CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY,
AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, 2600, AUSTRALIA

The Crystal and Molecular Structure of Racemic α-(Amminechlorotriethylenetetramine)cobalt(III) Nitrate

BY MARK DWYER AND IAN E. MAXWELL

Received August 11, 1969

The crystal and molecular structure of racemic α-(amminechlorotriethylenetetramine)cobalt(III) nitrate, α-[Co(trien)-NH_3Cl]$(NO_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $P2_1/c$ (C_{2h}^5, no. 14) with $a = 7.61$ (1) Å, $b = 14.50$ (2) Å, $c = 13.52$ (2) Å, $\beta = 98.17°$, and $Z = 4$. Measured and calculated densities are, respectively, 1.75 and 1.72 g cm^{-3}. The structure has been refined by full-matrix least-squares techniques to a final residual $R = 0.070$ for 1929 independent nonzero reflections. The crystal is composed of discrete α-Co(trien)NH_3Cl^{2+} cations and NO_3^- anions held together by hydrogen bonds and electrostatic forces. The coordination about the metal ion is octahedral, the trien ligand being coordinated quadridentate in the α configuration. A chloride ion and an ammonia molecule occupy the two remaining coordination sites. The conformations of the trien chelate rings are very puckered and are discussed in some detail.

Introduction

As part of studies on the stereochemistry and mechanisms of hydrolysis of CoN_5X^{2+} complexes (where N_5 may represent ammine groups or multidentate amine complexes or a mixture of both and X is an acido group) a series of complexes of the type Co(trien)NH_3Cl^{2+} were prepared (trien ≡ triethylenetetramine).[1]

There exists the possibility of 14 isomers including all enantiomeric forms; these include two α-trien, eight β-trien, and four *trans*-trien isomers[2] (see Figure 1). A knowledge of the structure of these isomers is essential to any comprehensive study of the mechanisms of hydrolysis in these complexes. In general it is difficult to assign structures to these types of complexes of low symmetry with certainty using spectroscopic and kinetic methods.

An accurate knowledge of the geometry of triethylenetetramine coordinated in various modes (*i.e.*, α, β, and *trans*) is important in understanding the interconversion reactions between the various forms. Further, precise molecular geometry is vital to our more recent studies on the prediction of molecular geometries of multidentate amine complexes using energy minimization techniques.[3]

In this paper we report the crystal structure analysis of the Co(trien)NH_3Cl^{2+} isomer which has the slowest rate of base hydrolysis. Crystals suitable for X-ray analysis were obtained by recrystallization of the dinitrate salt.

Experimental Section

Crystal Data.—Racemic α-[Co(trien)NH_3Cl]$(NO_3)_2$ crystallizes as well-formed red crystals which are stable to both air and X-irradiation. The unit cell is monoclinic with $a = 7.61$ (1) Å, $b = 14.50$ (2) Å, $c = 13.52$ (2) Å, $\beta = 98.17°$, $V = 1476.8$ Å^3, $D_m = 1.75$ (2) g cm^{-3} (by flotation in dibromopropane–isopropyl alcohol), $Z = 4$, $D_x = 1.72$ (1) g cm^{-3} for $C_6H_{21}N_7O_6ClCo$ with FW = 381.7, and $\mu_{Cu\ K\alpha} = 110$ cm^{-1}. The space group is $P2_1/c$ (no. 14) from systematic absences of reflections ($h0l$ absent for $l = 2n + 1$, $0k0$ for $k = 2n + 1$). Cell dimensions (given with standard deviations × 10^2 in parentheses) were calculated from values of θ for a number of high-angle reflections measured on an equiinclination diffractometer with Ni-filtered Cu Kα radiation [λ(Cu Kα_1) 1.5405 Å, λ(Cu Kα_2) 1.5443 Å].

X-Ray Data Collection and Reduction.—Two crystals of dimensions 0.22 × 0.13 × 0.13 mm and 0.17 × 0.22 × 0.20 mm parallel to a, b, and c were mounted about the a and b axes, respectively, for data collection. Data were collected with a Buerger–Supper equiinclination diffractometer, using the control program as described in Freeman, *et al.*[4]

A fully stabilized X-ray generator provided Ni-filtered Cu Kα radiation. A scintillation counter (Philips PW 1964/10) and pulse-height analyzer (Philips PW 4280) were used. The angle subtended at the crystal by the counter aperture was increased with increasing μ in the range (2° 50′–3° 40′). Reflections whose observed maximum count rate was outside the linear range of the counter were measured using an Al attenuator. The scan range was varied using a mosaicity factor of 1.0°.[4] This value was determined by measuring peak profiles of a number of zero-layer reflections. Scan speeds were calculated[4] so as to maintain a constant statistical $\sigma(F_o)/F_o$ ratio (4%) as obtained from counting statistics. The maximum and minimum scan speeds were 15.0 and 2.4°/min, respectively.

