

The mentioned stability preferences of the different crystal species, as well as the two crystal structures of the  $[(\text{HgCl}_2)_2(\text{ttp})]$  and  $[\text{HgI}_2(\text{ttp})]$  complexes, illustrate the importance of the size of the coordinated halogen ion in forming mercury complexes with the potentially tetradentate macrocyclic polythiather ttp. While in the  $[(\text{HgCl}_2)_2(\text{ttp})]$  complex ttp does not act as a tetradentate but as a doubly bidentate ligand, in  $[\text{HgI}_2(\text{ttp})]$  and probably in  $[\text{HgBr}_2(\text{ttp})]$ , where the halogen ions are larger, the Hg-halogen units are placed at the side of the macrocycle which acts as a doubly monodentate ligand.

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## Structure of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Perchlorate

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**Abstract.**  $[\text{CoCl}_2(\text{C}_2\text{H}_8\text{N}_2)_2]\text{ClO}_4$ ,  $M_r = 349.45$ ,  $P\bar{1}$ ,  $a = 8.519$  (2),  $b = 12.372$  (3),  $c = 6.341$  (1) Å,  $\alpha = 100.79$  (2),  $\beta = 105.09$  (2),  $\gamma = 77.40$  (2)°,  $V = 623.7$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.88$  (2),  $D_x = 1.86$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 20.71$  cm<sup>-1</sup>,  $F(000) = 356$ ,  $T = 296$  K,  $R = 0.035$  for 1575 unique observed data. There are two independent cations in the unit cell with nearly identical bond distances and angles. The cations are close to  $C_{2h}$  symmetry, the deviation arising from a twist of the ethylenediamine ligand. Each Co atom is found on an inversion center.

**Introduction.** Trivalent cobalt complexes are readily prepared from the oxygenation and subsequent oxidation of cobalt(II) compounds. Many *cis*- and *trans*-disubstituted cobalt(III) complexes may be synthesized from carbonatobis(ethylenediamine)cobalt(III) which is a product of the above reaction in the presence of

carbon dioxide (Springborg & Schaffer, 1973). The resulting cobaltic compounds are moderate oxidizing agents and isolation is usually performed at low temperature in order to minimize the production of cobalt(II) species. Thermal reactions of cobalt(III) complexes are important in the understanding of electron-transfer mechanisms. This report describes the product obtained in the thermal hydrolysis of carbonatobis(ethylenediamine)cobalt(III) in aqueous solutions of hydrochloric acid.

**Experimental.** Hydrolysis of carbonatobis(ethylenediamine)cobalt(III) chloride at 353 K in 6 M HCl resulted in a green crystalline material on standing at ambient temperature. The analysis of this product was in good agreement with that of the title compound. Crystal density by flotation in 1,2-dibromopropane–bromobenzene, crystal 0.08 × 0.09 × 0.10 mm, CAD-

4 automated diffractometer, 25 reflections at medium and high angles for determining lattice parameters. Scans by  $\theta-2\theta$  method,  $2-20^\circ \text{ min}^{-1}$ , scan width  $A + 0.347(\tan\theta_{\lambda_{a2}})$ , where  $\theta_{\lambda_{a2}}$  is determined from  $\theta_{\lambda_{a2}} = \theta_{\lambda_{a1}} + (\lambda_{a2} - \lambda_{a1})/\lambda_{a1} \cdot (360/2\pi)^\circ \tan\theta_{\lambda_{a1}}$  and  $A$  depends on the crystal mosaic spread and on the divergence of the primary beam. In this study  $A = 0.7^\circ (\theta)$ . Standard reflections ( $13\bar{1}$ ,  $22\bar{3}$ ,  $24\bar{3}$ ) every 110 measured, no drop-off in standards. No absorption correction as crystal shape regular. Intensities calculated as  $I = S(C - RB)$ , where  $S$  = scan rate,  $C$  = total integrated peak count,  $B$  = total background count, and  $R$  = ratio of the scan time for the peak to the scan time for the background; estimated error calculated as  $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$  where the value of  $p$  was 0.05. Lorentz and polarization corrections applied. Neutral-atom scattering factors used (Cromer & Waber, 1974), and metal atom corrected for both real and imaginary anomalous dispersion (Cromer, 1974). A total of 2186 unique data collected with  $0 < 2\theta < 50^\circ$  ( $h0$  to 10;  $k-14$  to 14;  $l-7$  to 7),

