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(Carbonato-*O,O'*)bis(1,2-ethanediamine-*N,N'*)cobalt(III) PerchlorateHUI-MING HU,^a HONG-SUI SUN,^a CHUN-YING DUAN,^a QUN ZHAO,^a XIAO-ZENG YOU,^a ZHONG-YUAN ZHOU^b and XIANG-GE ZHOU^b^aState Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China, and ^bChengdu Institute of Organic Chemistry, The Chinese Academy of Science, Chengdu 610041, People's Republic of China. E-mail: ccinu@netra.nju.edu.cn

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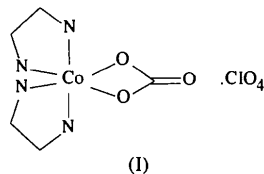
Abstract

The crystal structure determination of the title compound, [Co(CO₃)(C₂H₈N₂)₂]ClO₄, shows that the Co^{III} ion is approximately octahedral, with the two ethylenediamine N atoms and two carbonate O atoms in the equatorial positions, and the other ethylenediamine N atoms in axial positions. A hydrogen-bonding network is present in the crystal.

Comment

The exchange-reaction kinetics and mechanism in aqueous solution between the free uncoordinated carbonate ion and the corresponding ligand group in (carbonato)(tetraaza)cobalt(III) has been widely investigated (Van Eldik, Palmer & Harris, 1980; Harris & Hyde, 1978; Hyde, Fairchild & Harris, 1976; Van Eldik, Dasgupta & Harris, 1975; Dasgupta & Harris, 1969, 1971, 1974; Francis & Jordan, 1972; Holden & Harris, 1955).

The geometry around the Co^{III} ion in the title compound, (I), is approximately octahedral with the two N atoms of two ethylenediamine moieties and two carbonate O atoms in the equatorial positions, and the other two ethylenediamine N atoms in axial positions. Atoms Co(1), N(1), N(3), C(1), O(1), O(2) and O(3) are coplanar, the mean deviation from the plane being 0.030 Å.



The conformation of ethylenediamine in metal complexes is important in coordination chemistry. X-ray analyses on *trans*-[Co(en)₂Cl₂]Cl·HCl·2H₂O (Nakahara,

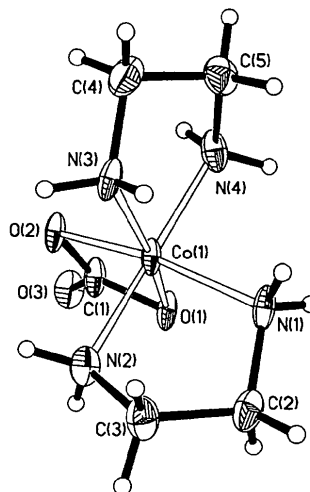


Fig. 1. The cation structure showing 50% probability displacement ellipsoids.

Saito & Kuroya, 1952) and other complexes indicate that the chelating ethylenediamine adopts a *gauche* conformation without exception. In this complex, both ethylenediamines also adopt *gauche* conformations. The carbonate ion coordinates to the Co^{III} ion in a bidentate fashion. The coordinated O—C(1) bond lengths are nearly equal at 1.306(5) and 1.300(5) Å, while the uncoordinated O(3)—C(1) bond length is 1.227(5) Å. The Co—N bond lengths fall in the range 1.941(3)–1.965(4) Å. The average Co—O bond length is 1.918(3) Å.

There is a two-dimensional intermolecular hydrogen-bonding network between the carbonate anion and the ethylenediamine ligands within the crystal lattice: O(1)···H(1Bⁱ)—N(1ⁱ) 2.899(5) Å and 148.1(4)°, O(2)···H(3Bⁱⁱⁱ)—N(3ⁱⁱ) 2.956(5) Å and 156.5(4)°, O(3)···H(1Aⁱⁱⁱ)—N(1ⁱⁱⁱ) 2.886(5) Å and 154.8(4)°, and O(3)···H(3Aⁱⁱⁱ)—N(3ⁱⁱⁱ) 2.904(5) Å and 160.7(4)° [symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$; (iii) $-1+x, y, z$].