Data were collected in the range $10° \leqslant \Upsilon \leqslant 140°$ for zones Hkl, $\bar{H}kl$ $(0 \leqslant H \leqslant 7)$ and hKl, $h\bar{K}l$ $(0 \leqslant K \leqslant 3)$. The net count $I(hkl)$ for each reflection was calculated as $I(hkl) = P - (B_1 + B_2)$ where P is the peak count and B_1 and B_2 are the first and second stationary background counts. A reflection was considered unobserved if $I(hkl) < 2(B_1 + B_2)^{1/2}$. On each layer a standard reflection was remeasured at regular intervals as a check on crystal decomposition, crystal alignment, and instrumental stability. (Variations in (F_o) were less than 3 times their statistical standard deviations.)

Lorentz, polarization, and absorption corrections were applied, the last by the method of Coppens, Leiserowitz, and Rabinovich,[5] with grid sizes of 10 × 6 × 6 (a-axis crystal) and 6 × 6 × 6 (b-axis crystal) parallel to a, b, and c axes, respectively. Transmission coefficients were in the ranges 0.15–0.40 and 0.18–0.34 for the a- and b-axis crystals, respectively. Estimated standard deviations in the relative structure factor amplitudes (observed and unobserved) were calculated using counting statistics.

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[1] A. R. Gainsford and D. A. House, *Inorg. Nucl. Chem. Letters*, **4**, 621 (1968); D. A. Buckingham, M. Dwyer, and A. M. Sargeson, to be submitted for publication.

[2] The nomenclature used to distinguish between the various modes of coordination of triethylenetetramine follows that used in a number of previous papers: *e.g.*, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

[3] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, to be submitted for publication.

[4] H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and A. Webster, in press.

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

Table I

Observed and Calculated Structure Amplitudes (in Electrons × 10) for α-[Co(trien)NH$_3$Cl](NO$_3$)$_2$

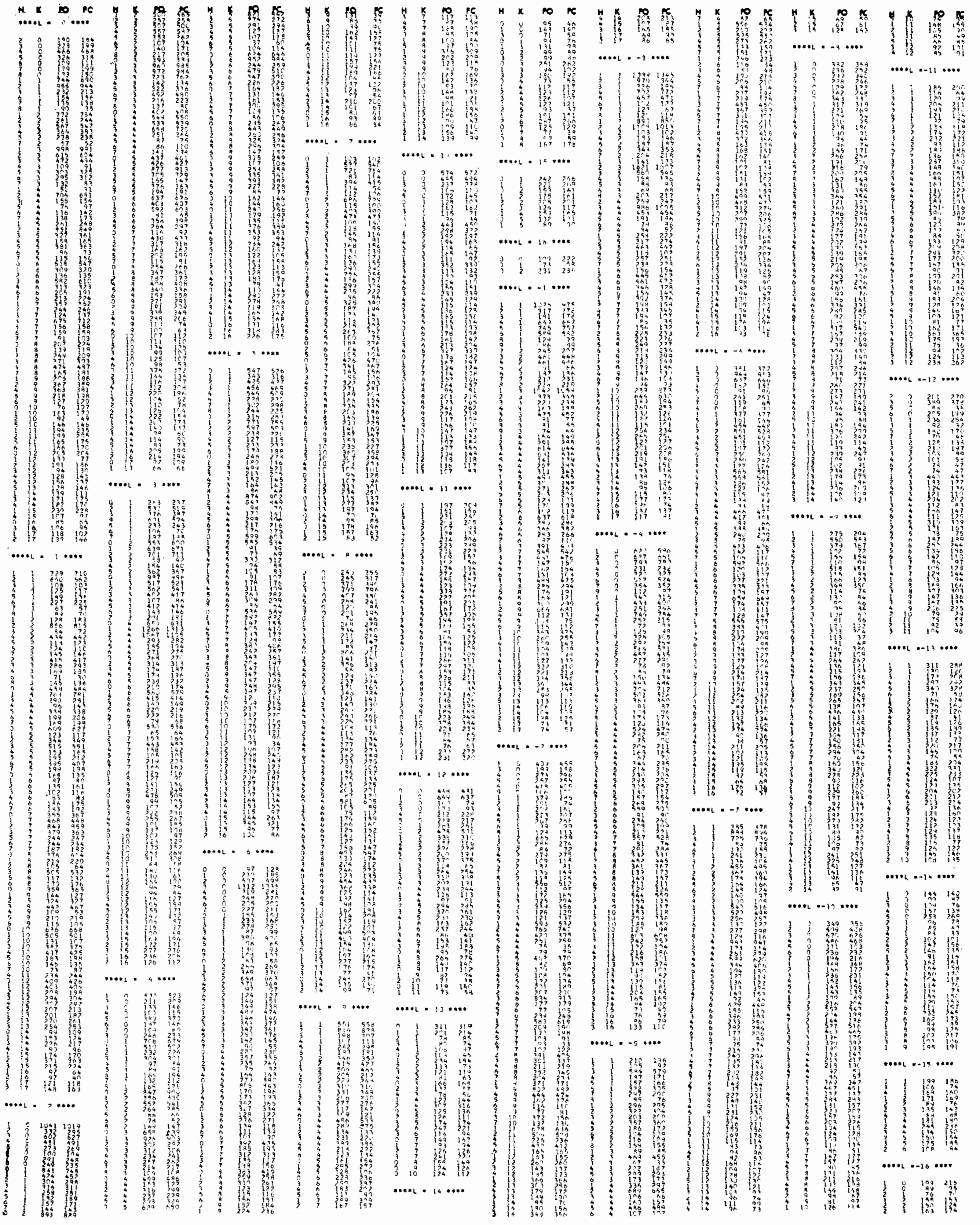
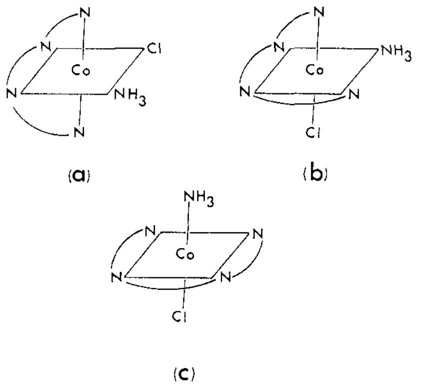


