

and have discussed the trends in terms of ligand–ligand and d-electron–ligand repulsions. New electron diffraction data<sup>35</sup> are now available on Fe(CO)<sub>5</sub>: the Fe–C (equatorial) bond length is 1.833 (4) Å and the Fe–C (axial) bond length is 1.806 (5) Å. This significant axial shortening in Fe(CO)<sub>5</sub> differs from the axial lengthening in Mn(NO)(CO)<sub>4</sub>. If one assumes that  $\pi$ -bonding properties of NO and CO differ but little, then one can look upon Mn(NO)(CO)<sub>4</sub> as completely analogous to the Mn(CO)<sub>5</sub><sup>–</sup> ion, with the charge residing on the metal. (No structural data are available for this ion.) Then axial shortening in Fe(CO)<sub>5</sub> and

(35) B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robiette, and G. M. Sheldrick, *Acta Cryst.*, in press, and references therein.

axial lengthening in Mn(NO)(CO)<sub>4</sub> are consistent with the idea that the d-electron–ligand repulsions should increase as the negative charge on the central metal increases. The fact that the average Fe–C distance of 1.822 Å is less than the average Mn–C distance of 1.868 Å is also consistent with this view.

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## The Crystal and Molecular Structure of Racemic *cis*- $\beta$ -(Chloroaquotriethylenetetramine)cobalt(III) Perchlorate

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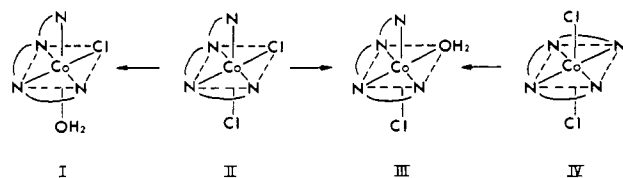
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The crystal and molecular structure of *cis*- $\beta$ -(chloroaquotriethylenetetramine)cobalt(III) perchlorate, [CoClOH<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group Pna2<sub>1</sub> (C<sub>2v</sub><sup>9</sup>, no. 33) of the orthorhombic system, with  $a = 12.09$  (1) Å,  $b = 8.34$  (1) Å,  $c = 15.74$  (2) Å, and  $Z = 4$ . Measured and calculated densities are, respectively, 1.90 and 1.91 g cm<sup>–3</sup>. The structure has been refined by full-matrix least-squares techniques to a final residual  $R = 0.070$  for 1125 independent nonzero reflections. The crystal is composed of  $\beta$ -Co(trien)ClOH<sub>2</sub><sup>2+</sup> cations and ClO<sub>4</sub><sup>–</sup> anions held together by hydrogen bonds and electrostatic forces. The coordination around Co is octahedral with the coordinated water molecule *trans* to those two chelate rings of  $\beta$ -trien which have a common coordination plane. Important bond distances are as follows: mean Co–N, 1.93  $\pm$  0.01 Å; Co–OH<sub>2</sub>, 1.98  $\pm$  0.01 Å; Co–Cl, 2.237  $\pm$  0.004 Å. The X-ray analysis confirms the structure of the complex cation as deduced from kinetic data.

### Introduction

It has been shown by Sargeson, *et al.*,<sup>1,2</sup> that  $\beta$ -Co(trien)Cl<sub>2</sub><sup>+</sup> (II, trien = triethylenetetramine) aquates to form two chloroaquo species (I and III) which can further aquate to form a common diaquo product. From a similar study on the aquation of *trans*-Co(trien)Cl<sub>2</sub><sup>+</sup> (IV) it could be reasoned<sup>1</sup> that isomer I was the only chloroaquo intermediate obtained in this case, and that this was the major chloroaquo isomer formed in the hydrolysis of  $\beta$ -Co(trien)Cl<sub>2</sub><sup>+</sup>. Correct structural assignments to the  $\beta$ -Co(trien)ClOH<sub>2</sub><sup>2+</sup> isomers are particularly important as these structures are the basis of a number of further studies on triethylenetetramine–cobalt(III) complexes.<sup>3–5</sup> A detailed knowledge of the stereochemistry of trien coordinated in the  $\beta$  geometry will also be of interest, particularly with respect to the configuration around that asymmetric secondary amine

nitrogen which connects the two chelate rings sharing a common coordination plane. (The nomenclature follows that of ref 1–3.) An X-ray crystal structure



analysis now removes the uncertainty hitherto attached to the structural assignment for isomer III. A brief report about the crystal structures of this compound and the related compound  $\beta$ -(triethylenetetramine-O-ethylglycylglycine)cobalt(III) perchlorate hydrate has been published.<sup>6</sup>

### Experimental Section

**Crystal Data.**—Racemic *cis*- $\beta$ -[Co(trien)ClOH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> forms dark red crystals. The unit cell is orthorhombic with  $a = 12.09$  (1) Å,  $b = 8.34$  (1) Å,  $c = 15.74$  (2) Å,  $V = 1586.9$  Å<sup>3</sup>,  $D_m =$

(1) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).  
(2) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).  
(3) D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *J. Am. Chem. Soc.*, **89**, 1082 (1967).  
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(5) D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, and A. M. Sargeson, unpublished work.

