

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

Tony D. Keene, Michael B. Hursthouse and Daniel J. Price*

School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England

Correspondence e-mail: daniel.price@soton.ac.uk

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.

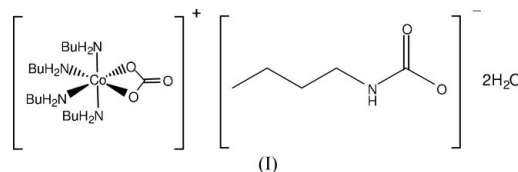
Received 2 March 2004

Accepted 4 March 2004

Online 20 March 2004

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

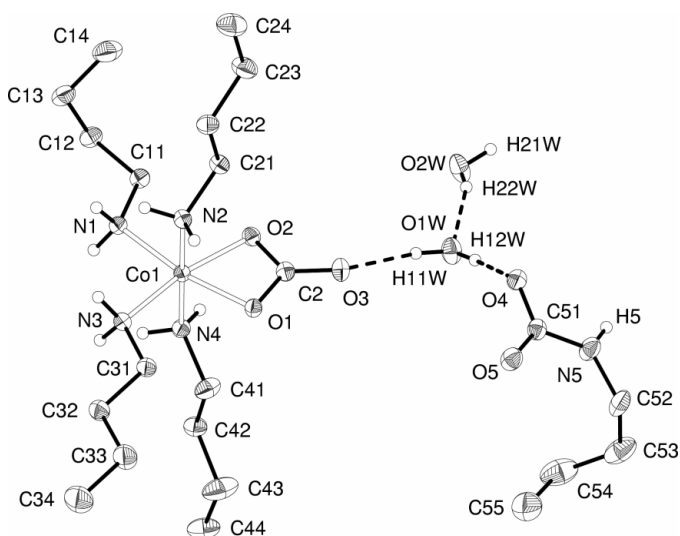
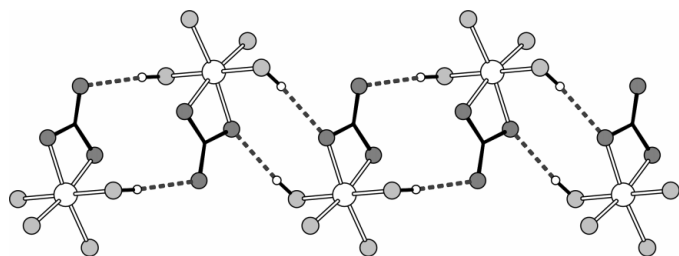


Figure 1

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 $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$. 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).

The authors are grateful to the EPSRC for the provision of X-ray crystallographic facilities and for the award of an Advanced Research Fellowship to DJP.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernal, I., Cai, J., Cetrullo, J. & Massoud, S. S. (1994). *Struct. Chem.* **5**, 265–275, and references therein.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Blacque, O., Brunner, H., Kubicki, M. M., Leblanc, J.-C., Meier, W., Moize, C., Mugnier, Y., Sadorge, A., Wachter, J. & Zabel, M. (2001). *J. Organomet. Chem.* **634**, 47–54.
- Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
- Duatti, A., Marchi, A., Bertalasi, V. & Ferretti, V. (1991). *J. Am. Chem. Soc.* **113**, 9680–9682.
- Dussart, Y., Harding, C., Dalgaard, P., McKenzie, C., Kadirvelraj, R., McKee, V. & Nelson, J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1704–1713, and references therein.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- García-Granda, S., Calvo-Pérez, V. & Gómez-Beltrán, F. (1993). *Acta Cryst.* **C49**, 322–324.
- Kaas, K. & Sorensen, A. M. (1973). *Acta Cryst.* **B29**, 113–120.
- Kovbasyuk, L. A., Fritsky, I. O., Kokozay, V. N. & Iskenderov, T. S. (1997). *Polyhedron*, **16**, 1723–1729.
- Nakamoto, K. (1968). *Spectroscopy and Structure of Metal Chelate Compounds*, edited by K. Nakamoto & P. J. McCarthy, ch. 4, p.26–285. New York: John Wiley & Sons, Inc.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Schmid, S. & Strähle, J. (1991). *Z. Naturforsch. Teil B*, **46**, 235–244.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Williams, D. H. & Fleming, I. (1987). *Spectroscopic Methods in Organic Chemistry*, 4th ed. London: McGraw-Hill Book Company.
- Zhu, H.-L. & Chen, X.-M. (1999). *Acta Cryst.* **C55**, 2010–2012.