TABLE II

FRACTIONAL ATOMIC POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS FOR α-[Co(trien)NH$_3$Cl](NO$_3$)$_2$[a,b]

ATOM	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	3649(2)	4306(1)	3034(1)	0129(2)	0028(1)	0024(1)	-0004(1)	0001(1)	-0004(1)
Cl	5806(3)	5268(1)	3767(1)	0180(4)	0044(1)	0038(1)	-0031(2)	0001(2)	-0007(1)
O(1)	10472(8)	3298(5)	4831(4)	0178(13)	0077(4)	0049(4)	-0023(6)	-0003(5)	-0008(3)
O(2)	8853(8)	3204(4)	3398(4)	0238(14)	0065(4)	0049(4)	0021(6)	-0010(6)	0005(3)
O(3)	7924(9)	2666(7)	4731(7)	0178(15)	0132(7)	0143(8)	-0052(9)	0020(9)	0061(6)
O(4)	4659(8)	1311(5)	3829(5)	0161(13)	0061(4)	0097(5)	-0003(6)	0027(6)	-0018(4)
O(5)	2830(10)	0181(4)	3810(5)	0385(20)	0037(4)	0093(5)	-0034(7)	0091(8)	-0010(3)
O(6)	1967(9)	1566(5)	3956(6)	0192(14)	0054(4)	0147(7)	0004(6)	0062(8)	-0013(4)
N(1)	1919(8)	4851(4)	3807(4)	0158(13)	0039(3)	0041(4)	-0004(6)	0022(5)	-0006(3)
N(2)	2829(8)	5243(4)	2030(4)	0169(13)	0035(3)	0037(4)	-0004(6)	0000(5)	0002(3)
N(3)	1985(9)	3458(4)	2274(4)	0170(14)	0035(3)	0039(4)	-0012(5)	-0004(6)	-0004(3)
N(4)	5387(8)	3798(4)	2252(4)	0146(13)	0038(3)	0042(4)	0017(6)	0012(5)	-0002(3)
N(5)	4245(9)	3397(4)	4127(4)	0178(14)	0038(4)	0035(4)	-0002(6)	-0005(5)	0004(3)
N(6)	9071(9)	3049(5)	4333(5)	0146(14)	0042(4)	0061(5)	0014(6)	0008(7)	0000(3)
N(7)	3158(10)	1015(5)	3862(5)	0196(16)	0040(4)	0040(4)	0013(7)	0023(6)	-0004(3)
C(1)	0796(12)	5555(6)	3231(6)	0197(18)	0054(5)	0050(5)	0016(8)	0030(8)	-0006(4)
C(2)	1924(12)	5990(6)	2523(6)	0223(20)	0034(4)	0054(5)	0024(8)	0000(8)	0000(4)
C(3)	1667(12)	4812(6)	1170(5)	0238(20)	0047(5)	0029(4)	0020(8)	-0030(7)	0001(4)
C(4)	0757(12)	3976(6)	1496(6)	0182(18)	0049(5)	0050(5)	0000(8)	-0021(8)	-0004(4)
C(5)	3016(12)	2713(6)	1861(6)	0227(20)	0029(4)	0060(6)	0006(8)	-0012(9)	-0022(4)
C(6)	4573(12)	3137(7)	1494(6)	0217(20)	0055(6)	0049(5)	0023(9)	0008(8)	-0008(4)

[a] Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding numbers. [b] The form of the anisotropic parameter is: $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.