611 unobserved [ $I < 3\sigma(I)$ ]. Structure solved by Patterson methods for Co, remaining atoms located by difference Fourier techniques. Full-matrix least-squares refinement of  $F$  magnitudes with positional and anisotropic thermal parameters. H positions geometrically calculated, included as a fixed contribution. Poor refinement of the perchlorate O atoms led to their removal and calculation of a difference Fourier map. Peaks in the map indicated an approximate 50:50 disorder of the three O atoms off the Cl(2)-O(1) axis. Refinement of the perchlorate was accomplished using this model.  $R = 0.035$ ,  $wR = 0.044$  where weights  $w = 1/\sigma(F_o)^2 = 4F_o^2/[\sigma(F_o^2)]^2$  and  $\sigma(F_o^2)$  is calculated from  $\sigma(I)$ . Ratio of maximum least-squares shift to e.s.d. in final refinement cycle 0.06. Final e.s.d. of an observation of unit weight 1.188. Maximum of  $0.89 \text{ e } \text{ \AA}^{-3}$  in final difference Fourier synthesis located about perchlorate anion. Secondary-extinction correction not applied. All computations on a PDP 11/60 computer with programs from Enraf-Nonius *SDP* (Enraf-Nonius, 1975).

Table 1. Positional and equivalent isotropic thermal parameters and their e.s.d.'s

	x	y	z	$B_{eq}^* (\text{\AA}^2)$
Co	1.0000	0.5000	0.0000	1.87 (2)
CoA	1.0000	1.0000	0.0000	1.84 (2)
Cl	0.9439 (1)	0.39975 (8)	0.2224 (2)	2.93 (2)
ClA	1.0269 (2)	0.87621 (8)	0.2294 (2)	3.31 (2)
N(1)	1.0938 (4)	0.5994 (3)	0.2572 (5)	2.70 (8)
N(2)	1.2216 (4)	0.4124 (3)	0.0304 (6)	3.02 (8)
N(1A)	1.0498 (4)	0.8760 (3)	-0.2274 (5)	2.37 (7)
N(2A)	1.2378 (4)	0.9987 (3)	0.0850 (6)	2.89 (8)
C(1)	1.2664 (6)	0.5487 (5)	0.3514 (8)	4.2 (1)
C(2)	1.3420 (6)	0.4824 (5)	0.1677 (9)	4.4 (1)
C(1A)	1.2302 (6)	0.8357 (4)	-0.1860 (8)	3.4 (1)
C(2A)	1.3148 (6)	0.9335 (4)	-0.0958 (8)	3.6 (1)
Cl(2)	1.3921 (1)	1.22134 (10)	1.5420 (2)	3.36 (3)
O(1)	1.3616 (6)	1.2225 (3)	1.3083 (6)	6.2 (1)
O(2)	1.3767 (13)	1.3362 (6)	1.6366 (12)	6.5 (2)
O(3)	1.2950 (10)	1.1651 (8)	1.5907 (17)	9.6 (3)
O(4)	1.5621 (10)	1.1755 (8)	1.6052 (15)	7.9 (3)
O(12)	1.4622 (17)	1.1107 (7)	1.5879 (17)	9.5 (4)
O(13)	1.2302 (11)	1.2458 (10)	1.5914 (15)	8.3 (3)
O(14)	1.4800 (12)	1.2942 (9)	1.6858 (21)	10.8 (4)

\*  $B_{eq}$  is calculated from anisotropic  $\beta$ 's (program *TEMPER*, Enraf-Nonius, 1975).

Table 2. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) and their e.s.d.'s for the  $[\text{CoCl}_2(\text{en})_2]^+$  complexes

Co-Cl	2.241 (1)	CoA-ClA	2.241 (1)
Co-N(1)	1.952 (3)	CoA-N(1A)	1.955 (3)
Co-N(2)	1.942 (3)	CoA-N(2A)	1.954 (4)
N(1)-C(1)	1.481 (6)	N(1A)-C(1A)	1.478 (6)
C(1)-C(2)	1.499 (7)	C(1A)-C(2A)	1.489 (6)
C(2)-N(2)	1.483 (6)	C(2A)-N(2A)	1.487 (5)
Cl-Co-N(1)	89.9 (1)	ClA-CoA-N(1A)	89.2 (1)
Cl-Co-N(2)	90.3 (1)	ClA-CoA-N(2A)	90.6 (1)
N(1)-Co-N(2)	86.2 (2)	N(1A)-CoA-N(2A)	85.8 (1)
Co-N(1)-C(1)	109.6 (3)	CoA-N(1A)-C(1A)	109.5 (3)
N(1)-C(1)-C(2)	108.8 (4)	N(1A)-C(1A)-C(2A)	108.5 (3)
C(1)-C(2)-N(2)	106.7 (4)	C(1A)-C(2A)-N(2A)	107.1 (4)
Co-N(2)-C(2)	109.2 (3)	CoA-N(2A)-C(2A)	109.2 (3)

