the C—As—C bond angle would have to be increased to 104° and the C—S—C angle would have to be increased to 114°. This additional distortion apparently requires more energy than would be gained by a planar-bonding scheme.

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Carbonato[tris(2-aminoethyl)amine]cobalt(III) Chloride Trihydrate, [Co(C₆H₁₈N₄)(CO₃)]Cl.3H₂O

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Abstract. $M_r = 354 \cdot 7$, monoclinic, $P2_1/c$, $a = 7 \cdot 177$ (1), $b = 19 \cdot 286$ (2), $c = 10 \cdot 743$ (3) Å, $\beta = 93 \cdot 86$ (4)°, $V = 1483 \cdot 6$ (8) Å³, $D_m = 1 \cdot 58$ (1), $D_x = 1 \cdot 588$ (1) g cm⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $\mu = 13 \cdot 6$ cm⁻¹, $T = 295$ (1) K, $F(000) = 744$. The final discrepancy factors were $R_F = 2 \cdot 0\%$ and $wR_F = 2 \cdot 7\%$ for those 1985 reflections $[F_o > 2\sigma(F_o)]$ in the range $3 \cdot 5° < 2\theta < 47°$. The Co^{III} ion is surrounded by four N atoms from the tetradentate amine ligand and by two O atoms from the chelated carbonate ligand in a somewhat distorted octahedron, *e.g.* the angle O—Co—O = 68·46 (5)°. One of the Co—O bonds is longer than the other, 1·931 (1) and 1·910 (1) Å, which suggests that the bond breaking during decarboxylation preferentially takes place at the site of the longer bond.

Introduction. In recent years, many interesting studies on cobalt(III) and chromium(III) complexes containing tris(2-aminoethyl)amine (β,β',β''-triaminotriethylamine, tren) as a tetradentate ligand have been undertaken (*e.g.* Dasgupta & Harris, 1971, 1978; Madan, Reiff & Bailar, 1965; Zipp & Madan, 1976) since the tripodal nature of the ligand offers a

stereochemically rigid system. It was observed that the acid-catalyzed Co—O bond breaking rate in [Co(tren)CO₃]⁺ is larger than that for the corresponding ethylenediamine and tetraammine analogues (Dasgupta & Harris, 1971). It was also observed that *cis*-[Co(tren)Cl₂]⁺ aquates much more rapidly than other dichlorocobalt(III) complexes containing organic amines. The enhancement of rate has been attributed to steric strains produced by the peculiar geometry of the complex (Madan, Reiff & Bailar, 1965). X-ray diffraction study of the complex [Ni(tren)(NCS)₂] has shown that the bonds between the metal and the primary amine nitrogens are drawn back towards the tertiary N atom (Rasmussen, 1959). Hence we were interested in finding the crystal structure of [Co(tren)CO₃]⁺ which might give us some clue about the reactivity of this complex.

Experimental. [Co(tren)CO₃]ClO₄ was prepared following the published procedure (Dasgupta & Harris, 1978). A saturated solution of sodium chloride was added to a solution of [Co(tren)CO₃]ClO₄ with stirring. The resultant solution was left at 293 K for several hours, after which bright-red crystals appeared which

were separated by suction filtration, washed with alcohol and air-dried. The purity of the crystals was checked by microanalysis and by visible spectroscopy. Analysis calculated for $[Co(C_6H_{18}N_4)(CO_3)]Cl.3H_2O$: C 23·05, H 6·59 and N 15·37%; found: C 23·61, H 6·83 and N 15·76%. The infrared spectrum of the compound was measured with a Perkin–Elmer Spectrometer, Model 735B (KBr-disc technique). The complex shows two strong peaks at 1600 and at 1260 cm^{-1}, comparable to the strong peaks at 1593 cm^{-1} {v[C—O(II)]} and 1265 cm^{-1} {v[C—O(I)] + δ[O(I)—C—O(II)]} obtained (Nakamoto, 1970) for [Co(NH$_3$)$_4$-CO$_3$]Cl.