Experimental

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared by the standard procedure (Bailar, 1946). An aqueous solution (10 ml) of Na₂CO₃ (106 mg, 1 mmol) was added to a boiling aqueous solution (10 ml) of [Co(en)₂Cl₂]Cl (286 mg, 1 mmol) and stirred for 1 h. NaClO₄ (123 mg, 1 mmol) dissolved in distilled water (5 ml) was added and the resulting solution was allowed to stand at room temperature for a few days whereupon crystals suitable for X-ray structure analysis were formed (found: C 17.59, H 4.62, N 16.94%; calculated for C₅H₁₆ClCoN₄O₇: C 17.74, H 4.76, N 16.55%).

Crystal data

[Co(CO₃)(C₂H₈N₂)₂]ClO₄
M_r = 338.60

Mo K α radiation
 λ = 0.71073 Å

Triclinic
 $P\bar{1}$
 $a = 7.356(1) \text{ \AA}$
 $b = 8.986(2) \text{ \AA}$
 $c = 9.544(2) \text{ \AA}$
 $\alpha = 74.37(3)^\circ$
 $\beta = 89.69(3)^\circ$
 $\gamma = 89.34(3)^\circ$
 $V = 607.5(2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.851 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens P4 diffractometer
 ω scans
Absorption correction: none
2452 measured reflections
1996 independent reflections
1499 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.0115$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.194$
 $S = 1.091$
1990 reflections
159 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0803P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 25
reflections
 $\theta = 10\text{--}25^\circ$
 $\mu = 1.666 \text{ mm}^{-1}$
 $T = 294 \text{ K}$
Cube
 $0.28 \times 0.26 \times 0.22 \text{ mm}$
Red

$\theta_{\text{max}} = 24.0^\circ$
 $h = -1 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 11$
3 standard reflections
every 100 reflections
intensity decay: 0.5%

$(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Co(1)—O(1)	1.917 (3)	Co(1)—N(4)	1.965 (4)
Co(1)—O(2)	1.919 (3)	O(1)—C(1)	1.306 (5)
Co(1)—N(1)	1.949 (3)	O(2)—C(1)	1.300 (5)
Co(1)—N(2)	1.942 (3)	O(3)—C(1)	1.227 (5)
Co(1)—N(3)	1.941 (3)		
O(1)—Co(1)—O(2)	68.4 (1)	N(2)—Co(1)—N(1)	86.6 (1)
O(1)—Co(1)—N(3)	166.6 (1)	O(1)—Co(1)—N(4)	91.1 (1)
O(2)—Co(1)—N(3)	98.7 (1)	O(2)—Co(1)—N(4)	90.6 (1)
O(1)—Co(1)—N(2)	92.3 (1)	N(3)—Co(1)—N(4)	85.4 (2)
O(2)—Co(1)—N(2)	90.9 (1)	N(2)—Co(1)—N(4)	176.6 (2)
N(3)—Co(1)—N(2)	91.3 (2)	N(1)—Co(1)—N(4)	92.8 (2)
O(1)—Co(1)—N(1)	97.6 (1)	O(3)—C(1)—O(2)	125.2 (4)
O(2)—Co(1)—N(1)	165.7 (1)	O(3)—C(1)—O(1)	123.0 (4)
N(3)—Co(1)—N(1)	95.5 (1)	O(2)—C(1)—O(1)	111.7 (3)

The O atoms of the disordered perchlorate anion were divided into two sets, each having 0.5 occupancy, and refined isotropically. All H atoms were fixed at ideal positions with a fixed U_{iso} of 0.08 \AA^2 . The largest difference peak (1.10 e \AA^{-3}) lies 1.01 \AA from the Co atom.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXTL (Sheldrick, 1995). Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1124). Services for accessing these data are described at the back of the journal.

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catena-Diaquatrakis(α -furancarboxylato)-lanthanum(III)

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Abstract

Each La^{3+} ion in *catena*-poly[[diaqua(2-furancarboxylato-*O, O'*)lanthanum(III)]- μ -(2-furancarboxylato-*O, O'*)-*O'*], $[\text{La}(\text{C}_5\text{H}_3\text{O}_3)_3(\text{H}_2\text{O})_2]_n$, is coordinated to seven O atoms from furancarboxylato groups and to two O atoms of water molecules in a distorted monocapped square-