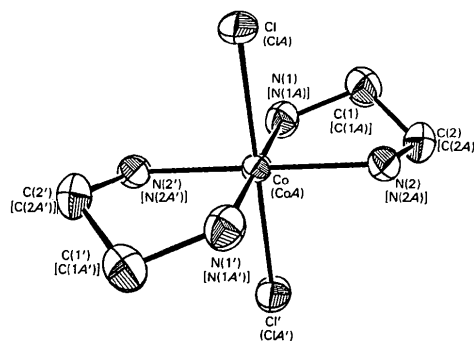


Fig. 1. ORTEP projection (Johnson, 1976) of one of the independent cations. The numbering scheme given in brackets is for the second cation. Atoms labeled with a prime denote that they are related through the inversion center (Co atom). Probability ellipsoids are at the 30% level.

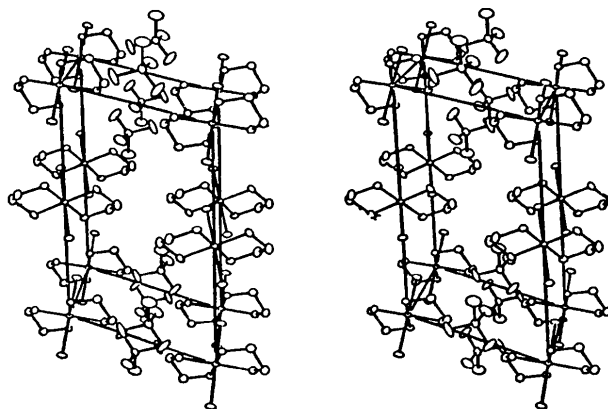


Fig. 2. Stereoscopic projection of the unit-cell packing (a approximately horizontal, b vertical, c into plane of page).

**Discussion.** Positional and equivalent isotropic thermal parameters are given in Table 1.\* Bond distances and angles for the two independent cobalt(III) cations are nearly identical as is demonstrated in Table 2 and are in good agreement with the less accurate structures of *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl (Becker, Grosse & Plieth, 1959), *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl.HCl.2H<sub>2</sub>O (Nakahara, Saito & Kuroya, 1952), and *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]<sub>2</sub>-[CoCl<sub>4</sub>] (Schubert, Zimmer-Gasser, Dash & Chaudhury, 1981). The cations are close to C<sub>2h</sub> symmetry, the deviation arising from a twist of the ethylenediamine ligand. The closest contact distances between the perchlorate anion and the cobalt chelates are N(2)···O(1) 3.047 (5) and N(2A)···O(1) 3.132 (5) Å. Figs. 1 and 2 illustrate the molecular structure of the cations and the unit-cell packing, respectively. Each Co atom occupies a special position (inversion center) in the unit cell. The ethylenediamine ligands must then adopt both  $\delta$  and  $\lambda$  conformations in each molecule with Cl(C1A) and its symmetry-related pair making up the coordination. However, the two

molecules are crystallographically different since the inversion centers occupy either corner or edge positions. This results in alternating layers of cations which are rotated and tilted with respect to the previous set. The perchlorate anions are situated between the layers.

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\* Lists of anisotropic thermal parameters and H-atom parameters and a table of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42716 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## *cis/trans* Disorder in (5-Bromo-4-pentenyl)triphenylphosphonium Iodide

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**Abstract.** C<sub>23</sub>H<sub>23</sub>BrP<sup>+</sup>.I<sup>-</sup>, *M<sub>r</sub>* = 537.2, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.196 (1), *b* = 18.494 (1), *c* = 14.576 (1) Å,

$\beta = 116.53 (1)^\circ$ , *V* = 2217.9 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.609 g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ ,  $\mu = 143.2 \text{ cm}^{-1}$ , *F*(000) = 1056, room temperature, *R* = 0.069 for 3786 observed reflections. The configuration of the triphenylphosphonium ion deviates substantially from that of a symmetrical propeller. The extended alkyl chain is disordered between the *cis* and *trans*

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