

Structure Redetermination of Carbonatobis(ethylenediamine)cobalt(III) Chloride

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Abstract. (OC-6-22)-Carbonato- κ^2O -bis(ethylenediamine- κ^2N)cobalt(III) chloride, $[\text{Co}(\text{CO}_3)(\text{C}_2\text{H}_8\text{N}_2)_2]\text{Cl}$, $M_r = 274.59$, orthorhombic, $Pca2_1$, $a = 10.754$ (4), $b = 11.084$ (3), $c = 8.564$ (2) Å, $V = 1020.8$ (5) Å³, $Z = 4$, $D_x = 1.79$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 19.3$ cm⁻¹, $F(000) = 568$, $T = 293$ K, final conventional $R = 0.022$ for 1051 observed reflections and 184 variables. The structure of the title compound and its orientation with respect to the polar axis were determined by X-ray diffraction. The average Co—N distance is 1.955 (3) Å and the average Co—O distance is 1.911 (3) Å. The O(1)—Co—O(2) bite angle is 69.2 (1)° and the average N—Co—N bite angle is 85.9 (3)°. The Co^{III} coordination is pseudo-octahedral, consisting of two oxygen ligands in *cis* positions and two adjacent ethylenediamine ligands. The two enantiomers, showing Λ and Δ configurations around the metal centre, are in the unit cell. The ethylenediamine ligands show a λ chelate ring conformation in the Λ enantiomer and a δ conformation in the Δ enantiomer, with N—C—C—N torsion angles of 53.2 (5) and 51.1 (5)°. The ideal Co(1)—O(1)···O(2) plane was found to be 4.9 (1)° out of the ideal O(1)—C(5)—O(2)···O(3) plane.

Experimental. Crystals were obtained by slow evaporation at room temperature of a dilute (0.05M) solution of the title complex in ethanol/water (1:1). A red prism-shaped crystal of dimensions 0.26 × 0.19 × 0.19 mm was selected for data measurements. Mo K α radiation, graphite-crystal monochromator, Enraf-Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions determined from the angular

settings of 25 reflections with $12 < \theta < 25^\circ$. Space group $Pca2_1$ from systematic absences and structure determination. 5452 reflections were collected using the ω - 2θ scan technique, with a variable scan rate and a maximum scan time of 60 s per reflection, within the angular limits $0 \leq \theta \leq 25^\circ$ and the h, k, l range $-12, -13, -6$ to $12, 13, 10$. Intensity checked throughout data collection by monitoring three standard reflections every 60 min, drift corrections from 0.91 to 1.11. Profile analysis performed on all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction applied using ψ scans (North, Philips & Mathews, 1968), resulting in maximum and minimum correction factors of 0.98 and 1.00, respectively. Symmetry-equivalent reflections averaged, $R_{\text{int}} = 0.036$, giving 1140 unique reflections of which 1051 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values. Structure newly solved by Patterson interpretation using the program *SHELXS86* (Sheldrick, 1985) and Fourier synthesis. Isotropic least-squares refinement, using *SHELX76* (Sheldrick, 1976). Additional empirical absorption correction applied at this stage (Walker & Stuart, 1983), with correction factors within the range 0.90 to 1.12. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of all the H atoms. Positional parameters and anisotropic thermal parameters of non-H atoms refined. All H atoms refined free, except those of C(3) and N(2), which were refined riding on their parent atoms. The final conventional agreement factors $R = 0.022$, $wR = 0.021$ for 184 refined parameters. Function minimized $\sum w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0.00010F_o^2]$ with $\sigma(F_o)$ from counting statistics. Maximum shift to e.s.d. ratio in the last full-matrix

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Table 1. Fractional positional and thermal parameters with *e.s.d.*'s in parentheses
$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{Å}^2 \times 10^2)$
Co(1)	0.06969 (3)	0.21093 (3)	0.00485	1.93 (1)
Cl(1)	0.23886 (7)	0.54204 (7)	0.5122 (2)	3.66 (3)
O(1)	0.2360 (2)	0.1882 (2)	0.0767 (3)	2.57 (7)
O(2)	0.1418 (2)	0.0698 (2)	-0.0867 (3)	2.84 (8)
O(3)	0.3444 (2)	0.0337 (2)	-0.0306 (3)	3.5 (1)
N(1)	0.1298 (3)	0.3090 (3)	-0.1693 (4)	2.45 (9)
N(2)	-0.0900 (3)	0.2083 (3)	-0.1055 (4)	2.6 (1)
N(3)	0.0033 (3)	0.1162 (3)	0.1786 (4)	2.5 (1)
N(4)	0.0314 (3)	0.3528 (3)	0.1304 (4)	2.40 (9)
C(3)	-0.0681 (4)	0.1970 (4)	0.2828 (7)	3.3 (2)
C(2)	-0.0646 (4)	0.2381 (5)	-0.2714 (6)	2.9 (1)
C(5)	0.2471 (3)	0.0923 (3)	-0.0154 (5)	2.4 (1)
C(1)	0.0235 (5)	0.3440 (4)	-0.2697 (6)	3.0 (1)
C(4)	0.0039 (5)	0.3133 (4)	0.2932 (5)	2.9 (1)

