of a distorted octahedron. The small angle of 68.9 (1)° subtended by the chelating carbonate group is largely responsible for this distortion. This small angle has been observed in other cobalt carbonate compounds (Schlemper, Sen Gupta & Desgupta, 1983). The average angle subtended by the trien ligand is 86.3 (3)° as observed in related compounds (Freeman & Maxwell, 1969, 1970; Freeman, Marzilli & Maxwell, 1970). The Co—N bond lengths range from 1.924 (2)–1.960 (2) Å (Table 2) and compare favourably with reported Co—N (amine) bond lengths (Freeman & Maxwell, 1969; Schlemper, Sen Gupta & Desgupta, 1983). Notably the bond to the planar nitrogen N(3) is the shortest (Table 2). This feature has been observed in the complexes *A-cis- $\beta_2$* -(SSS)-[Co(trien){(*S*)-Pro}]ZnCl<sub>4</sub> (Freeman & Maxwell, 1970), *cis- $\beta$* -[Co(trien)-ClOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (Freeman & Maxwell, 1969). It has been argued that the shortened bond reduces angular strain at the secondary N atom (Buckingham, Cresswell, Dellaca, Dwyer, Gainsford, Marzilli, Maxwell,

Robinson, Sargeson & Turnbull, 1974). In cases where the chelating carbonate group is present it has been suggested that the shortened bond may result from a *trans* influence of the carbonate ion (Schlemper, Sen Gupta & Desgupta, 1983; Toriumi & Saito, 1975). Since the structure under investigation contains a carbonate group, it seems reasonable to suggest that both factors are at play.

Within the trien ligand the mean C—N and C—C distances respectively (Table 2) compare with values found in related complexes (Buckingham *et al.*, 1974; Buckingham, Freeman, Maxwell & Sargeson, 1970). Endocyclic Co—N—C and N—C—C angles have values close to the regular tetrahedral value (Table 2). Significant angular distortions occur at the secondary N atoms: C(2)—N(2)—C(3) 113.1 (2) and C(4)—N(3)—C(5) 114.3 (2)°. These angles are very similar to those observed in other cobalt(III) complexes with *cis- $\beta$*  coordination. The absolute configuration adopted at both asymmetric N atoms is *R*. In this configuration the proton at N(3) is directed toward the apical ring supporting the conclusion that, in general, this is the more stable configuration (Buckingham, Marzilli & Sargeson, 1967; Sargeson & Searle, 1967).

A puckering of the  $\beta$ -trien chelate rings is clearly evident in Fig. 1. The two outer rings adopt unsymmetrical skew conformations and the central ring adopts an unsymmetrical envelope conformation. Torsion angles about the C—C bond and chiralities of the five-membered rings are: C(1)—C(2) 49.0  $\delta$ ; C(3)—C(4) 46.9  $\delta$ ; C(5)—C(6) 51.5°  $\lambda$ . This result is consistent with the general preference for the apical ring to take the  $\delta$  absolute configuration in  $\Delta$ -*cis- $\beta$* -cobalt(III) trien systems (Buckingham *et al.*, 1975; Buckingham, Freeman, Maxwell & Sargeson, 1970). Small variations in the torsional angles about C(3)—C(4) compared with other complexes (Freeman & Maxwell, 1969; Buckingham, Freeman, Maxwell & Sargeson, 1970) are most likely due to a difference in hydrogen bonding involving the N—H groups. That the overall structure is repeated in a number of complexes suggests that it is not critically influenced by crystal packing and intermolecular bonding.

The dimensions of the coordinated carbonate group (Table 2) are typical (Schlemper, Sen Gupta & Desgupta, 1983). The atom groupings O(1), O(2), C(7), O(3) and O(1), O(2), Co, N(1), N(3) are planar, the maximum deviations being 0.001 (3) and -0.027 (2) Å respectively. The dihedral angle between the planes of 1.1° is less than that found in some other cobalt carbonate compounds (Toriumi & Saito, 1975; Geue & Snow, 1971; Hoskins & Urban, 1987). Within the perchlorate group the average Cl—O distance is 1.41 (3) Å. This is slightly shorter than the usual bond distance of 1.43 Å (Ito, Marumo