Prisms, 0·25 × 0·35 × 0·4 mm, Enraf–Nonius CAD-4 diffractometer, 25 reflections with 20° < 2θ < 40° used for cell parameters (Mo $K\alpha_1$, $\lambda = 0·70926$ Å), empirical (ψ-scan) absorption correction ($T = 0·93$–$1·00$), hkl range: h 0–8, k 0–21, l −11–11, 4619 hkl with 2θ < 47°, 2119 unique reflections, three standards every 2 h of X-ray exposure (3% range); 1985 reflections with $F_o > 2\sigma(F_o)$ used in refinement; solution, including H atoms, by Patterson and difference Fourier methods, $\sum w(|F_o| - |F_c|)$ minimized, $w^{-1} = (\sigma_{counting} + 0·05\, F_o^2)/4F_o^2$, anisotropic (isotropic H's) full matrix, $R = 0·020$, $R_w = 0·027$, maximum shift/error = 0·01, maximum $\Delta\rho$ on final difference Fourier map 0·4 e Å^{-3}, scattering factors including f' and f'' values from International Tables for X-ray Crystallography (1974) and Stewart, Davidson & Simpson (1965), computations on PDP11/34 computer using Enraf–Nonius SDP programs. The final parameters are in Table 1.*

* Lists of structure factors, H-atom parameters, distances and angles involving H atoms and anisotropic thermal parameters, Fig. 3 and Tables 3, 4 and 5 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38540 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The molecular structure and the numbering scheme are given in Fig. 1. Table 2 gives the more important bond distances and angles. The structure of $[Co(tren)CO_3]^+Cl^-.3H_2O$ is built up from discrete $[Co(tren)CO_3]^+$ cations, chloride anions and waters of hydration held together by electrostatic interaction and hydrogen bonding (Fig. 2). The cation has Co^{III} complexed to an asymmetric bidentate, chelated carbonate group and four N atoms from the tren ethylenediamine groups. Thus, the Co atom is surrounded by four N atoms and two O atoms at the apices of a distorted octahedron. The chelating carbonate ligand causes distortion in the octahedral environment about Co. This is evident from the angle O(1)—Co—O(2) = 68·46 (5)°. This value is found to be consistent with related cobalt complexes (Table 3).*
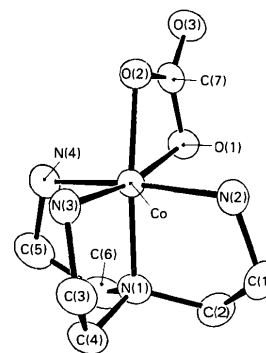
* See deposition footnote.

Fig. 1. Thermal ellipsoids (50% probability level) and atom labelling for [Co(tren)CO$_3$]$^+$.

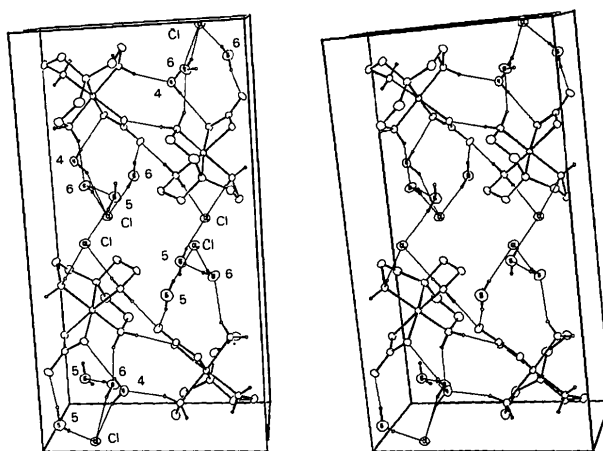Table 1. *Positional parameters in* [Co(tren)CO$_3$]Cl.-3H$_2$O