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1.90 (1) g cm<sup>-3</sup> (by flotation in bromoform-toluene),  $Z = 4$ ,  $D_x = 1.91$  g cm<sup>-3</sup> for C<sub>6</sub>H<sub>20</sub>N<sub>4</sub>O<sub>9</sub>ClCo with FW = 455.5, and  $\mu_{\text{Cu } K\alpha} = 135$  cm<sup>-1</sup>. The space group is Pna2<sub>1</sub> (no. 33) or Pnam (equivalent to Pnma, no. 62) from systematic absences of reflections ( $h0l$  absent for  $h = 2n + 1$ ,  $0kl$  for  $k + l = 2n + 1$ ). The centrosymmetric space group can be eliminated on the basis that the compound contains dissymmetric molecules which cannot have the required point group symmetry (C<sub>s</sub> or C<sub>i</sub>). The solution and refinement of the structure have confirmed the true space group as Pna2<sub>1</sub>.

The unit-cell dimensions (with standard deviations  $\times 10^2$  in parentheses) were calculated from the values of  $\theta$  for a number of zero and upper layer reflections, measured on an equi-inclination diffractometer with Ni-filtered Cu K $\alpha$  radiation [ $\lambda$  (Cu K $\alpha_1$ ) 1.5405 Å,  $\lambda$  (Cu K $\alpha_2$ ) 1.5443 Å].

**X-Ray Data Collection and Reduction.**—A well-formed crystal of dimensions 0.20  $\times$  0.17  $\times$  0.11 mm parallel to  $a$ ,  $b$ , and  $c$  was mounted about its  $b$  axis for data collection. Intensity data were collected with a Buerger-Supper equi-inclination diffractometer using Ni-filtered Cu K $\alpha$  radiation from a fully stabilized X-ray generator. A scintillation counter (Philips PW 1964/10) and pulse-height analyzer (Philips PW 4280) were used. The aperture and collimating system were such that an angle of 2° 50' was subtended at the crystal by the counter aperture. Attenuation of the X-ray beam was not necessary as the maximum count rate was below the region where coincidence losses were significant.

The procedure for measuring the intensity  $I(hkl)$  of a reflection  $hkl$ , given settings of the equi-inclination angles  $\mu$  (crystal) and  $\nu$  (counter) appropriate for a reciprocal lattice zone,<sup>7</sup> was as follows: (1) The counter was brought manually to the position  $\Upsilon(hkl)$ . (2) The crystal was manually rotated to the angle  $\phi_1 = \phi_0(hkl) - \omega(hkl)/2$ , where  $\phi_0(hkl)$  was the calculated setting for the diffraction maximum. The scan angle  $\omega(hkl)$  was normally set at 3° but was increased (and a remeasurement was made) whenever the chart-recorder trace of the rate meter output showed that a reflection had been truncated. (3) The first background,  $B_1$ , was measured for  $t$  sec. (4) The crystal was moved by motor through an angle  $\omega(hkl)$  at 3°/min to  $\phi_2 = \phi_0(hkl) + \omega(hkl)/2$ . Total scan time was  $2t$  sec and the integrated count was  $P$ . (5) The second background,  $B_2$ , was measured for  $t$  sec at the angle  $\phi_2$ .

Steps 3–5 were controlled by an automated stepping mechanism. Peak profiles for all reflections were recorded on a chart recorder to check on peak centering and possible overlapping of adjacent reflections. Data were collected in the range  $10^\circ \leq \Upsilon \leq 140^\circ$  for the zones  $hkl$  ( $0 \leq K \leq 9$ ). Ten strong zero-layer reflections were remeasured at regular intervals.

For each reflection, the net count  $I(hkl)$  was calculated as  $I(hkl) = P - (B_1 + B_2)$ . This corrected count was then tested for significance above background, *i.e.*,  $I(hkl) \geq 2(B_1 + B_2)^{1/2}$ . The usual corrections for Lorentz-polarization effects were applied and a set of corrected relative structure amplitudes  $|F(hkl)|$  was obtained.