supporting information

Acta Cryst. (2004). E60, m381–m383 [https://doi.org/10.1107/S1600536804005070]

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

Tony D. Keene, Michael B. Hursthouse and Daniel J. Price

(I)

Crystal data

[Co(CO₃)(C₄H₁₁N)₄](C₅H₁₀NO₂)·2H₂O

$M_r = 563.66$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 8.7948$ (2) Å

$b = 12.9638$ (4) Å

$c = 13.9288$ (4) Å

$\alpha = 88.187$ (2)°

$\beta = 89.525$ (2)°

$\gamma = 75.210$ (2)°

$V = 1534.69$ (7) Å³

$Z = 2$

$F(000) = 616$

$D_x = 1.22$ Mg m⁻³

Melting point: N/A K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 33407 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 0.60$ mm⁻¹

$T = 120$ K

Block, red

$0.16 \times 0.14 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer

φ and ω scans to fill Ewald Sphere

Absorption correction: multi-scan (SORTAV; Blessing, 1997)

$T_{\min} = 0.634$, $T_{\max} = 0.953$

30921 measured reflections

7050 independent reflections

6003 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.092$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 2.9$ °

$h = -11 \rightarrow 11$

$k = -16 \rightarrow 16$

$l = -17 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.108$

$S = 1.03$

7050 reflections

332 parameters

6 restraints

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.8409P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.31$ e Å⁻³

$\Delta\rho_{\min} = -0.73$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.85979 (14)	0.44465 (9)	0.45133 (9)	0.0171 (3)
O2	0.67427 (14)	0.48892 (9)	0.55706 (9)	0.0181 (3)
O3	0.74239 (15)	0.61932 (10)	0.46808 (10)	0.0226 (3)
N2	0.95987 (17)	0.35553 (11)	0.62436 (11)	0.0176 (3)
H2A	0.9859	0.2942	0.6596	0.021*
H2B	1.0448	0.3584	0.5889	0.021*
N3	0.92955 (17)	0.21136 (11)	0.49077 (11)	0.0179 (3)
H3A	0.9847	0.1765	0.5414	0.021*
H3B	0.8687	0.1705	0.4698	0.021*
N1	0.70029 (17)	0.26660 (12)	0.63460 (11)	0.0176 (3)
H1A	0.6608	0.2180	0.6057	0.021*
H1B	0.7776	0.2309	0.6742	0.021*
N4	0.62597 (17)	0.33398 (12)	0.44355 (10)	0.0178 (3)
H4A	0.6098	0.2686	0.4527	0.021*
H4B	0.5369	0.3812	0.4613	0.021*
C1	0.7582 (2)	0.52382 (14)	0.49041 (13)	0.0182 (4)
C21	0.9321 (2)	0.44442 (14)	0.69205 (13)	0.0199 (4)
H21A	0.8348	0.4480	0.7267	0.024*
H21B	0.9205	0.5112	0.6560	0.024*
C22	1.0659 (2)	0.43058 (15)	0.76355 (14)	0.0230 (4)
H22A	1.1628	0.4291	0.7291	0.028*
H22B	1.0795	0.3629	0.7985	0.028*
C23	1.0341 (3)	0.52060 (17)	0.83435 (15)	0.0317 (5)
H23A	1.0261	0.5876	0.7993	0.038*
H23B	0.9337	0.5246	0.8655	0.038*
C24	1.1607 (3)	0.5066 (2)	0.91081 (17)	0.0395 (5)
H24A	1.1343	0.5654	0.9533	0.059*
H24B	1.2600	0.5044	0.8806	0.059*
H24C	1.1678	0.4411	0.9468	0.059*
C34	1.3229 (3)	0.0251 (2)	0.24777 (19)	0.0472 (6)
H34A	1.3918	0.0386	0.1978	0.071*
H34B	1.2490	-0.0096	0.2216	0.071*
H34C	1.3836	-0.0200	0.2972	0.071*
C33	1.2352 (3)	0.12968 (17)	0.28996 (17)	0.0356 (5)
H33A	1.1763	0.1754	0.2393	0.043*
H33B	1.3107	0.1650	0.3149	0.043*
C32	1.1226 (2)	0.11647 (15)	0.36990 (14)	0.0240 (4)
H32A	1.0437	0.0844	0.3446	0.029*
H32B	1.1802	0.0686	0.4197	0.029*
C31	1.0424 (2)	0.22201 (14)	0.41307 (13)	0.0201 (4)
H31A	1.1216	0.2535	0.4389	0.024*
H31B	0.9865	0.2701	0.3628	0.024*
C11	0.5737 (2)	0.33496 (14)	0.69341 (13)	0.0194 (4)
H11A	0.4844	0.3663	0.6522	0.023*
H11B	0.6118	0.3928	0.7182	0.023*