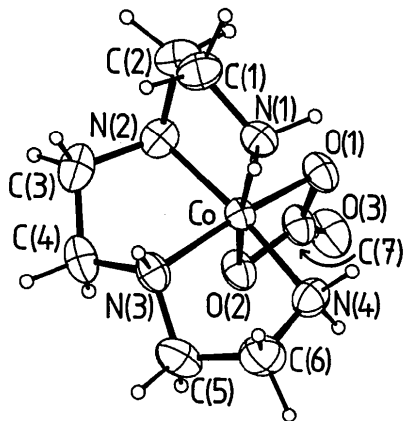


Fig. 1. A perspective view of the (-)<sub>5a6</sub>-*cis- $\beta$* -[Co(trien)CO<sub>3</sub>] cation with thermal ellipsoids scaled to 50% probability. H atoms are included as spheres of arbitrary radius.

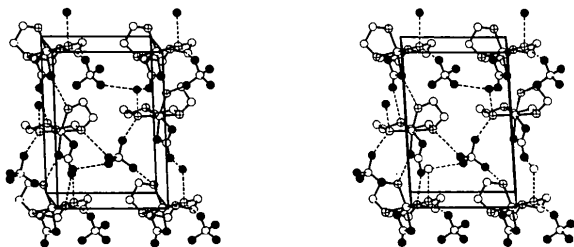


Fig. 2. Stereoview of the crystal packing. Direction of projection is along the *a* axis, the *b* axis is vertical.

& Saito, 1970; Loehlin & Fleischer, 1976). The relatively large thermal parameters probably account for the individual deviations from the average. The bond angles approximate to the regular tetrahedral angle (Table 2). No orientational disorder of the O atoms is observed.

All six H atoms bonded to the N atoms participate in intermolecular hydrogen bonding (Table 2). Five act as donors to the O atoms in the carbonate group and perchlorate anion, and one donates to the O atom of the water molecule. The two H atoms from the water are also involved in intermolecular hydrogen bonding.

The authors are grateful to Professor A. M. Sargeson for supplying the  $(-)_{546}$ -*cis*- $\beta$ -[Co(trien)-CO<sub>3</sub>]ClO<sub>4</sub>.H<sub>2</sub>O sample.

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## Structure of Di- $\mu$ -tetrasulfido-bis{bis[ $\mu$ -(dimethylene)diphenylphosphoranyl-*C,C'*]-digold(II)(*Au–Au*)}

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**Abstract.** [ $\{\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2\}_2\text{S}_4\}_2$ ,  $M_r = 1897.2$ , triclinic,  $P\bar{1}$ ,  $a = 12.048(3)$ ,  $b = 13.243(3)$ ,  $c = 10.756(3)$  Å,  $\alpha = 113.42(2)$ ,  $\beta = 110.92(2)$ ,  $\gamma = 85.40(2)^\circ$ ,  $V = 1467.1(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 2.147$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 10.4$  mm<sup>-1</sup>,  $F(000) = 896$ ,  $T = 298$  K,  $R = 0.0674$  and  $wR = 0.0940$  for 137 variable parameters and 2062 reflections with  $I > 3\sigma(I)$ . The unit cell contains one centrosymmetric molecule consisting of two dimeric Au<sup>II</sup> ylides linked together by pairs of four-atom polysulfide bridges forming a 12-atom heterocyclic ring. The Au–Au distance is 2.671(2) Å and the Au–S bond lengths range from 2.34(2) to 2.41(2) Å.

**Introduction.** We recently described the syntheses and X-ray crystal structures of two unusual products obtained from reactions involving the addition of either H<sub>2</sub>S or Na<sub>2</sub>S to the Au<sup>II</sup> ylide dimer, [Au(CH<sub>2</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Br]<sub>2</sub> (Fackler & Porter, 1986). The products obtained from these reactions were unexpected: instead of simply substituting the axial Br<sup>-</sup> ligands with HS<sup>-</sup>, we obtained instead two compounds in which pairs of Au<sup>II</sup> ylide dimers were linked by four- and five-atom polysulfide bridges. One of these adducts, the more symmetrical of the two consisting of pairs of Au<sup>II</sup> ylide dimers linked by a pair of four-atom polysulfide bridges, crystallized with two molecules of water per unit cell,