Standard deviations in the relative structure amplitudes (both observed and unobserved) were assigned using an expression due to Hoard and Jacobson.<sup>8</sup> The constants  $K_T$ ,  $K_B$ , and  $K_D$  in this expression were given values 0.02, 0.05, and 0, respectively. Using accurate measurements of the crystal dimensions, absorption corrections were applied by the method of Coppens, Leiserowitz, and Rabinovich,<sup>9</sup> using a 4  $\times$  6  $\times$  6 grid with axes parallel to  $a$ ,  $b$ , and  $c$ , respectively. Calculated transmission coefficients ranged from 0.17 to 0.43. Finally, scale factors between the ten sets of ten standard reflections (see above) were calculated by a least-squares method.<sup>10</sup> These scale factors indicated a time-

dependent decrease in the intensities of the standard reflections during the period of X irradiation. Appropriate corrections were applied. A total of 1591 reflections was recorded, of which 466 were unobservably weak.

**Solution and Refinement of the Structure.**—The structure was solved using a sharpened Patterson synthesis and standard Fourier syntheses. It was evident from the spread of electron density around the perchlorate oxygen atoms that they were not rigidly fixed.

Least-squares refinement was then carried out, minimizing the function  $\sum w(|F_o| - s|F_c|)^2$  where the weights  $w = 1/\sigma^2(F)$  and  $s =$  inverse of scale factor to be applied to the  $|F_o|$ . Unobservably weak reflections were given zero weights. After three cycles in which only the coordinates and isotropic temperature factors were varied, the residuals  $R_1 = \sum \Delta/\sum |F_o|$  and  $R_2 = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$  were 0.156 and 0.059, respectively ( $\Delta = ||F_o| - s|F_c||$ ).

Before commencing anisotropic refinement, new weights were derived from an analysis of the variation of  $(1/\Delta^2)$  in ranges of  $|F_o|$  and  $(\sin \theta)/\lambda$ . The  $|F_o|$  dependence could be adequately described by a modified Cruickshank function<sup>11</sup> of the type  $w = K/[1 + ((F_o - p_2)/p_1)^2]$ . The angular dependence was shown to be negligibly small. The weighting scheme was revised after each subsequent refinement cycle. The weighting parameters converged to the values  $K = 0.203$ ,  $p_1 = 34.0$ , and  $p_2 = 53.0$ .

A  $(F_o - F_c)$  synthesis, computed after two cycles of anisotropic refinement, had positive regions of electron density in all 18 expected hydrogen atom positions of the trien ligand. The inclusion of hydrogen atoms at their calculated positions caused an improvement in the residual  $R_1$  from 0.090 to 0.077 and in  $R_2$  from 0.120 to 0.096. The hydrogen atom positions were recalculated after each cycle, but otherwise the hydrogen atom parameters were not refined. After five cycles, the anisotropic refinement converged with residuals  $R_1 = 0.070$  and  $R_2 = 0.076$ . No parameter changed by more than 0.3 of its standard deviation in the last refinement cycle. A final difference Fourier had no positive maxima greater than 0.4 e<sup>-</sup>/Å<sup>3</sup>, the standard deviation of the electron density being 0.15 e<sup>-</sup>/Å<sup>3</sup>.

The atomic scattering factors of Cromer and Waber<sup>12</sup> were used for Co<sup>3+</sup>, Cl, O, N, and C. The values for H were taken from the tabulation by Ibers.<sup>13</sup> In view of the polar nature of the space group, the Co and Cl atoms were treated as anomalous scatterers,<sup>14,14a</sup> with  $\Delta f'$  and  $\Delta f''$  values listed by Cromer.<sup>15</sup> The observed and calculated structure factors are compared in Table I. [Structure factors for unobservably weak reflections have not been reproduced in Table I. None of the calculated values differed from the value assigned to the corresponding  $|F_{\text{unobsd}}|$  by more than  $3\sigma(F_{\text{unobsd}})$ .] The final atomic positions and anisotropic thermal parameters are presented in Table II. Although the refinement was based on data recorded about only one crystal axis, the vibrational parameters correspond to physically reasonable thermal vibrational ellipsoids (Figures 1 and 2).

**Computer Programs.**—Data reduction, Fourier syntheses, and subsidiary calculations were carried out on a CDC 3600 computer using programs written by Dr. J. F. Blount. Isotropic full-matrix least-squares refinement was performed on a CDC 3600 computer, and anisotropic refinement was done on an IBM 360/50 computer, using modified versions of the program

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(14a) NOTE ADDED IN PROOF.—As the result of a discussion with Dr. B. Foxman, we later repeated the refinement in the space group of reverse polarity. The resulting atomic shifts were of the order predicted by Cruickshank and McDonald,<sup>14</sup> and led to unacceptable bond lengths [*e.g.*, Co-N(1) = 2.14 Å, Co-N(3) = 1.71 Å], showing that the original choice of space group was correct.

