

Tetra-*n*-butylamine(carbonato- κ^2O,O')cobalt(III) *n*-butylcarbamate dihydrate

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Key indicators

Single-crystal X-ray study

$T = 120\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.041

wR factor = 0.108

Data-to-parameter ratio = 21.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Co}(\text{CO}_3)(\text{C}_4\text{H}_{11}\text{N})_4](\text{C}_5\text{H}_{10}\text{NO}_2)\cdot 2\text{H}_2\text{O}$, is a coordination complex with an N_4O_2 coordination sphere around the central Co^{III} ion. The small bite angle of the chelating carbonate causes a distortion of the octahedral geometry to an approximately C_{2v} local symmetry. Hydrogen-bonding between the carbonate, carbamate and amine groups, and the water of crystallization, results in a complex two-dimensional network.

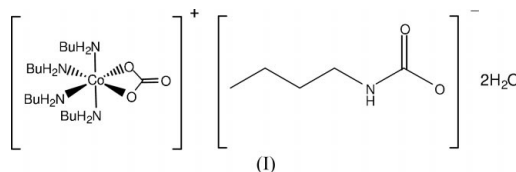
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Comment

The title complex, (I) (Fig. 1), crystallized very slowly from a mixture of cobalt(II) oxalate dihydrate, *n*-butylamine and water. This synthesis involves the aerobic oxidation of Co^{II} to Co^{III} , which is facilitated by the strong-field amine ligands. In addition, the oxalate is oxidized to CO_2 , which is sequestered in this basic reaction mixture and converted into carbonate and *n*-butylcarbamate.



Compound (I) contains monocationic $[\text{Co}(\text{BuNH}_2)_4(\text{CO}_3)]^+$ units and non-coordinating *n*-butylcarbamate anions. The Co^{III} ion has a distorted octahedral coordination environment

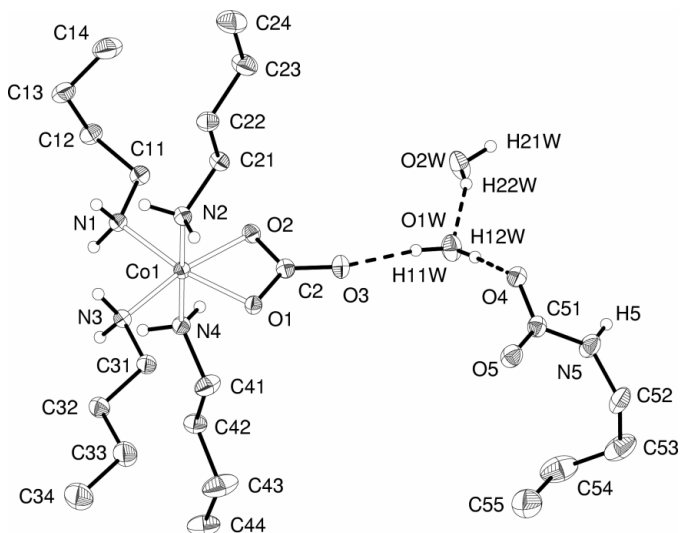
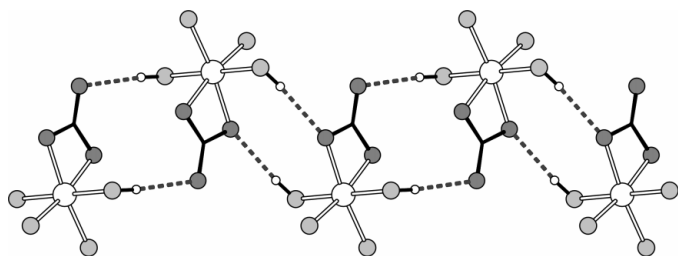


Figure 1

A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. Alkyl H atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines.


Figure 2

A view of the amine-carbonate hydrogen-bonded ribbon, looking down the *c* axis, showing an alternation of the two distinct types of cyclic hydrogen-bonded motif making up the ribbon structure.