Table 2. Bond lengths (Å), angles (°) and possible H-bond parameters with *e.s.d.*'s in parentheses

Co(1)—O(1)	1.908 (2)	O(3)—C(5)	1.238 (4)	
Co(1)—N(2)	1.960 (3)	O(2)—C(5)	1.311 (4)	
Co(1)—C(5)	2.324 (3)	N(1)—C(1)	1.482 (5)	
Co(1)—O(2)	1.914 (3)	N(2)—C(2)	1.483 (6)	
Co(1)—N(3)	1.956 (3)	N(3)—C(3)	1.479 (6)	
Co(1)—N(1)	1.956 (3)	N(4)—C(4)	1.491 (5)	
Co(1)—N(4)	1.948 (3)	C(2)—C(1)	1.508 (6)	
O(1)—C(5)	1.329 (4)	C(3)—C(4)	1.506 (6)	
O(2)—Co(1)—O(1)	69.2 (1)	N(1)—Co(1)—O(1)	90.5 (1)	
N(1)—Co(1)—O(2)	90.5 (1)	N(2)—Co(1)—O(1)	167.1 (1)	
N(2)—Co(1)—O(2)	98.4 (1)	N(2)—Co(1)—N(1)	86.0 (1)	
N(3)—Co(1)—O(1)	91.5 (1)	N(3)—Co(1)—O(2)	91.2 (1)	
N(3)—Co(1)—N(1)	177.7 (1)	N(3)—Co(1)—N(2)	92.2 (1)	
N(4)—Co(1)—O(1)	97.3 (1)	N(4)—Co(1)—O(2)	166.2 (1)	
N(4)—Co(1)—N(1)	92.4 (1)	N(4)—Co(1)—N(2)	95.3 (1)	
N(4)—Co(1)—N(3)	86.4 (1)	C(5)—Co(1)—O(1)	34.9 (1)	
C(5)—Co(1)—O(2)	34.3 (1)	C(5)—Co(1)—N(1)	89.2 (1)	
C(5)—Co(1)—N(2)	132.4 (1)	C(5)—Co(1)—N(3)	93.0 (1)	
C(5)—Co(1)—N(4)	132.2 (1)	C(5)—O(1)—Co(1)	89.9 (2)	
C(5)—O(2)—Co(1)	90.2 (2)	C(1)—N(1)—Co(1)	109.4 (3)	
C(2)—N(2)—Co(1)	107.3 (2)	C(3)—N(3)—Co(1)	108.8 (3)	
C(4)—N(4)—Co(1)	108.7 (2)	C(4)—C(3)—N(3)	106.7 (4)	
C(1)—C(2)—N(2)	106.2 (4)	O(1)—C(5)—Co(1)	55.2 (2)	
O(2)—C(5)—Co(1)	55.4 (2)	O(2)—C(5)—O(1)	110.5 (3)	
O(3)—C(5)—Co(1)	176.8 (3)	O(3)—C(5)—O(1)	123.9 (3)	
O(3)—C(5)—O(2)	125.6 (3)	C(2)—C(1)—N(1)	106.6 (4)	
C(3)—C(4)—N(4)	107.3 (4)			
D—H...A	D—H	H...A	D...A	D—H...A
N(1)—H(1)...O(1 ⁱ)	0.931 (4)	2.06 (4)	2.934 (4)	155 (4)
N(1)—H(2)...Cl(1 ⁱ)	0.86 (5)	2.49 (5)	3.329 (3)	161 (4)
N(4)—H(7)...Cl(1 ⁱ)	0.91 (4)	2.53 (4)	3.396 (3)	158 (4)
N(2)—H(3)...Cl(1 ⁱⁱ)	1.080 (4)	2.316 (3)	3.352 (3)	160.1 (3)
N(4)—H(8)...Cl(1 ⁱⁱ)	0.82 (4)	2.49 (4)	3.291 (3)	164 (4)
N(2)—H(4)...O(3 ⁱⁱⁱ)	1.080 (4)	1.805 (4)	2.847 (4)	160 (4)
N(3)—H(5)...O(3 ⁱⁱⁱ)	0.89 (4)	2.18 (5)	2.981 (4)	150 (4)
N(3)—H(6)...O(3 ⁱⁱⁱ)	0.94 (4)	2.24 (4)	3.118 (4)	155 (3)

Symmetry code: (i) $-x + \frac{1}{2}, +y, +z - \frac{1}{2}$; (ii) $-x, -y + 1, +z - \frac{1}{2}$; (iii) $+x - \frac{1}{2}, -y, +z$; (iv) $-x + \frac{1}{2}, +y, +z + \frac{1}{2}$.

least-squares cycle was 0.002 and the final difference Fourier map showed no peaks higher than 0.49 or deeper than $-0.41 e \text{ Å}^{-3}$. The orientation with respect to the polar axis was assigned using a new version of the program *BIJVOET* (Beurskens, Noordik & Beurskens, 1980), the Bijvoet coefficient (for 150 pairs) was 0.928 (6). Atomic scattering

factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional and thermal parameters are given in Table 1.* Molecular geometry data are collected in Table 2. Fig. 1 shows the cobalt(III) coordination and the atomic numbering scheme for the two enantiomeric configurations.