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(9) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, **18**, 1035 (1965).

(10) (a) A. D. Rae, *ibid.*, **19**, 683 (1965); (b) A. D. Rae and A. B. Blake, *ibid.*, **20**, 586 (1966).

TABLE I  
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR β-[Co(trien)ClO<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC				
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H = 1	.....	.....	H = 2	.....	.....	.....	H = 3	.....	.....	.....	H = 4	.....	.....	.....	H = 5	.....	.....	.....	H = 6	.....	.....	.....	H = 7	.....	.....	.....	H = 8	.....	.....	.....	H = 9	.....	.....	.....	H = 10	.....	.....	.....
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TABLE II  
FRACTIONAL ATOMIC POSITIONAL PARAMETERS<sup>a-c</sup> AND ANISOTROPIC TEMPERATURE FACTORS<sup>d,e</sup> FOR β-[Co(trien)ClO<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

Atom	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z	10 <sup>4</sup> β <sub>11</sub>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>	Atom	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z
O <sub>0</sub>	2125(2)	1274(3)	25058 <sup>b</sup>	23(1)	103(3)	22(1)	3(2)	0(1)	4(2)	H(1)	2908	-0023	1241
Cl(1)	0386(3)	1938(6)	2171(3)	23(2)	174(8)	33(2)	11(4)	-3(2)	5(3)	H(2)	1758	0670	1005
Cl(2)	4570(3)	6694(6)	4225(3)	50(3)	170(8)	24(1)	-1(4)	5(2)	-1(3)	H(3)	3840	2130	0989
Cl(3)	4828(4)	7838(6)	1074(3)	60(3)	133(8)	39(2)	15(4)	-8(2)	-8(3)	H(4)	4735	2309	0258
O(1)	1618(8)	9047(12)	2685(8)	53(7)	111(18)	42(6)	-18(9)	5(6)	21(9)	H(5)	3084	4755	1211
O(2)	4742(13)	5153(21)	3876(13)	117(16)	229(32)	89(12)	46(18)	4(11)	-70(16)	H(6)	1712	4014	1208
O(3)	3594(13)	7285(18)	3887(12)	99(14)	187(27)	116(12)	40(15)	-44(11)	15(15)	H(7)	3373	3385	2401
O(4)	0529(15)	1665(31)	0093(11)	108(15)	466(57)	48(9)	47(24)	-14(9)	10(18)	H(8)	2538	5670	2902
O(5)	0520(13)	7330(26)	3996(11)	74(12)	412(50)	68(11)	114(22)	21(9)	7(17)	H(9)	1246	4781	2661
O(6)	0922(15)	7816(29)	1141(14)	107(16)	466(51)	78(12)	-104(24)	-5(13)	-16(23)	H(10)	2850	4007	4039
O(7)	4218(26)	7344(45)	1798(19)	269(39)	614(102)	122(20)	55(49)	107(25)	75(35)	H(11)	1400	4279	4095
O(8)	4293(23)	7265(38)	0407(18)	225(32)	525(78)	111(18)	-63(37)	-98(20)	-78(30)	H(12)	1209	1732	3815
O(9)	4835(21)	9441(28)	1040(27)	189(27)	238(45)	274(37)	23(27)	-6(26)	-42(38)	H(13)	2713	1646	4829
N(1)	2431(10)	0869(17)	1304(6)	36(9)	142(24)	15(5)	-12(11)	-4(5)	-5(9)	H(14)	2369	-0156	4298
N(2)	2657(10)	3377(17)	2299(9)	32(8)	111(23)	43(8)	6(11)	-7(6)	15(10)	H(15)	4108	2284	3770
N(3)	1895(9)	1295(17)	3662(8)	38(9)	127(22)	22(6)	-10(12)	2(5)	11(10)	H(16)	4339	0280	4095
N(4)	3558(10)	0903(15)	2872(6)	53(9)	111(20)	21(5)	3(11)	-7(6)	11(9)	H(17)	4113	0913	2499
O(1)	2960(14)	2241(22)	0926(11)	60(12)	166(33)	31(9)	13(17)	-2(9)	13(13)	H(18)	3567	-0634	2849
O(2)	2562(15)	3752(22)	1386(14)	62(13)	137(32)	38(10)	-18(16)	1(10)	34(16)				
O(3)	2076(16)	4550(22)	2885(12)	69(13)	126(29)	44(10)	-6(18)	8(11)	-8(13)				
O(4)	2070(15)	3782(23)	3731(13)	61(13)	133(30)	50(9)	5(19)	5(10)	-27(15)				
O(5)	2658(12)	1064(20)	4205(11)	33(10)	131(30)	33(6)	0(14)	2(7)	29(12)				
O(6)	3763(13)	1073(23)	3750(13)	35(12)	195(34)	38(9)	26(17)	8(9)	26(16)				