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$\tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Co	0·22807 (3)	0·17260 (1)	−0·25757 (2)	1·809 (4)
Cl	−0·09662 (6)	−0·01269 (2)	−0·22979 (4)	3·704 (9)
O(1)	0·2428 (1)	0·23599 (5)	−0·39571 (9)	2·33 (2)
O(2)	0·0094 (1)	0·22890 (5)	−0·27939 (9)	2·28 (2)
O(3)	−0·0122 (2)	0·30139 (6)	−0·4437 (1)	3·17 (2)
O(4)	−0·0335 (3)	0·15375 (7)	−0·6115 (1)	5·39 (3)
O(5)	−0·2610 (2)	0·40131 (7)	−0·3783 (1)	4·75 (3)
O(6)	0·4496 (2)	0·38563 (7)	−0·2116 (1)	4·87 (3)
N(1)	0·4615 (2)	0·12307 (7)	−0·2560 (1)	2·54 (2)
N(2)	0·3608 (2)	0·24082 (6)	−0·1497 (1)	2·34 (2)
N(3)	0·1654 (2)	0·11674 (6)	−0·1174 (1)	2·22 (2)
N(4)	0·1308 (2)	0·10345 (6)	−0·3781 (1)	2·57 (3)
C(1)	0·5620 (2)	0·22262 (9)	−0·1295 (2)	3·53 (4)
C(2)	0·6114 (2)	0·17626 (9)	−0·2346 (2)	3·62 (4)
C(3)	0·3378 (2)	0·08744 (8)	−0·0554 (1)	2·82 (3)
C(4)	0·4684 (2)	0·06920 (8)	−0·1542 (2)	3·04 (3)
C(5)	0·2821 (3)	0·05586 (9)	−0·4129 (2)	3·64 (4)
C(6)	0·4667 (3)	0·09014 (9)	−0·3811 (2)	3·46 (4)
C(7)	0·0747 (2)	0·25842 (7)	−0·3770 (1)	2·21 (3)

Fig. 2. Unit-cell contents of [Co(tren)CO$_3$]Cl.3H$_2$O. Hydrogen bonds are indicated by the thinner lines. Water oxygens are numbered, and chloride ions are labelled.

Table 2. *Bond distances* (Å) *and angles* (°) *in* [Co(tren)CO₃]⁺ (*with e.s.d.'s in parentheses*)

Co—O(1)	1·931 (1)	N(1)—C(2)	1·493 (2)
Co—O(2)	1·910 (1)	N(1)—C(4)	1·507 (2)
Co—N(1)	1·928 (1)	N(1)—C(6)	1·490 (2)
Co—N(2)	1·958 (1)	N(2)—C(1)	1·488 (2)
Co—N(3)	1·929 (1)	N(3)—C(3)	1·478 (2)
Co—N(4)	1·955 (1)	N(4)—C(5)	1·488 (2)
O(1)—C(7)	1·310 (2)	C(1)—C(2)	1·501 (3)
O(2)—C(7)	1·308 (2)	C(3)—C(4)	1·504 (3)
O(3)—C(7)	1·236 (2)	C(5)—C(6)	1·499 (3)

O(1)—Co—O(2)	68·46 (5)	Co—N(1)—C(4)	109·5 (1)
O(1)—Co—N(1)	103·19 (5)	Co—N(1)—C(6)	106·1 (1)
O(1)—Co—N(2)	88·83 (6)	C(2)—N(1)—C(4)	112·0 (2)
O(1)—Co—N(3)	168·84 (6)	C(2)—N(1)—C(6)	111·7 (2)
O(1)—Co—N(4)	87·61 (6)	C(4)—N(1)—C(6)	111·1 (1)
O(2)—Co—N(1)	171·65 (5)	Co—N(2)—C(1)	110·9 (1)
O(2)—Co—N(2)	93·07 (5)	Co—N(3)—C(3)	109·5 (1)
O(2)—Co—N(3)	100·40 (5)	Co—N(4)—C(5)	110·7 (1)
O(2)—Co—N(4)	93·02 (6)	N(2)—C(1)—C(2)	107·9 (2)
N(1)—Co—N(2)	86·54 (6)	N(1)—C(2)—C(1)	108·7 (2)
N(1)—Co—N(3)	87·96 (6)	N(3)—C(3)—C(4)	108·3 (1)
N(1)—Co—N(4)	86·52 (6)	N(1)C(4)—C(3)	111·0 (1)
N(2)—Co—N(3)	92·48 (7)	N(4)—C(5)—C(6)	108·6 (2)
N(2)—Co—N(4)	171·28 (7)	N(1)—C(6)—C(5)	108·5 (2)
N(3)—Co—N(4)	92·55 (7)	O(1)—C(7)—O(2)	111·3 (1)
Co—O(1)—C(7)	89·57 (9)	O(1)C(7)—O(3)	124·5 (2)
Co—O(2)—C(7)	90·57 (9)	O(2)—C(7)—O(3)	124·2 (2)
Co—N(1)—C(2)	106·1 (1)		