C12	0.5185 (2)	0.27547 (16)	0.77728 (14)	0.0231 (4)
H12A	0.4893	0.2140	0.7527	0.028*
H12B	0.4246	0.3219	0.8042	0.028*
C13	0.6376 (2)	0.23714 (17)	0.85790 (14)	0.0271 (4)
H13A	0.5940	0.1957	0.9048	0.033*
H13B	0.7316	0.1902	0.8315	0.033*
C14	0.6835 (3)	0.3266 (2)	0.90867 (16)	0.0389 (5)
H14A	0.7584	0.2968	0.9583	0.058*
H14B	0.5917	0.3725	0.9366	0.058*
H14C	0.7294	0.3670	0.8632	0.058*
C41	0.6445 (2)	0.35029 (18)	0.33954 (14)	0.0285 (4)
H41A	0.7453	0.3059	0.3195	0.034*
H41B	0.6448	0.4241	0.3263	0.034*
C42	0.5159 (2)	0.32408 (16)	0.28131 (14)	0.0241 (4)
H42A	0.5139	0.2509	0.2964	0.029*
H42B	0.4156	0.3697	0.3007	0.029*
C43	0.5330 (3)	0.3371 (2)	0.17450 (16)	0.0448 (6)
H43A	0.6370	0.2964	0.1558	0.054*
H43B	0.5257	0.4117	0.1589	0.054*
C44	0.4130 (3)	0.3021 (2)	0.11633 (16)	0.0380 (5)
H44A	0.4314	0.3132	0.0492	0.057*
H44B	0.3095	0.3431	0.1330	0.057*
H44C	0.4213	0.2278	0.1296	0.057*
O4	0.83001 (16)	0.90478 (10)	0.37696 (10)	0.0239 (3)
O5	1.00761 (16)	0.84550 (11)	0.26221 (10)	0.0267 (3)
N5	0.8177 (2)	0.99862 (13)	0.23680 (12)	0.0279 (4)
H5	0.7373	1.0432	0.2602	0.034*
C51	0.8895 (2)	0.91169 (15)	0.29292 (14)	0.0210 (4)
C52	0.8676 (3)	1.02092 (17)	0.14077 (15)	0.0324 (5)
H52A	0.9688	0.9721	0.1280	0.039*
H52B	0.8814	1.0928	0.1376	0.039*
C53	0.7524 (3)	1.0107 (2)	0.06337 (17)	0.0439 (6)
H53A	0.6520	1.0605	0.0758	0.053*
H53B	0.7902	1.0313	0.0019	0.053*
C54	0.7270 (3)	0.9001 (2)	0.05617 (19)	0.0502 (7)
H54A	0.6965	0.8772	0.1188	0.060*
H54B	0.6409	0.9034	0.0122	0.060*
C55	0.8703 (4)	0.8183 (2)	0.0221 (2)	0.0522 (7)
H55A	0.8465	0.7502	0.0189	0.078*
H55B	0.9554	0.8130	0.0662	0.078*
H55C	0.8999	0.8395	-0.0405	0.078*
O1W	0.57777 (17)	0.82925 (11)	0.44237 (11)	0.0280 (3)
O2W	0.31962 (18)	0.90202 (12)	0.55808 (12)	0.0328 (3)
Co1	0.79257 (3)	0.345151 (18)	0.534965 (16)	0.01531 (8)
H21W	0.276 (3)	0.9662 (14)	0.5723 (18)	0.043 (7)*
H22W	0.407 (2)	0.897 (2)	0.529 (2)	0.059 (9)*
H11W	0.623 (3)	0.7642 (14)	0.456 (2)	0.053 (8)*
H12W	0.646 (3)	0.859 (2)	0.420 (2)	0.054 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0174 (6)	0.0157 (6)	0.0183 (6)	-0.0044 (5)	0.0009 (5)	0.0005 (5)
O2	0.0167 (6)	0.0168 (6)	0.0200 (6)	-0.0028 (5)	0.0010 (5)	-0.0016 (5)
O3	0.0225 (6)	0.0167 (6)	0.0279 (7)	-0.0041 (5)	-0.0013 (5)	0.0020 (5)
N2	0.0165 (7)	0.0166 (7)	0.0194 (7)	-0.0038 (6)	-0.0019 (6)	-0.0009 (6)