(a) (b) (c)

Figure 1.—Some topographical isomers of Co(trien)NH$_3$Cl^{2+}: (a) α isomer; (b) β_2 isomer; (c) *trans* isomer.

Scale factors were calculated between different reciprocal layers by a least-squares procedure.[6,7] A total of 2559 independent reflections were obtained (630 were unobservably weak).

Solution and Refinement of the Structure.—The structure solution was carried out by the usual sharpened Patterson and Fourier syntheses. An ($F_o - F_c$) synthesis in the final stages of solution indicated no water of crystallization. Full-matrix least-squares refinement was used to minimize the function $\Sigma w(|F_o| - s|F_c|)^2$ where w is the weight given to each reflection and s is the inverse of the scale factor to be applied to $|F_o|$. Unobserved data were assigned zero weights. Two cycles were carried out using unit weights and varying an overall scale factor, atomic coordinates, and isotropic temperature factors. The residuals $R_1 = \Sigma\Delta/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ were 0.144 and 0.174, respectively ($\Delta = ||F_o| - s|F_c||$). After a further cycle in which the Co and Cl atoms were given anisotropic temperature factors the residuals were $R_1 = 0.116$ and $R_2 = 0.151$.

An analysis of $\langle 1/\Delta^2\rangle$ in ranges of $|F_o|$ and $(\sin\theta)/\lambda$ at this stage indicated no systematic dependence on $|F_o|$; hence unit weights were maintained. This type of analysis was repeated at the end of each subsequent least-squares cycle. All atoms were assigned anisotropic temperature factors in the next cycle which resulted in residuals $R_1 = 0.099$ and $R_2 = 0.154$.

An ($F_o - F_c$) synthesis indicated the presence of significant electron density in the regions expected for hydrogen atoms of the trien ring. The inclusion of 18 trien hydrogen atoms in calculated positions (tetrahedral primary N, $d_{\text{N-H}} = 0.95$ Å; tetrahedral secondary N, $d_{\text{N-H}} = 0.89$ Å; methylene C, $d_{\text{C-H}} = 1.084$ Å) decreased the residuals to $R_1 = 0.095$ and $R_2 = 0.139$. Hence these hydrogen atoms were included in all subsequent cycles with fixed coordinates and temperature factors, the H atom coordinates being recalculated after each cycle. After three more cycles of anisotropic refinement a small F_o dependence was observed from the weighting-scheme analysis. New weights were assigned by fitting the $|F_o|$ dependence to a modified Cruickshank function[8] of the type $w = K/[1 + ((F_o - P_2)/P_1)^2]$. After two more cycles the refinement converged with residuals $R_1 = 0.070$ and $R_2 = 0.074$. The weighting-scheme parameters converged to the values $K = 0.265$, $P_1 = 32.2$, and $P_2 = 38.0$. The maximum parameter shift in the final cycle was 0.25σ. A final difference Fourier map had no positive maxima greater than 0.48 e$^-$/Å^3 except in the vicinity of the cobalt atom (maximum 0.55 e$^-$/Å^3).

Scattering factor tables used for Co^{3+}, Cl$^-$, O, N, and C were those of Cromer and Waber[9] and the anomalous scattering terms $\Delta f'$ and $\Delta f''$ for Co and Cl were those listed by Cromer.[10] Calculated and observed structure factor amplitudes are compared in Table I and the final atomic positions and anisotropic thermal parameters with standard deviations are presented in Table II.

A perspective diagram of the complex cation, showing atom numbering and ellipsoids of thermal motion, is given in Figure 2.

Computer Programs.—Data reduction, Fourier synthesis,

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(6) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(7) A. D. Rae and A. B. Blake, *ibid.*, **20**, 586 (1966).

(8) J. S. Rollett and O. S. Mills in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 117.

(9) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(10) D. T. Cromer, *ibid.*, **18**, 17 (1965).

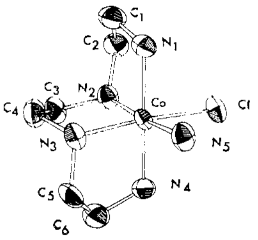

Figure 2.—Perspective view of the α-$Co(trien)NH_3Cl^{2+}$ cation showing ellipsoids of thermal motion.

and subsidiary calculations were carried out on a CDC 3600 computer using programs written by Dr. J. F. Blount. Full-matrix least-squares refinement was carried out on an IBM 360/50 computer, using a version of program ORFLS[11] which included a rigorous anomalous dispersion option. Figures 2 and 3 were produced using program ORTEP.[12]

Description of the Structure

This structural analysis has shown that the $Co(trien)NH_3Cl^{2+}$ isomer with the slowest rate of base hydrolysis has trien coordinated in the α form.