(Table 1), due to the constraints imposed by the chelating carbonate group. While the O1—Co1—O2 angle is very acute, at 68.86 (5)°, all other angles not involving the carbonate group are close to the ideal octahedral values. The Co—N and Co—O bond lengths are typical for a low-spin Co^{III} ion and this assignment is supported by electronic spectroscopy, from which we calculate $\Delta_{\text{oct}} = 19\,600\text{ cm}^{-1}$. We note that three of the four coordinated butylamine ligands adopt a fully extended all-*anti* conformation, while one of these and the butyl chain on the carbamate show a *gauche* conformational geometry.

The structure of (I) shows a very distinct two-dimensional character, with layers of the non-polar alkyl chains alternating with layers that contain more polar functionalities, in particular the complex cation core, the carbamate anion and the water of crystallization. The complex cations are hydrogen-bonded through the amine H atoms and the carbonate groups to form ribbons running parallel to the *a* axis (Fig. 2). These ribbons are further hydrogen-bonded through the water of crystallization and the carbamate units into a two-dimensional structure in the *ab* plane. In total, 11 distinct linear hydrogen bonds are involved in this very complex network (Table 2).

Metal carbonate-containing compounds are of interest as possible fixatives of atmospheric CO₂ (Zhu & Chen, 1999), and biologically in relation to carbonic anhydrases (Dussart *et al.*, 2002). A search of the Cambridge Structural Database (CSD, Version 5.42 of November 2002; Allen, 2002) for discrete metal carbonate-containing structures reveals that octahedral Co^{III} complexes outnumber all other types (see, for example, Bernal *et al.*, 1994; Kaas & Sorensen, 1973; García-Granda *et al.*, 1993). It is particularly interesting that, in most cases, while the carbonate occupies two coordination sites, the other four sites are occupied by *N*-donor ligands.

Due to their tendency for thermal decarboxylation, carbamic acids and free carbamate are not common in crystal structures. There are a number of reports where carbamate is found to be coordinated to a metal centre (Blacque *et al.*, 2001; Duatti *et al.*, 1991; Schmid & Strähle, 1991). Compound (I) represents a rare example where a carbamate group simply acts as a non-coordinating counterion (Kovbasyuk *et al.*, 1997).

Experimental

Co(C₂O₄)·2H₂O (183 mg, 1.00 mmol), *n*-butylamine (1.0 ml) and distilled water (10 ml) were stirred in a test tube and left to react for six months. Although initially a green precipitate was formed, eventually small red crystals of (I) appeared. These were separated manually. IR (diffuse reflectance, cm⁻¹): 3378–3233 *br m* (NH and OH stretch), 2958 *m* (CH), 2924 *m* (CH), 2868 *m* (CH), 2409 *w*, 2319 *w*, 2213 *w*, 1790 *w*, 1614 *br s* (CO₃ ν₃; carbamate and NH bend), 1465 *s* (CH₂ def.), 1373 *s* (CH₃ sym. def.), 1306 *s* (carbamate), 1275 *s* (CO₃ ν₃; OH bend), 1217 *s*, 1105 *s*, 1038 (CO₃ ν₁) 990 *s*, 817 *s* (CO₃ ν₂), 755 *s* (CO₃ ν₄), 674 *s* (CO₃ ν₄), 582 *s*, 492 *m*, 473 *m*, 458 *m*, 422 *m* (MO); UV/VIS/NIR (diffuse reflectance, cm⁻¹): 19 000 and 20 100 (¹A_{1g} → ¹T_{1g} split by reduced symmetry), 27 000 (→ ¹T_{2g}). IR assignments were based on the literature values of comparable compounds (Nakamoto, 1968; Williams & Fleming, 1987)