N3	0.0201 (7)	0.0159 (7)	0.0177 (7)	-0.0044 (6)	0.0001 (6)	-0.0013 (6)
N1	0.0188 (7)	0.0171 (7)	0.0169 (7)	-0.0045 (6)	-0.0008 (6)	0.0000 (6)
N4	0.0179 (7)	0.0181 (7)	0.0176 (7)	-0.0052 (6)	-0.0007 (6)	-0.0002 (6)
C1	0.0160 (8)	0.0185 (9)	0.0199 (9)	-0.0042 (7)	-0.0041 (7)	0.0001 (7)
C21	0.0195 (9)	0.0196 (9)	0.0208 (9)	-0.0050 (7)	-0.0004 (7)	-0.0028 (7)
C22	0.0226 (9)	0.0263 (10)	0.0204 (9)	-0.0066 (8)	-0.0027 (7)	-0.0017 (7)
C23	0.0354 (11)	0.0315 (11)	0.0287 (11)	-0.0084 (9)	-0.0032 (9)	-0.0089 (9)
C24	0.0432 (13)	0.0477 (14)	0.0311 (12)	-0.0168 (11)	-0.0065 (10)	-0.0091 (10)
C34	0.0537 (15)	0.0386 (13)	0.0445 (15)	-0.0028 (11)	0.0211 (12)	-0.0098 (11)
C33	0.0409 (12)	0.0285 (11)	0.0360 (12)	-0.0061 (9)	0.0181 (10)	-0.0048 (9)
C32	0.0262 (10)	0.0215 (9)	0.0238 (10)	-0.0053 (8)	0.0040 (8)	-0.0029 (8)
C31	0.0205 (9)	0.0196 (9)	0.0196 (9)	-0.0043 (7)	0.0022 (7)	-0.0015 (7)
C11	0.0171 (8)	0.0208 (9)	0.0194 (9)	-0.0035 (7)	0.0006 (7)	-0.0001 (7)
C12	0.0196 (9)	0.0281 (10)	0.0216 (9)	-0.0066 (7)	0.0041 (7)	0.0003 (8)
C13	0.0288 (10)	0.0320 (11)	0.0195 (9)	-0.0063 (8)	0.0034 (8)	0.0023 (8)
C14	0.0479 (14)	0.0515 (15)	0.0225 (11)	-0.0223 (12)	-0.0018 (10)	-0.0018 (10)
C41	0.0290 (10)	0.0409 (12)	0.0200 (10)	-0.0173 (9)	-0.0028 (8)	0.0034 (8)
C42	0.0228 (9)	0.0279 (10)	0.0216 (10)	-0.0061 (8)	-0.0015 (7)	-0.0036 (8)
C43	0.0427 (13)	0.0767 (19)	0.0230 (11)	-0.0302 (13)	-0.0034 (10)	0.0002 (11)
C44	0.0349 (12)	0.0568 (15)	0.0229 (11)	-0.0117 (11)	-0.0037 (9)	-0.0065 (10)
O4	0.0276 (7)	0.0209 (7)	0.0219 (7)	-0.0043 (5)	0.0016 (5)	0.0012 (5)
O5	0.0245 (7)	0.0256 (7)	0.0259 (7)	0.0005 (6)	0.0015 (6)	0.0031 (6)
N5	0.0277 (9)	0.0253 (9)	0.0251 (9)	0.0026 (7)	0.0017 (7)	0.0064 (7)
C51	0.0209 (9)	0.0201 (9)	0.0229 (9)	-0.0070 (7)	-0.0030 (7)	0.0014 (7)
C52	0.0354 (12)	0.0296 (11)	0.0298 (11)	-0.0056 (9)	0.0029 (9)	0.0118 (9)
C53	0.0348 (12)	0.0568 (16)	0.0292 (12)	0.0068 (11)	0.0002 (10)	0.0114 (11)
C54	0.0411 (14)	0.084 (2)	0.0329 (13)	-0.0289 (14)	-0.0042 (11)	0.0011 (13)
C55	0.0665 (18)	0.0509 (16)	0.0424 (15)	-0.0208 (14)	-0.0060 (13)	-0.0002 (12)
O1W	0.0233 (7)	0.0212 (7)	0.0384 (9)	-0.0039 (6)	0.0029 (6)	0.0012 (6)
O2W	0.0305 (8)	0.0194 (7)	0.0493 (10)	-0.0075 (6)	0.0096 (7)	-0.0060 (7)
Co1	0.01598 (13)	0.01440 (13)	0.01542 (13)	-0.00362 (9)	-0.00036 (9)	-0.00055 (9)