The three ethylenediamine chelate rings share a common edge Co—N(1). The N—Co—N angles of these five-membered rings are smaller [mean value 87·0 (7)°] than the idealized 90° angle for an undistorted octahedral coordination about the Co atom. The four Co—N(en) bond lengths range from 1·928 (1) to 1·958 (1) Å, the mean value being 1·942 (14) Å. This value is essentially the same as the average Co—N(amine) distance in other cobalt amine salts (Table 3).* There is, however, a large range of distances in the present compound. The longer distances [1·958 (1) and 1·955 (1) Å] involve terminal N atoms which are *trans* to each other while the shortest distance [1·928 (1) Å] involves the central tren nitrogen which is *trans* to a carbonate oxygen. The terminal nitrogen which is *trans* to the other carbonate oxygen also has a short Co—N distance [1·929 (1) Å]. A similar effect was observed by Toriumi & Saito (1975) in *cis-β*-carbonato[(3S,8S)-3,8-dimethyltriethyltetramine]cobalt(III) perchlorate and may be related to relative *trans*-directing abilities. The C—N bond distances range from 1·478 (2) to 1·507 (2) Å, with the mean value of 1·491 (7) Å. This value nearly agrees with that of the paraffin–quaternary amine bond length of 1·479 Å given in Sutton's (1958) tabulation. The three C—C bond distances, ranging from 1·499 (3) to 1·504 (3) Å with a mean value of 1·501 (3) Å, are shorter than the usual paraffinic C—C bond distances of 1·54 Å but are comparable to those in related compounds (Table 3).* Table 3* shows comparable Co—N (average), Co—O, C—O, N—C (average), C—C (average) distances and the angle O(1)—Co—O(2) for a series of [CoN₄CO₃]⁺ complexes; all these are comparable, but the present study is the most precise. The Co—N—C and N—C—C angles inside

the chelate ethylenediamine rings [average 108·8 (1·8) and 108·9 (8)° respectively] are all close to the normal tetrahedral angle of 109·5°, the maximum deviation being −3·4° [Co—N(1)—C(6) = 106·1 (1)°].

The Co—O(1) and Co—O(2) bond distances are 1·931 (1) and 1·910 (1) Å respectively; these are comparable to values in other cobalt complexes (Table 3).* The carbonate ligand exhibits a geometry indicative of a valence-bond structure near:

$$\begin{array}{c} O(3) \\ \parallel \\ C(7) \\ \diagup \quad \diagdown \\ O(1) \qquad O(2) \end{array}.$$
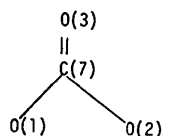
The O(3) atom, not bonded to the Co atom, has an apparent double bond with C(7) [C(7)—O(3) = 1·236 (2) Å] while the two O atoms bonded to Co are involved in longer C—O bonds [C(7)—O(2) = 1·308 (2), C(7)—O(1) = 1·310 (2) Å].

As expected, none of the ethylenediamine chelating rings are planar (Table 4).* the maximum and minimum deviations of atoms from the least-squares planes through the rings are 0·402 (2) Å at C(2) and −0·296 (2) Å at C(3). The dihedral angles between rings *A*[N(1), N(2)] with *B*[N(1), N(3)], *A*[N(1), N(2)] with *C*[N(1), N(4)], and *B*[N(1), N(3)] with *C*[N(1), N(4)] are 90·7 (2), 8·1 (2), and 98·7 (2)°, respectively. Fig. 3* shows torsion angles within the ethylenediamine chelating rings *A*[N(1), N(2)], *B*[N(1), N(3)], and *C*[N(1), N(4)]. The puckering parameters (Cremer & Pople, 1975) for rings *A*, *B* and *C* are [q_2 = 0·43 (1) Å, φ_2 = 119 (1)°], [q_2 = 0·35 (1) Å, φ_2 = 249 (1)°], and [q_2 = 0·43 (1) Å, φ_2 = 302 (1)°], respectively. Thus ring *B* is very close to a perfect (252°) envelope (*C_s*) conformation, while *C* is near a twist (*C₂*) conformation (306°) and *A* is intermediate.