<sup>a</sup> Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number. <sup>b</sup> Cobalt z coordinate was chosen arbitrarily and remained fixed throughout refinement at 0.25058. <sup>c</sup> Hydrogen atom positions were calculated as follows: tetrahedral primary N, d<sub>N-H</sub> = 0.95 Å; tetrahedral secondary N, d<sub>N-H</sub> = 0.89 Å; methylene C, d<sub>C-H</sub> = 1.084 Å. <sup>d</sup> The form of the anisotropic temperature parameter T is: T = exp{-[h<sup>2</sup>β<sub>11</sub> + k<sup>2</sup>β<sub>22</sub> + l<sup>2</sup>β<sub>33</sub> + 2hkβ<sub>12</sub> + 2hlβ<sub>13</sub> + 2klβ<sub>23</sub>]} . <sup>e</sup> Hydrogen atoms were all assigned fixed isotropic temperature factors of 6.0 Å<sup>2</sup>. <sup>f</sup> The numbering of the perchlorate anions is as follows: atoms O(2)-O(5) are bonded to Cl(1) and atoms O(6)-O(9) are bonded to Cl(2). <sup>g</sup> Hydrogen atoms are numbered sequentially around the trien rings from atom N(1) to atom N(4).

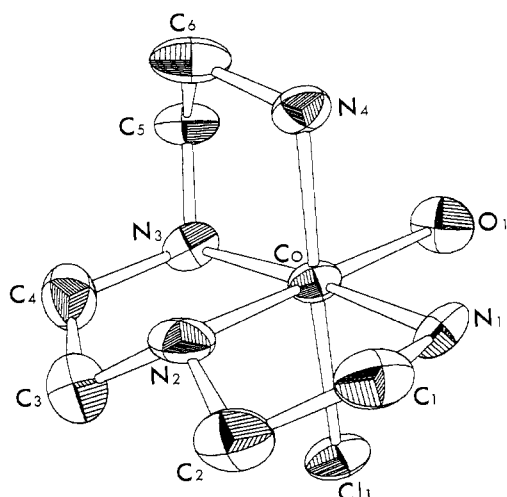


Figure 1.—Perspective view of the  $\beta$ -Co(trien)ClOH<sub>2</sub><sup>2+</sup> cation, showing the thermal vibration ellipsoids.

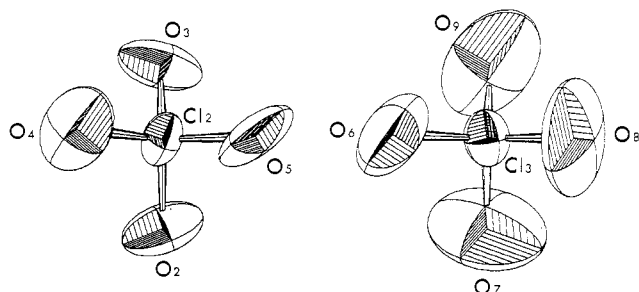


Figure 2.—Perchlorate ions in  $\beta$ -[Co(trien)ClOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, drawn to show ellipsoids of thermal vibration.

ORFLS.<sup>18</sup> The modifications<sup>17</sup> included a rigorous anomalous dispersion option. Estimated standard deviations (including correlation terms) of interatomic parameters were calculated by means of the program ORFFE,<sup>18</sup> adapted for use on an IBM 360/50 computer.

### Description of the Structure

The crystal structure can be described in terms of successive layers of cations and anions in which the Co-Cl bonds of the cations are roughly parallel to the *a* axis. A stereoscopic diagram of the unit cell as viewed down the *b* axis is shown in Figure 3. The crystal contains no water of crystallization. Thermal ellipsoids for the perchlorate anions (Figure 2) indicate high thermal motion or slight disorder of the oxygen atoms. This feature of the structure, the relatively large percentage of unobserved reflections, the effects of fluorescent radiation, and the use of single-axis data have combined to reduce the precision and accuracy of the structure analysis.

**Description of the  $\beta$ -Co(trien)ClOH<sub>2</sub><sup>2+</sup> Cation.**—Intramolecular bond distances and angles with their estimated standard deviations are given in Tables III and IV. The Co<sup>III</sup>-N bond distances are all equal within three standard deviations, although the bonds are not chemically equivalent. Their mean is  $1.93 \pm 0.03$  Å, com-

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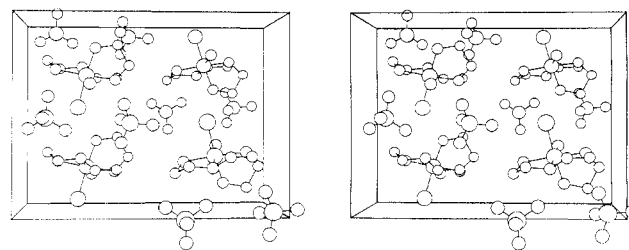


Figure 3.—A stereoscopic diagram of the unit cell of  $\beta$ -[Co(trien)ClOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> viewed down the *b* axis. The *a* axis is vertical and the *c* axis is horizontal.