Geometric parameters (\AA , $^\circ$)

O1—Co1	1.9113 (12)	C32—H32B	0.9700
O2—Co1	1.9214 (12)	C31—H31A	0.9700
N1—Co1	1.9838 (15)	C31—H31B	0.9700
N2—Co1	1.9687 (14)	C11—C12	1.523 (2)
N3—Co1	1.9563 (14)	C11—H11A	0.9700
N4—Co1	1.9849 (15)	C11—H11B	0.9700
O1—C1	1.306 (2)	C12—C13	1.524 (3)

O2—C1	1.321 (2)	C12—H12A	0.9700
O3—C1	1.240 (2)	C12—H12B	0.9700
O4—C51	1.288 (2)	C13—C14	1.518 (3)
O5—C51	1.249 (2)	C13—H13A	0.9700
N5—C51	1.367 (2)	C13—H13B	0.9700
N2—C21	1.482 (2)	C14—H14A	0.9600
N2—H2A	0.9000	C14—H14B	0.9600
N2—H2B	0.9000	C14—H14C	0.9600
N3—C31	1.489 (2)	C41—C42	1.510 (3)
N3—H3A	0.9000	C41—H41A	0.9700
N3—H3B	0.9000	C41—H41B	0.9700
N1—C11	1.491 (2)	C42—C43	1.503 (3)
N1—H1A	0.9000	C42—H42A	0.9700
N1—H1B	0.9000	C42—H42B	0.9700
N4—C41	1.471 (2)	C43—C44	1.503 (3)
N4—H4A	0.9000	C43—H43A	0.9700
N4—H4B	0.9000	C43—H43B	0.9700
C1—Co1	2.3230 (18)	C44—H44A	0.9600
C21—C22	1.520 (2)	C44—H44B	0.9600
C21—H21A	0.9700	C44—H44C	0.9600
C21—H21B	0.9700	N5—C52	1.448 (3)
C22—C23	1.521 (3)	N5—H5	0.8600
C22—H22A	0.9700	C52—C53	1.517 (3)
C22—H22B	0.9700	C52—H52A	0.9700
C23—C24	1.521 (3)	C52—H52B	0.9700
C23—H23A	0.9700	C53—C54	1.512 (4)
C23—H23B	0.9700	C53—H53A	0.9700
C24—H24A	0.9600	C53—H53B	0.9700
C24—H24B	0.9600	C54—C55	1.509 (4)
C24—H24C	0.9600	C54—H54A	0.9700
C34—C33	1.512 (3)	C54—H54B	0.9700
C34—H34A	0.9600	C55—H55A	0.9600
C34—H34B	0.9600	C55—H55B	0.9600
C34—H34C	0.9600	C55—H55C	0.9600
C33—C32	1.518 (3)	O1W—H11W	0.851 (17)
C33—H33A	0.9700	O1W—H12W	0.845 (17)
C33—H33B	0.9700	O2W—H21W	0.851 (16)
C32—C31	1.511 (2)	O2W—H22W	0.853 (17)
C32—H32A	0.9700		
O1—Co1—O2	68.86 (5)	C33—C32—H32A	109.3
O1—Co1—N3	99.99 (6)	C31—C32—H32B	109.3
O2—Co1—N3	168.74 (6)	C33—C32—H32B	109.3
O1—Co1—N2	87.94 (6)	H32A—C32—H32B	107.9
O2—Co1—N2	92.50 (6)	N3—C31—C32	112.84 (15)
N3—Co1—N2	88.56 (6)	N3—C31—H31A	109.0
O1—Co1—N1	169.00 (6)	C32—C31—H31A	109.0
O2—Co1—N1	100.34 (6)	N3—C31—H31B	109.0