The plots in Fig. 1 were made with the *PLUTO* program (Motherwell & Clegg, 1978). Geometrical calculations were made with *PARST* (Nardelli, 1983). All calculations were made on a MicroVAX-3400 at the Scientific Computer Center, University of Oviedo.

Related literature. Since no absolute structure was assigned to carbonatobis(ethylenediamine)cobalt(III) chloride (Healy, Kennard, Smith & White, 1981) we undertook a redetermination of the compound seeking to improve the reported structural data and determine the orientation with respect to the polar axis.

The central Co atom is pseudo-octahedrally coordinated by two ethylenediamine ligands and a carbonate showing Λ and Δ configurations about the Co^{III} atom. The N(1)—Co—N(2) bite angle of $86.0(1)^\circ$ and N(3)—Co—N(4) of $86.4(1)^\circ$ are very close to the values of $85.9(3)$ and $86.0(3)^\circ$ found by García-Granda, Calvo-Pérez & Gómez-Beltrán (1992) for (2-butene-1,4-diolato)bis(ethylenediamine)cobalt(III) dichloride dihydrate. The Co—O distances are $1.910(3)$ Å, similar to that found in (+)-[bis(ethylenediamine)(oxalato)cobalt] (Kiryama & Igaki, 1988) of $1.93(4)$ Å and in (2-butene-1,4-diolato)bis(ethylenediamine)cobalt(III). The atoms

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, selected torsion angles, least-squares-plane angles and H-atom geometries have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55502 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0389]

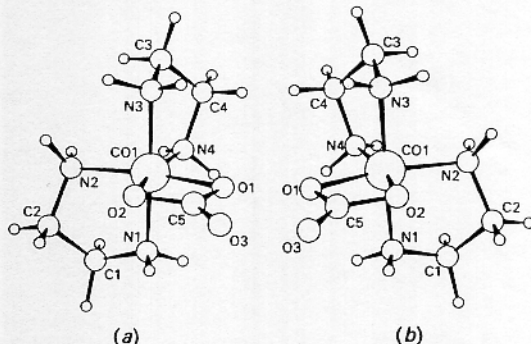


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) diagrams of both enantiomers, (a) Λ and (b) Δ , of the title compound. The Co^{III} coordination and atomic labelling scheme are shown for each.

C(5), O(1), O(2), O(3) lie in a plane. The C(5)—O(1) [1.329 (4) Å] and C(5)—O(2) [1.311 (4) Å] bonds are longer than C(5)—O(3) [1.238 (4) Å], which has some double-bond character. However, the carbonate chelation is symmetrical, in contrast to the results previously reported for this structure. The carbonate plane makes an angle of 4.9 (1)° with the plane formed by Co(1), O(1), O(2).

Both ethylenediamine molecules show a similar disposition of their chelate rings (λ conformation in the Λ enantiomer), with torsion angles N(1)—C(1)—C(2)—N(2) and N(3)—C(3)—C(4)—N(4) of 53.2 (5) and 51.1 (5)°, respectively, very close to the value of 51.6° found in the (+)-[Co(en)₂Cl₂]Cl·H₂O complex (Matsumoto, Ooi & Kuroya, 1970). In addition, this complex shows the same configuration about the central atom as that in Λ $\delta\delta$ (+)-[Co^{III}(en)₂Cl₂]Cl while the other enantiomer is Δ $\delta\delta$. Hydrogen bonding includes the chloride ion and the O(1) and O(3) atoms of the carbonate ligand, which are hydrogen bonded to the H atoms of the amine. Symmetry operations and geometrical data for this network are collected in Table 2.

References

- BEURSKENS, G., NOORDIK, J. H. & BEURSKENS, P. T. (1980). *Cryst. Struct. Commun.* **9**, 23–28.
- GARCÍA-GRÁNDA, S., CALVO-PÉREZ, V. & GÓMEZ-BELTRÁN, F. (1992). *Acta Cryst.* Submitted.
- GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
- HEALY, P. C., KENNARD, C. H. L., SMITH, G. & WHITE, A. H. (1981). *Cryst. Struct. Commun.* **10**, 883–889.
- KIRIYAMA, K. & IGAKI, M. (1988). *Bull. Chem. Soc. Jpn*, **61**, 2817–2823.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- MATSUMOTO, K., OOI, S. & KUROYA, H. (1970). *Bull. Chem. Soc. Jpn*, **43**, 3801–3804.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- NORTH, A. C. T., PHILIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.