TABLE III

INTRAMOLECULAR DISTANCES FOR α-$[Co(trien)NH_3Cl](NO_3)_2$

Atoms	Dist, Å	Atoms	Dist, Å
Distances within the α-$Co(trien)NH_3Cl^{2+}$ Cation			
Co–Cl	2.271 (2)	C(2)–N(2)	1.49 (1)
Co–N(1)	1.960 (6)	N(2)–C(3)	1.49 (1)
Co–N(2)	1.959 (6)	C(3)–C(4)	1.49 (1)
Co–N(3)	1.950 (6)	C(4)–N(3)	1.51 (1)
Co–N(4)	1.952 (6)	N(3)–C(5)	1.49 (1)
Co–N(5)	1.984 (6)	C(5)–C(6)	1.48 (1)
N(1)–C(1)	1.48 (1)	C(6)–N(4)	1.47 (1)
C(1)–C(2)	1.51 (1)		
Distances within the Nitrate Anions			
N(6)–O(1)	1.23 (1)	N(7)–O(4)	1.23 (1)
N(6)–O(2)	1.27 (1)	N(7)–O(5)	1.24 (1)
N(6)–O(3)	1.22 (1)	N(7)–O(6)	1.23 (1)

Intramolecular bond distances and angles with their estimated standard deviations are given in Tables III and IV. The Co^{III}–N bond distances of the α-trien ring do not differ by more than one standard deviation from their mean (1.955 (9) Å). Comparable values are 1.955 (9) Å in Dβ$_2$-(*SSS*)-[Co(trien)(*S*)-pro]$ZnCl_4$,[13] 1.96 (1) Å in Lβ$_2$-(*SSS*)-[Co(trien)(*S*)-pro]$I_2 \cdot 2H_2O$,[14] and 1.93 (1) Å in β-$[Co(trien)ClOH_2](ClO_4)_2$.[15] However, the Co–N(5) distance appears to be significantly longer than those of the trien ring. This bond length (1.984 (6) Å) is five standard deviations longer than the mean Co–N(trien) distance. This distance is considerably longer than 1.936 (15) Å which has been found in $[Co(NH_3)_6]I_3$.[16] The absence of H atom contributions to the NH_3 may account for some of this difference. However, nonbonded interactions with H atoms on the trien rings may also be involved.

TABLE IV

INTRAMOLECULAR BOND ANGLES FOR α-$[Co(trien)NH_3Cl](NO_3)_2$

Atoms	Angle, deg	Atoms	Angle, deg
Angles within the α-$Co(trien)NH_3Cl^{2+}$ Cation			
N(1)–Co–N(2)	85.3 (3)	N(1)–C(1)–C(2)	106.5 (6)
N(1)–Co–N(3)	95.8 (2)	C(1)–C(2)–N(2)	108.7 (7)
N(1)–Co–Cl	91.0 (2)	C(2)–N(2)–C(3)	113.1 (6)
N(1)–Co–N(5)	88.3 (3)	Co–N(2)–C(2)	108.4 (4)
N(4)–Co–N(2)	93.4 (2)	Co–N(2)–C(3)	110.1 (5)
N(4)–Co–N(3)	85.2 (2)	N(2)–C(3)–C(4)	111.0 (6)
N(4)–Co–N(5)	93.0 (3)	C(3)–C(4)–N(3)	110.1 (6)
N(4)–Co–Cl	88.0 (2)	C(4)–N(3)–C(5)	114.0 (6)
Cl–Co–N(5)	90.5 (2)	Co–N(3)–C(5)	108.5 (4)
Cl–Co–N(2)	90.9 (2)	Co–N(3)–C(4)	110.2 (5)
N(3)–Co–N(5)	92.0 (3)	N(3)–C(5)–C(6)	108.2 (7)
N(3)–Co–N(2)	87.3 (3)	C(5)–C(6)–N(4)	108.3 (7)
Co–N(1)–C(1)	112.3 (5)	C(6)–N(4)–Co	111.8 (4)
Angles within the Nitrate Anions			
O(1)–N(6)–O(2)	118.2 (6)	O(4)–N(7)–O(5)	121.5 (7)
O(1)–N(6)–O(3)	120.6 (8)	O(4)–N(7)–O(6)	118.8 (7)
O(2)–N(6)–O(3)	121.2 (7)	O(5)–N(7)–O(6)	119.7 (7)

The average C–N (1.49 (1) Å) and C–C (1.49 (1) Å) distances in the α-trien ligand are similar to those found in other trien structures.[13–15]

The Co–Cl distance 2.271 (2) Å compares with 2.286 (2) Å found in $[Co(NH_3)_5Cl]Cl_2$[17] and is significantly longer than 2.237 (4) Å in β-$[Co(trien)ClOH_2](ClO_4)_2$.[15]

Conformations of α-trien Chelate Rings.—The angles subtended at the cobalt atom by the outer two trien rings (85.3 (3) and 85.2 (3)°) are equal to within one standard deviation. However, the angle subtended by the inner chelate ring is expanded to 87.3 (3)°, about seven standard deviations from the angle subtended at each of the other rings. All these angles are within the range of values found in other Co^{III}–trien complexes.[13–15] These chelate angles combine to produce significant distortions from regular octahedral coordination about the cobalt ion. The distortion is evident in the deviations from planarity of atoms Co, Cl, N(2), N(3), and N(5) (plane 1, Table V).