N3—Co1—N1	90.86 (6)	C32—C31—H31B	109.0
N2—Co1—N1	90.57 (6)	H31A—C31—H31B	107.8
O1—Co1—N4	91.70 (6)	N1—C11—C12	113.96 (15)
O2—Co1—N4	87.97 (6)	N1—C11—H11A	108.8
N3—Co1—N4	90.86 (6)	C12—C11—H11A	108.8
N2—Co1—N4	179.26 (6)	N1—C11—H11B	108.8
N1—Co1—N4	89.90 (6)	C12—C11—H11B	108.8
O1—Co1—C1	34.22 (6)	H11A—C11—H11B	107.7
O2—Co1—C1	34.64 (6)	C11—C12—C13	115.57 (15)
N3—Co1—C1	134.21 (6)	C11—C12—H12A	108.4
N2—Co1—C1	89.60 (6)	C13—C12—H12A	108.4
N1—Co1—C1	134.91 (6)	C11—C12—H12B	108.4
N4—Co1—C1	90.47 (6)	C13—C12—H12B	108.4
C1—O1—Co1	90.41 (10)	H12A—C12—H12B	107.4
C1—O2—Co1	89.55 (10)	C14—C13—C12	113.96 (18)
C21—N2—Co1	119.84 (11)	C14—C13—H13A	108.8
C21—N2—H2A	107.4	C12—C13—H13A	108.8
Co1—N2—H2A	107.4	C14—C13—H13B	108.8
C21—N2—H2B	107.4	C12—C13—H13B	108.8
Co1—N2—H2B	107.4	H13A—C13—H13B	107.7
H2A—N2—H2B	106.9	C13—C14—H14A	109.5
C31—N3—Co1	115.76 (11)	C13—C14—H14B	109.5
C31—N3—H3A	108.3	H14A—C14—H14B	109.5
Co1—N3—H3A	108.3	C13—C14—H14C	109.5
C31—N3—H3B	108.3	H14A—C14—H14C	109.5
Co1—N3—H3B	108.3	H14B—C14—H14C	109.5
H3A—N3—H3B	107.4	N4—C41—C42	112.96 (16)
C11—N1—Co1	114.75 (11)	N4—C41—H41A	109.0
C11—N1—H1A	108.6	C42—C41—H41A	109.0
Co1—N1—H1A	108.6	N4—C41—H41B	109.0
C11—N1—H1B	108.6	C42—C41—H41B	109.0
Co1—N1—H1B	108.6	H41A—C41—H41B	107.8
H1A—N1—H1B	107.6	C43—C42—C41	114.52 (17)
C41—N4—Co1	121.01 (11)	C43—C42—H42A	108.6
C41—N4—H4A	107.1	C41—C42—H42A	108.6
Co1—N4—H4A	107.1	C43—C42—H42B	108.6
C41—N4—H4B	107.1	C41—C42—H42B	108.6
Co1—N4—H4B	107.1	H42A—C42—H42B	107.6
H4A—N4—H4B	106.8	C42—C43—C44	114.48 (19)
O3—C1—O1	124.59 (16)	C42—C43—H43A	108.6
O3—C1—O2	124.26 (16)	C44—C43—H43A	108.6
O1—C1—O2	111.14 (15)	C42—C43—H43B	108.6
O3—C1—Co1	178.59 (14)	C44—C43—H43B	108.6
O1—C1—Co1	55.36 (8)	H43A—C43—H43B	107.6
O2—C1—Co1	55.80 (8)	C43—C44—H44A	109.5
N2—C21—C22	111.89 (15)	C43—C44—H44B	109.5
N2—C21—H21A	109.2	H44A—C44—H44B	109.5
C22—C21—H21A	109.2	C43—C44—H44C	109.5