TABLE III

INTRAMOLECULAR DISTANCES FOR  $\beta$ -[Co(trien)ClOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub><sup>a,b</sup>

Atoms	Distance, Å	Atoms	Distance, Å
Distances within the $\beta$ -Co(trien)ClOH <sub>2</sub> <sup>2+</sup> Cation			
Co-Cl(1)	2.237 (4)	N(2)-C(2)	1.47 (2)
Co-O(1')	1.976 (10)	N(2)-C(3)	1.52 (2)
Co-N(1)	1.957 (12)	C(3)-C(4)	1.48 (3)
Co-N(2)	1.896 (14)	N(3)-C(4)	1.54 (2)
Co-N(3)	1.927 (13)	N(3)-C(5)	1.46 (2)
Co-N(4)	1.936 (12)	C(5)-C(6)	1.51 (2)
N(1)-C(1)	1.44 (2)	N(4)-C(6)	1.48 (2)
C(1)-C(2)	1.53 (3)		
Distances within Perchlorate Anions			
Cl(2)-O(2)	1.41 (2)	Cl(3)-O(6''')	1.43 (2)
Cl(2)-O(3)	1.39 (1)	Cl(3)-O(7)	1.42 (2)
Cl(2)-O(4'')	1.37 (2)	Cl(3)-O(8)	1.32 (2)
Cl(2)-O(5''')	1.45 (1)	Cl(3)-O(9)	1.34 (2)

<sup>a</sup> Symmetry transformations are as follows: prime:  $x, -1 + y, z$ ; double prime:  $1/2 - x, 1/2 + y, 1/2 + z$ ; triple prime:  $1/2 + x, 3/2 - y, z$ . <sup>b</sup> Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number.

parable with 1.96 (2) Å in *trans*-[Co(en)<sub>2</sub>Cl]S<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O,<sup>19</sup> 1.97 (2) Å in D-[Co(en)<sub>2</sub>(L-OOCCH(NH<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>-COO)]ClO<sub>4</sub>,<sup>20</sup> 1.97 (1) Å in [Co(en)<sub>2</sub>CH<sub>3</sub>NHCH<sub>2</sub>CO<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O,<sup>21</sup> and 1.94 (2) Å in *trans*-[Co(en)<sub>2</sub>SO<sub>3</sub>NCS]·2H<sub>2</sub>O.<sup>22</sup> Our Co<sup>III</sup>-Cl bond length, 2.237 (4) Å, lies in the range of other recent determinations: 2.230 (10) Å,<sup>19</sup> 2.303 (6) Å in [Co(NH<sub>3</sub>)<sub>5</sub>Cl]SiF<sub>6</sub>,<sup>23</sup> and 2.286 (2) Å in [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>.<sup>24</sup> (A number of earlier determinations<sup>25-29</sup> of Co<sup>III</sup>-N and Co<sup>III</sup>-Cl bond lengths have been omitted from the comparisons. The reported values were significantly greater but were based on limited data and refinements.) We have been unable to find a value for comparison with our Co<sup>III</sup>-OH<sub>2</sub> distance, 1.98 (1) Å. To our knowledge, the only previously re-

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TABLE IV  
 INTRAMOLECULAR BOND ANGLES FOR  $\beta$ -[Co(trien)ClOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub><sup>a,b</sup>