Crystal data

[Co(CO ₃)(C ₄ H ₁₁ N) ₄]- (C ₅ H ₁₀ NO ₂)·2H ₂ O	<i>Z</i> = 2
<i>M_r</i> = 563.66	<i>D_x</i> = 1.22 Mg m ⁻³
Triclinic, <i>P</i> 1	Mo <i>K</i> α radiation
<i>a</i> = 8.7948 (2) Å	Cell parameters from 33 407 reflections
<i>b</i> = 12.9638 (4) Å	θ = 2.9–27.5°
<i>c</i> = 13.9288 (4) Å	μ = 0.60 mm ⁻¹
α = 88.187 (2)°	<i>T</i> = 120 (2) K
β = 89.525 (2)°	Block, red
γ = 75.210 (2)°	0.16 × 0.14 × 0.08 mm
<i>V</i> = 1534.69 (7) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	7050 independent reflections
φ and ω scans	6003 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	<i>R</i> _{int} = 0.092
<i>T</i> _{min} = 0.634, <i>T</i> _{max} = 0.953	θ_{max} = 27.6°
30 921 measured reflections	<i>h</i> = -11 → 11
	<i>k</i> = -16 → 16
	<i>l</i> = -17 → 18

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.8409P]$
<i>R</i> (<i>F</i>) = 0.041	where $P = (F_o^2 + 2F_c^2)/3$
$wR[F^2 > 2\sigma(F^2)] = 0.108$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.03	$\Delta\rho_{\text{max}} = 0.31\text{ e \AA}^{-3}$
7050 reflections	$\Delta\rho_{\text{min}} = -0.73\text{ e \AA}^{-3}$
332 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

O1—Co1	1.9113 (12)	N2—Co1	1.9687 (14)
O2—Co1	1.9214 (12)	N3—Co1	1.9563 (14)
N1—Co1	1.9838 (15)	N4—Co1	1.9849 (15)
O1—Co1—O2	68.86 (5)	N3—Co1—N1	90.86 (6)
O1—Co1—N3	99.99 (6)	N2—Co1—N1	90.57 (6)
O2—Co1—N3	168.74 (6)	O1—Co1—N4	91.70 (6)
O1—Co1—N2	87.94 (6)	O2—Co1—N4	87.97 (6)
O2—Co1—N2	92.50 (6)	N3—Co1—N4	90.86 (6)
N3—Co1—N2	88.56 (6)	N2—Co1—N4	179.26 (6)
O1—Co1—N1	169.00 (6)	N1—Co1—N4	89.90 (6)
O2—Co1—N1	100.34 (6)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2A \cdots O5 ⁱ	0.90	2.07	2.956 (3)	167
N2—H2B \cdots O3 ⁱ	0.90	2.11	2.996 (3)	168
N3—H3A \cdots O4 ⁱ	0.90	2.03	2.898 (4)	160
N3—H3B \cdots O2W ⁱⁱ	0.90	2.14	3.026 (3)	166
N1—H1B \cdots O5 ⁱ	0.90	2.09	2.967 (4)	166
N4—H4A \cdots O2W ⁱⁱ	0.90	2.15	2.974 (2)	152
N4—H4B \cdots O2 ⁱⁱ	0.90	2.18	3.024 (2)	157
O2W—H21W \cdots O4 ⁱⁱⁱ	0.851 (16)	1.854 (19)	2.695 (4)	169.7 (18)
O2W—H22W \cdots O1W	0.853 (17)	1.96 (2)	2.754 (4)	154 (2)
O1W—H11W \cdots O3	0.851 (17)	1.907 (17)	2.751 (3)	171 (2)
O1W—H12W \cdots O4	0.845 (17)	1.94 (3)	2.780 (3)	170 (3)

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, 2-y, 1-z$.

H atoms bound to C or N atoms were positioned geometrically and refined as riding, with C—H = 0.96–0.97 and N—H = 0.90 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$. H atoms bound to O atoms were located in difference maps, but their distances and angles were restrained to literature values.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT* (Nonius, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999).

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