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 Cl N(2) N(3) N(5)	1	0.7640	−0.3665	−0.5310	2.7627
Co N(1) N(2) N(4) N(5)	2	−0.6399	−0.6269	−0.4444	7.1212
Co Cl N(1) N(3) N(4)	3	−0.1474	0.6874	0.7112	−1.1068

(b) Distances of Atoms from Planes

	Dev (Å) from		
Atoms	Plane 1	Plane 2	Plane 3
Co	−0.01	0.00	−0.03
Cl	0.11	. . .	0.01
N(1)	. . .	−0.02	0.00
N(2)	−0.12	0.02	. . .
N(3)	0.13	. . .	0.02
N(4)	. . .	−0.02	0.00
N(5)	−0.11	0.02	. . .

The configurations at the two asymmetric nitrogen atoms N(2) and N(3) are fixed by the α-trien geometry. The outer two chelate rings adopt unsymmetrical-skew

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(11) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(13) H. C. Freeman, L. G. Marzilli, and I. E. Maxwell, to be submitted for publication.

(14) H. C. Freeman and I. E. Maxwell, in press.

(15) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **8**, 1293 (1969).

(16) N. E. Kime and J. A. Ibers, *Acta Cryst.*, **B25**, 168 (1969).

(17) G. G. Messmer and E. L. Amma, *ibid.*, **B24**, 417 (1968).

conformations whereas the central chelate ring is almost in a symmetrical-skew form. Distances of carbon atoms from their relevant N–Co–N planes are: C(1), 0.17 and C(2) −0.46 Å; C(3), −0.22 and C(4), 0.27 Å; C(5), 0.50 and C(6), −0.10 Å. These conformations are such that the α-trien moiety, excluding the other two substituents, has an approximate twofold axis through the cobalt ion and bisecting the C(3)–C(4) bond.

Dihedral angles about the C–C bonds are: C(1)–C(2), 46.5°; C(3)–C(4), 37.2°; C(5)–C(6), 44.9°. Ligand angular strain is further evidenced at the two asymmetric N centers, N(2) and N(3). The C(2)–N(2)–C(3) [113.1 (6)°] and C(4)–N(3)–C(5) [114.0 (6)°] angles are 6σ and 7σ, respectively, from the strain-free tetrahedral value.

The most marked conformational difference between α-trien and β-trien occurs at the central chelate ring. This ring adopts an unsymmetrical envelope conformation for β-trien,[13–15] in contrast to the almost symmetrical-skew conformation found in the present structure. It is interesting that the dihedral angle about the C–C bond of this chelate ring is rather small in both α and β forms.

A detailed analysis of the conformational strain for trien coordinated in various forms, using energy-minimization techniques, is in progress.[18]

Hydrogen Bonding and Nonbonded Contacts in the α-[Co(trien)NH$_3$Cl](NO$_3$)$_2$ Crystal.—Table VI lists the hydrogen bonds and identifies the proton-donor and -acceptor atoms along with the relevant bonding angles. Nonbonded contacts less than 3.5 Å are listed in Table VII and the unit cell as viewed down the a axis is shown in Figure 3.

TABLE VI

HYDROGEN BONDING IN THE α-[Co(trien)NH$_3$Cl](NO$_3$)$_2$ CRYSTAL

Atoms X–H···Y	d(X···Y), Å	Atoms X–H···Y	d(X···Y), Å
N(1)–H···O(1)^{vi}	2.94	N(5)–H···O(3)	3.00
N(2)–H···O(4)^{iii}	2.83	N(5)–H···O(1)^{vi}	3.16
N(3)–H···O(2)^{vi}	3.03	N(5)–H···O(4)	3.07
N(4)–H···O(5)^{iii}	2.91	N(5)–H···O(6)	3.16
N(4)–H···O(2)	2.99		

Atoms	Angle, deg	Atoms	Angle, deg
Co–N(1)···O(1)^{vi}	106	C(6)–N(4)···O(2)	115
C(1)–N(1)···O(1)^{vi}	123	Co–N(4)···O(2)	116
Co–N(2)···O(4)^{iii}	120	Co–N(5)···O(3)	123
C(3)–N(2)···O(4)^{iii}	106	Co–N(5)···O(4)	125
C(2)–N(2)···O(4)^{iii}	100	Co–N(5)···O(1)^{vi}	98
C(5)–N(3)···O(2)^{vi}	126	Co–N(5)···O(6)	116
C(4)–N(3)···O(2)^{vi}	88	O(3)···N(5)···O(1)	139
Co–N(4)···O(2)^{vi}	108	O(3)···N(5)···O(4)	65
C(6)–N(4)···O(5)	107	O(1)···N(5)···O(6)	58
Co–N(4)···O(5)	114	O(6)···N(5)···O(4)	40

☛ Each complex cation has nine hydrogen bonds to the oxygen atoms of four adjacent nitrate groups. The cations and anions form chains running approximately parallel to the a and b axes and intersecting at the cations. There are hydrogen bonds neither between cations nor in the c-axis direction. Thus the cations and anions form hydrogen-bonded sheets perpendicular to the c axis.