N2—C21—H21B	109.2	H44A—C44—H44C	109.5
C22—C21—H21B	109.2	H44B—C44—H44C	109.5
H21A—C21—H21B	107.9	C51—N5—C52	124.60 (17)
C21—C22—C23	111.42 (16)	C51—N5—H5	117.7
C21—C22—H22A	109.3	C52—N5—H5	117.7
C23—C22—H22A	109.3	O5—C51—O4	123.82 (17)
C21—C22—H22B	109.3	O5—C51—N5	119.85 (17)
C23—C22—H22B	109.3	O4—C51—N5	116.32 (17)
H22A—C22—H22B	108.0	N5—C52—C53	113.43 (18)
C24—C23—C22	113.19 (18)	N5—C52—H52A	108.9
C24—C23—H23A	108.9	C53—C52—H52A	108.9
C22—C23—H23A	108.9	N5—C52—H52B	108.9
C24—C23—H23B	108.9	C53—C52—H52B	108.9
C22—C23—H23B	108.9	H52A—C52—H52B	107.7
H23A—C23—H23B	107.8	C54—C53—C52	114.60 (19)
C23—C24—H24A	109.5	C54—C53—H53A	108.6
C23—C24—H24B	109.5	C52—C53—H53A	108.6
H24A—C24—H24B	109.5	C54—C53—H53B	108.6
C23—C24—H24C	109.5	C52—C53—H53B	108.6
H24A—C24—H24C	109.5	H53A—C53—H53B	107.6
H24B—C24—H24C	109.5	C55—C54—C53	113.5 (2)
C33—C34—H34A	109.5	C55—C54—H54A	108.9
C33—C34—H34B	109.5	C53—C54—H54A	108.9
H34A—C34—H34B	109.5	C55—C54—H54B	108.9
C33—C34—H34C	109.5	C53—C54—H54B	108.9
H34A—C34—H34C	109.5	H54A—C54—H54B	107.7
H34B—C34—H34C	109.5	C54—C55—H55A	109.5
C34—C33—C32	113.36 (19)	C54—C55—H55B	109.5
C34—C33—H33A	108.9	H55A—C55—H55B	109.5
C32—C33—H33A	108.9	C54—C55—H55C	109.5
C34—C33—H33B	108.9	H55A—C55—H55C	109.5
C32—C33—H33B	108.9	H55B—C55—H55C	109.5
H33A—C33—H33B	107.7	H11W—O1W—H12W	108 (2)
C31—C32—C33	111.81 (16)	H21W—O2W—H22W	112 (2)
C31—C32—H32A	109.3		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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	0.85 (2)	1.85 (2)	2.695 (4)	170 (2)
O2W—H22W \cdots O1W	0.85 (2)	1.96 (2)	2.754 (4)	154 (2)

O1W—H11W··O3	0.85 (2)	1.91 (2)	2.751 (3)	171 (2)
O1W—H12W··O4	0.85 (2)	1.94 (3)	2.780 (3)	170 (3)

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