The least-squares plane (Table 4)* passing through atoms O(1)—O(2)—C(7)—O(3), O(1)—O(2)—Co—N(1)—N(3) and O(3)—C(7)—O(1)—O(2)—Co—N(1)—N(3) indicate that each of these atom groups is nearly planar. Deviations are less than 0·011 (1) Å for the first two planes and maximum deviations are 0·067 (1) Å for O(3) and −0·041 (1) Å for O(2) from the latter plane. However, the dihedral angle between the first two planes is 4·4 (2)°. In the tetraamminecarbonato-cobalt(III) ion (Barclay & Hoskins, 1962) and in the carbonatobis(trimethylenediamine)cobalt(III) ion (Gene & Snow, 1971), an angle of 7° was found between the carbonato group and the O—O—Co—N—N plane.

As can be seen in Table 5* (hydrogen-bond parameters) each of the amine and water hydrogen atoms is involved in one hydrogen bond with another water oxygen, a carbonate oxygen, or the ionic chloride. Each oxygen is the acceptor for at least one hydrogen bond, and the uncoordinated carbonate

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* See deposition footnote.   * See deposition footnote.

oxygen [O(3)] is the acceptor for the two shortest hydrogen bonds [to O(5), 2·750 (2) Å and to N(3), 2·815 (2) Å]. The chloride ion is the acceptor for five hydrogen bonds with $X \cdots Cl$ from 3·207 (2) to 3·375 (2) Å. All $Y-H \cdots X$ angles are reasonable [range 148 (1) to 177 (1)°].

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Structure of a Complex of *trans*-Dichlorobis(triphenylphosphine)palladium(II) with *p*-Dichlorobenzene, [PdCl₂{P(C₆H₅)₃}₂]·½(*p*-C₆H₄Cl₂)

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Abstract. $M_r = 775\cdot39$, monoclinic, $P2_1/n$, $a = 16\cdot565$ (1), $b = 18\cdot692$ (2), $c = 11\cdot676$ (1) Å, $\beta = 105\cdot39$ (3)°, $V = 3485\cdot6$ Å³, $Z = 4$, $D_m = 1\cdot470$, $D_x = 1\cdot478$ Mg m⁻³, $\lambda(Cu\,K\alpha) = 1\cdot5405$ Å, $\mu = 7\cdot58$ mm⁻¹, $F(000) = 1572$, $T = 298$ K. The final R was 0·057 for 5308 independent reflections. The crystal structure analysis showed that *p*-dichlorobenzene is selectively incorporated into the cavity formed by two PdCl₂{P(C₆H₅)₃}₂ from the mixed solution of *ortho* and *para* isomers to form the stable title complex. The Pd atom possesses an essentially *trans* square-planar coordination with mean Pd–Cl 2·289 (1), and Pd–P 2·349 (1) Å.

Introduction. By the recrystallization of dichlorobis(triphenylphosphine)palladium(II) from a mixed solution of *o*- and *p*-dichlorobenzene, a new crystalline complex has been obtained in high yield (Kajimoto & Hara, 1983). The analysis of the complex suggested that one mole of dichlorobenzene was apparently incorporated per two PdCl₂{P(C₆H₅)₃}₂ in this complex. This structural analysis confirmed that a *p*-dichlorobenzene is trapped in the cavity formed by two PdCl₂{P(C₆H₅)₃}₂.

Experimental. Needle-like hexagonal orange-yellow prisms of a size suitable for X-ray analysis obtained by recrystallization of PdCl₂{P(C₆H₅)₃}₂ from hot *o*-dichlorobenzene which contained about 20% of *para* isomer. Density measured by flotation in an ethyl iodide–toluene mixture at 298 K. Data collection: Rigaku automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation; single crystal, 0·12 × 0·05 × 0·20 mm, mounted with *c* coincident with the goniostat axis; unit-cell dimensions determined by least-squares refinement of angular settings of 15