Atoms	Angle, deg	Atoms	Angle, deg
Angles within the $\beta$ -Co(trien)ClOH <sub>2</sub> <sup>2+</sup> Cation			
N(2)-Co-N(1)	86.0(6)	Co-N(1)-C(1)	110.3(1.0)
N(2)-Co-N(3)	86.4(6)	N(1)-C(1)-C(2)	108.6(1.3)
N(3)-Co-N(4)	86.9(5)	C(1)-C(2)-N(2)	105.2(1.4)
N(1)-Co-O(1')	92.0(5)	C(2)-N(2)-Co	109.7(1.1)
N(3)-Co-O(1')	95.6(5)	Co-N(2)-C(3)	109.6(1.0)
N(2)-Co-N(4)	93.1(5)	N(2)-C(3)-C(4)	105.7(1.4)
N(1)-Co-N(4)	93.5(5)	C(3)-C(4)-N(3)	111.4(1.5)
N(4)-Co-O(1')	85.6(5)	C(4)-N(3)-Co	109.8(1.1)
Cl(1)-Co-N(2)	92.8(4)	Co-N(3)-C(5)	108.1(1.0)
Cl(1)-Co-N(1)	89.6(4)	N(3)-C(5)-C(6)	106.1(1.3)
Cl(1)-Co-O(1')	88.6(3)	C(5)-C(6)-N(4)	107.0(1.4)
Cl(1)-Co-N(3)	90.8(4)	C(6)-N(4)-Co	108.7(1.0)
Angles within Perchlorate Anions			
O(2)-Cl(2)-O(5''')	107.2(1.1)	O(6''')-Cl(3)-O(9)	112.2(1.4)
O(2)-Cl(2)-O(4'')	112.6(1.5)	O(6''')-Cl(3)-O(8)	111.8(1.7)
O(2)-Cl(2)-O(3)	107.4(1.0)	O(6''')-Cl(3)-O(7)	108.0(1.7)
O(4'')-Cl(2)-O(5''')	109.1(1.1)	O(7)-Cl(3)-O(8)	106.1(2.0)
O(3)-Cl(2)-O(4'')	108.3(1.3)	O(8)-Cl(3)-O(9)	109.5(2.2)
O(3)-Cl(2)-O(5''')	112.2(1.1)	O(7)-Cl(3)-O(9)	109.0(2.2)

<sup>a</sup> Symmetry transformations are as follows: prime:  $x, -1 + y, z$ ; double prime:  $1/2 - x, 1/2 + y, 1/2 + z$ ; triple prime:  $1/2 + x, 3/2 - y, z$ . <sup>b</sup> The numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number.

 TABLE V  
 LEAST-SQUARES PLANES

(a) Equations of Planes  $AX + BY + CZ + D = 0$ , Where  $X = ax, Y = by, Z = cz$

—Atoms included in plane—	Plane No.	A	B	C	D
Co, O(1'), N(1), N(2), N(3)	1	-0.9303	0.2843	-0.2318	3.0124
Co, Cl(1), N(1), N(3), N(4)	2	0.3331	0.9281	-0.1665	-1.1940
Co, Cl(1), O(1'), N(2), N(4)	3	0.2003	-0.2308	-0.9522	3.4917

(b) Distances of Atoms from Planes

Atoms	Dev (Å) from		
	Plane 1	Plane 2	Plane 3
Co	0.01	-0.01	0.01
Cl(1)	...	-0.11	-0.04
O(1')	-0.01	...	0.04
N(1)	0.01	0.12	...
N(2)	-0.01	...	0.04
N(3)	0.01	0.12	...
N(4)	...	-0.12	-0.05

ported structures containing such bonds have been disordered.<sup>30-32</sup>

**Conformations of Chelate Rings.**—Since the angles subtended at the cobalt atom by the trien chelate rings are all close to 86° (as in simple ethylenediamine complexes<sup>19,22</sup>), the coordination geometry cannot be that of a precisely regular octahedron. The bonds from Co to N(1), N(2), N(3), and O(1') [=OH<sub>2</sub>] are coplanar (plane 1, Table V), but the four donor atoms in each of the other two coordination planes deviate significantly from them (planes 2 and 3, Table V).

The two outer chelate rings have unsymmetrical skew conformations. The ring carbon atoms C(1) and C(2) lie at -0.12 and 0.54 Å, respectively, from the N(1)-Co-N(2) plane. The corresponding deviations of C(5)

and C(6) from the N(3)-Co-N(4) plane are -0.48 and 0.22 Å. In the central chelate ring, on the other hand, the methylene carbons C(3) and C(4) lie on the same side of the N(2)-Co-N(3) plane (unsymmetrical envelope conformation, deviations 0.73 and 0.23 Å). Models suggest that, given the configuration found at the asymmetric atom N(2), both the distorted coordination geometry and the conformations of the chelate rings in this structure minimize the distortions of the bond angles in the ligand from their normal values. Ibers, *et al.*,<sup>33</sup> recently examined the dihedral angles formed by the C-N and C-C bonds (defined in their paper as angle  $\beta$ ) in a number of tris-ethylenediamine complexes of Co(III), Cr(III), and Ni(II). The most accurately known values of  $\beta$  were quoted for a number of Cr(en)<sub>3</sub><sup>3+</sup> complexes with different anions. The  $\beta$  angles in three independently

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TABLE VI  
 HYDROGEN BONDS IN THE  $\beta$ -[Co(trien)ClOH<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> CRYSTAL