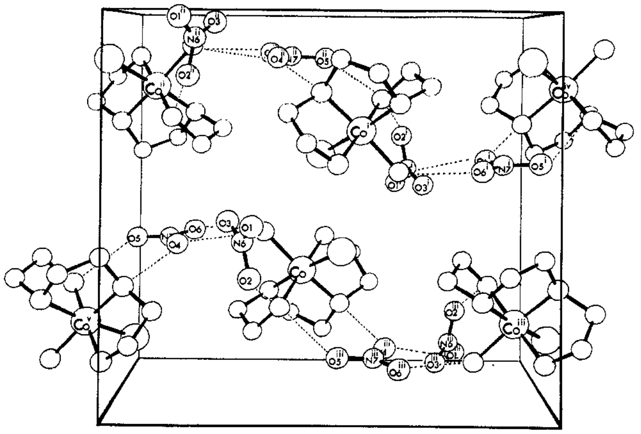

Figure 3.—Perspective view of the unit cell of racemic α-[Co(trien)NH$_3$Cl](NO$_3$)$_2$ down the a axis. The b axis is horizontal and the c axis is vertical. Symmetry transformations are given in footnote a, Table VII.

TABLE VII

CLOSE CONTACTS IN THE α-[Co(trien)NH$_3$Cl](NO$_3$)$_2$ CRYSTAL[a]

Atoms X···Y	d(X···Y), Å	Atoms X···Y	d(X···Y), Å
C(1)···O(1)^{i}	3.36	C(4)···O(2)^{vi}	3.32
C(2)···O(2)^{iii}	3.46	C(4)···O(5)^{ix}	3.22
C(2)···O(4)^{iii}	3.42	C(5)···O(1)^{viii}	3.45
C(2)···O(6)^{ix}	3.43	C(5)···O(6)	3.47
C(3)···O(5)^{ix}	3.47	Cl···N(5)^{i}	3.45
C(3)···O(5)^{x}	3.43	Cl···N(1)^{i}	3.49

[a] Symmetry transformations with respect to the coordinates listed in Table II are as follows: none, x, y, z; i, $1 - x, 1 - y, 1 - z$; ii, $x, {}^1/_2 - y, {}^1/_2 + z$; iii, $1 - x, {}^1/_2 + y, {}^1/_2 - z$; iv, $x, 1.5 - y, {}^1/_2 + z$; v, $1 - x, y - {}^1/_2, {}^1/_2 - z$; vi, $x - 1, y, z$; vii, $1 + x, y, z$; viii, $x - 1, {}^1/_2 - y, z - {}^1/_2$; ix, $-x, {}^1/_2 + y, {}^1/_2 - z$; x, $x, {}^1/_2 - y, z - {}^1/_2$.

There are four H bonds of approximately equal length from nitrate oxygen atoms to the ammine nitrogen atom N(5) containing only three protons. Model building indicates that the bonding can best be explained by a bifurcated interaction between N(5) and the oxygen atoms O(4) and O(6) of the same nitrate group. The proton on atom N(5) which is involved in the bifurcated interaction has been located on a final ($F_o - F_c$) synthesis. A peak ($\sim$0.4 e$^-$/Å^3) was found 1 Å away from atom N(5) along the bisector of angle O(4)–N(5)–O(6), 40°. This very small angle is consistent with such a hydrogen-bonding scheme. A similar geometry was found in Lβ_2-[Co(trien)(S)-pro)]I$_2$·2H$_2$O[14] crystals where a proton on a water molecule interacts equally with two oxygen atoms of the same coordinated carboxyl group.

Acknowledgments.—The authors are very grateful to Dr. H. C. Freeman for making available his automated diffractometer and for kindly reading the manuscript and also to Dr. M. Sterns for the use of her single-crystal camera facilities. The interest and encouragement offered by Drs. A. M. Sargeson and D. A. Buckingham are gratefully acknowledged. Cal-

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[18] D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, work in progress.

culations were carried out on the CDC 3200/3600 computers of the CSIRO Division of Computing Research, using programs written or adapted by Dr. J. F. Blount, and on an IBM 360/50 computer at the Computer Centre, Australian National University, with refinement and function-error programs supplied by Dr. W. T. Robinson. The diffraction data were recorded on an automatic diffractometer operated under Grant 65/15552 from the Australian Research Grants Committee.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CENTER FOR ADVANCED STUDIES,
THE UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA 22901