Atoms <sup>a</sup> X-H...Y	Atoms <sup>a</sup> Y...H-X	<i>d</i> (X-H), Å	<i>d</i> (X...Y), Å
O(1')-H-O(5')			2.84
O(1')-H-O(6')			2.77
N(2)-H(7)...Cl(1 <sup>iv</sup> )	Cl(1)...H(7 <sup>v</sup> )-N(2 <sup>v</sup> )	2.5	3.32
N(4)-H(17)...Cl(1 <sup>iv</sup> )	Cl(1)...H(17 <sup>v</sup> )-N(4 <sup>v</sup> )	2.4	3.27

Atoms <sup>a</sup>	Angle, deg	Atoms <sup>a</sup>	Angle, deg
Co-O(1')...O(5')	136	CoN-(2)...Cl(1 <sup>iv</sup> )	106
Co-O(1')...O(6')	109	C(2)-N(2)...Cl(1 <sup>iv</sup> )	92
O(5')...O(1')...O(6')	108	C(3)-N(2)...Cl(1 <sup>iv</sup> )	123
O(1')...O(5')-Cl(2 <sup>v</sup> )	106	N(2)-H(7)...Cl(1 <sup>iv</sup> )	160
O(1')...O(6')-Cl(3 <sup>v</sup> )	119	Co-N(4)...Cl(1 <sup>iv</sup> )	107
Co-Cl(1)...N(2 <sup>v</sup> )	154	C(6)-N(4)...Cl(1 <sup>iv</sup> )	90
Co-Cl(1)...N(4 <sup>v</sup> )	136	N(4)-H(17)...Cl(1 <sup>iv</sup> )	148

<sup>a</sup> Symmetry transformations with respect to the coordinates listed in Table II are as follows: prime:  $x, -1 + y, z$ ; iv:  $1/2 + x, 1/2 - y, z$ ; v:  $-1/2 + x, 1/2 - y, z$ .

determined cations varied from 48.4 to 55.0° (mean value 51.6°). We find that the  $\beta$  angles for the two outer chelate rings in  $\beta$ -trien<sup>34</sup> have values (47.4, 51.8°) similar to those found by Ibers, in contrast to the central chelate ring which has a much smaller  $\beta$  (37.0°).

These conformational features of coordinated  $\beta$ -trien are repeated in a number of other structures containing  $\beta$ -trien complexes (unpublished work). We deduce that the conformation of  $\beta$ -trien is influenced only to a minor extent by the specific crystal packing and hydrogen bonding found in the present complex.

**Intermolecular Contacts.**—Each complex cation makes six hydrogen-bonded contacts (Table VI). Two of these are between the coordinated H<sub>2</sub>O molecule and perchlorate oxygen atoms. The ligand nitrogen atoms N(2) and N(4) are donors, and the coordinated chloride Cl(1) is the acceptor, in two pairs of N-H...Cl bonds which link each complex to the two complexes related to it by the *a*-glide operation.

The shortest nonbonded contacts ( $2.3 \pm 0.1$  Å) are all between hydrogens attached to ligand nitrogen atoms, and perchlorate oxygens: H(2)...O(4), H(12)...O(2<sup>v</sup>), H(18)...O(3), H(1)...O(9). Not surprisingly, if hydrogens are omitted, then the shortest nonbonded contacts of each complex are still with perchlorate oxygens: Cl(1)...O(4), 3.28 Å, Cl(1)...O(2<sup>iv</sup>), 3.30 Å.

### Chemical Significance of This Structure

This crystal structure analysis has shown that the major chloroaquo isomer obtained from the partial hydrolysis of the  $\beta$ -Co(trien)Cl<sub>2</sub><sup>+</sup> ion is that in which the coordinated water molecule is *trans* to those two chelate rings which have a common coordination plane (Figure 3). The X-ray result confirms the structure deduced

from kinetic data and provides the basis for the assignment of structures to a number of other related compounds.<sup>3-5</sup> It is now further established that the trien ligand remains in the  $\beta$  configuration during the hydrolysis of  $\beta$ -Co(trien)Cl<sub>2</sub><sup>+</sup>. The structure analysis has not provided any information which might explain the large difference between the relative rates of formation of the two chloroaquo isomers,<sup>2</sup> although it does rule out the possibility of steric effects.

It has been reasoned from kinetic and stereochemical data that one configuration of  $\beta$ -trien, namely, that in which the proton on atom N(2) (Figure 3) is directed toward the apical chelate ring, is more stable than that in which the configuration at atom N(2) is inverted.<sup>1,2,35-37</sup> The structure analyses of the present complex and of the related cation<sup>3</sup>  $\beta$ -Co(trien)(Gly-GlyOC<sub>2</sub>H<sub>5</sub>)<sup>3+</sup> lead to the same conclusion.

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