The Crystal and Molecular Structure of the Dicesium Salt of the Di-μ-carbonyl-bis[π-(3)-1,2-dicarbollylcarbonyliron] Anion, $Cs_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe_2(CO)_4\cdot(CH_3)_2CO\cdot H_2O$

BY PETER T. GREENE AND ROBERT F. BRYAN

Received October 28, 1969

The crystal and molecular structure of the dicesium salt of the di-μ-carbonyl-bis[π-(3)-1,2-dicarbollylcarbonyliron] anion, $Cs_2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe_2(CO)_4$, has been determined as its acetone hydrate by single-crystal X-ray diffraction methods. Of the 4639 reflections measured by counter diffractometry, 2500 were included in the refinement. The crystal system is triclinic, space group $P\bar{1}$. Crystal data are: $a = 11.57$ (2), $b = 15.19$ (3), $c = 9.35$ (2) Å, $\alpha = 88°\ 48\ (5)'$, $\beta = 76°\ 54\ (5)'$, $\gamma = 112°\ 18\ (5)'$, $d_m = 1.86$ (1) g cm^{-3}, $Z = 2$, $d_o = 1.87$ (1) g cm^{-3}. Structure determination was by the heavy-atom method and refinement was carried out by the block-diagonal least-squares technique with anisotropic thermal parameters for the cesium and iron atoms. Hydrogen atoms were included in calculated positions but not refined. Final values of R and R_1 are 0.045 and 0.052 (0.080 and 0.068 for all 4639 reflections). The anion consists of two $B_9C_2H_{11}Fe(CO)_2$ fragments joined through a double carbonyl bridged Fe–Fe bond of length 2.591 (5) Å. It has a cisoid, almost totally eclipsed, conformation with a close approach to C_2 symmetry. The bridge is asymmetric with Fe–C distances of 1.90, 1.98, 1.90, and 1.99 Å (esd's 0.01 Å) around the bridge. The two Fe–Fe–C planes in the bridge make an angle of 164° about the Fe–Fe axis and are inclined away from the icosahedra. The normals from the basal planes of the cages to the Fe atoms make angles of 140 and 142° with the Fe–Fe axis. These angles are larger than in analogous cyclopentadienyl complexes and are presumably so because of H · · · H repulsions between the cages. The normals from Fe to the basal planes of the cages pass through the center of gravity of the plane in each case and are 1.57 and 1.59 (1) Å. The terminal Fe–C carbonyl distances are 1.69 and 1.70 (1) Å. C–O distances are in the range 1.16–1.18 (2) Å. The mean B–B bond length is 1.787 (5) Å; mean B–C is 1.721 (8) Å. Within the crystal the Cs ions are irregularly coordinated to the oxygen atoms of the solvent molecules. The anions pack so that the icosahedra come into contact across the centers of symmetry along the c axis.

Introduction

Hawthorne and his collaborators have shown that the dicarbollyl anion $B_9C_2H_{11}^{2-}$ forms stable complexes with a variety of transition metal derivatives.[1,2] X-Ray analysis of some of these compounds has revealed that the dicarbollyl cage may be symmetrically π bonded to the metal atom to form a completed icosahedron.[3-5]

Recently, the tetramethylammonium salt of $[B_9C_2H_{11}Fe(CO)_2]_2^{2-}$ was synthesized by Hawthorne and Rühle,[6] who suggested that the anion had a stereochemistry similar to the isoelectronic complex *trans*-$[\pi\text{-}C_5H_5Fe(CO)_2]_2$ which has been structurally characterized by X-ray diffraction methods.[7] This analysis of the crystal structure of the dicesium salt of the same anion, undertaken to establish its solid-state stereochemistry, has shown that in this case the anion adopts a cisoid conformation analogous to that found in the newly isolated and characterized *cis*-$[\pi\text{-}C_5H_5Fe(CO)_2]_2$.[8]

Measurement of Crystal and Intensity Data

Professor M. F. Hawthorne kindly supplied a sample of dicesium di-μ-carbonyl-bis[π-(3)-1,2-dicarbollylcarbonyliron]. The crystals were thin, elongated, dark red platelets from which suitable specimens for X-ray study had to be cut. The crystals have been shown by the X-ray analysis to contain one molecule each of acetone and of water of solvation in the asymmetric unit.

Crystal Data.—For $Cs_2[B_9C_2H_{11}(CO)_2Fe]_2\cdot(CH_3)_2CO\cdot H_2O$ the data are: mol wt 830.4, triclinic, $a = 11.57$ (2), $b = 15.19$ (3), $c = 9.35$ (2) Å, $\alpha = 88°\ 48\ (5)'$, $\beta = 76°\ 54\ (5)'$, $\gamma = 112°\ 18\ (5)'$, $V = 1471$ Å^3, $F(000) = 788$, $\mu = 35.2$ cm^{-1}, λ 0.7107 Å.

The unit cell parameters were derived from 25° pre-

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