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# Tetra-*n*-butylamine(carbonato-$\kappa^2O,O'$)cobalt(III) *n*-butylcarbamate dihydrate

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**Key indicators**

Single-crystal X-ray study
*T* = 120 K
Mean $\sigma$(C–C) = 0.003 Å
*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.

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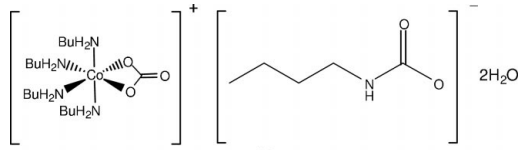
The title compound, $[Co(CO_3)(C_4H_{11}N)_4](C_5H_{10}NO_2)\cdot 2H_2O$, is a coordination complex with an $N_4O_2$ coordination sphere around the central $Co^{III}$ ion. The small bite angle of the chelating carbonate causes a distortion of the octahedral geometry to an approximately $C_{2v}$ local symmetry. Hydrogen-bonding between the carbonate, carbamate and amine groups, and the water of crystallization, results in a complex two-dimensional network.

## 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.




(I)

Compound (I) contains monocationic $[Co(BuNH_2)_4(CO_3)]$ units and non-coordinating *n*-butylcarbamate anions. The $Co^{III}$ ion has a distorted octahedral coordination environment

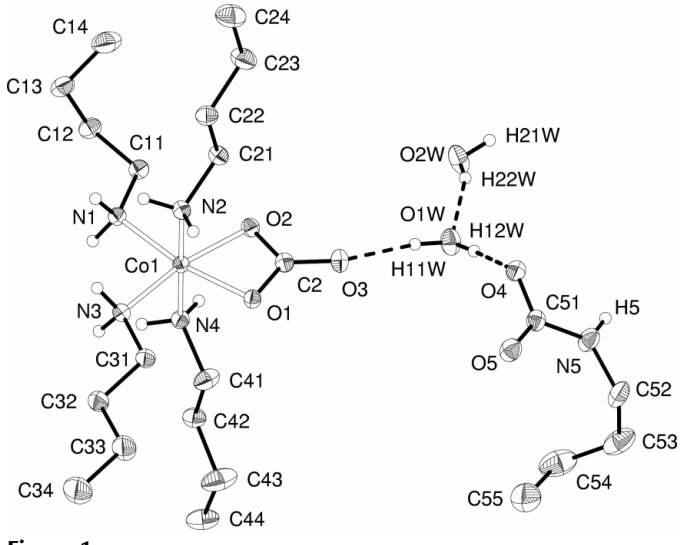



**Figure 1**
A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. Alkyl H atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

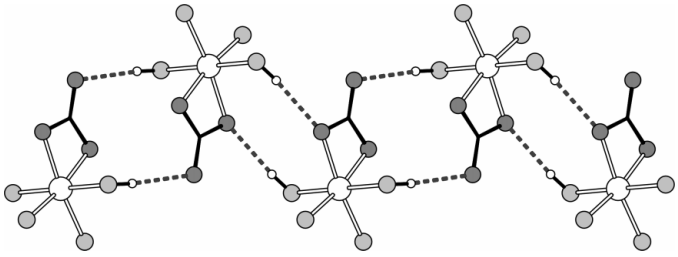


**Figure 2**
A view of the amine–carbonate hydrogen-bonded ribbon, looking down the *c* axis, showing an alternation of the two distinct types of cyclic hydrogen-bonded motif making up the ribbon structure.

(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 $\Delta_{oct}$ = 19 600 $cm^{-1}$. 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 $CO_2$ (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

$Co(C_2O_4)\cdot 2H_2O$ (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* ($CO_3$ $\nu_3$; carbamate and NH bend), 1465 *s* ($CH_2$ def.), 1373 *s* ($CH_3$ sym. def.), 1306 *s* (carbamate), 1275 *s* ($CO_3$ $\nu_{3'}$; OH bend), 1217 *s*, 1105 *s*, 1038 ($CO_3$ $\nu_1$) 990 *s*, 817 *s* ($CO_3$ $\nu_2$), 755 *s* ($CO_3$ $\nu_4$), 674 *s* ($CO_3$ $\nu_{4'}$), 582 *s*, 492 *m*, 473 *m*, 458 *m*, 422 *m* (*M*O); UV/VIS/NIR (diffuse reflectance, $cm^{-1}$): 19 000 and 20 100 ($^1A_{1g} \rightarrow {}^1T_{1g}$ split by reduced symmetry), 27 000 ($\rightarrow {}^1T_{2g}$). IR assignments were based on the literature values of comparable compounds (Nakamoto, 1968; Williams & Fleming, 1987)

*Crystal data*

$[Co(CO_3)(C_4H_{11}N)_4]$-$(C_5H_{10}NO_2)\cdot 2H_2O$
$M_r$ = 563.66
Triclinic, $P\overline{1}$
$a$ = 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) $Å^3$
$Z$ = 2
$D_x$ = 1.22 Mg $m^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 33 407 reflections
$\theta$ = 2.9–27.5°
$\mu$ = 0.60 $mm^{-1}$
$T$ = 120 (2) K
Block, red
0.16 × 0.14 × 0.08 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{min}$ = 0.634, $T_{max}$ = 0.953
30 921 measured reflections
7050 independent reflections
6003 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.092
$\theta_{max}$ = 27.6°
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 18$

*Refinement*

Refinement on $F^2$
$R(F)$ = 0.041
$wR[F^2 > 2\sigma(F^2)]$ = 0.108
$S$ = 1.03
7050 reflections
332 parameters
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 $Å^{-3}$

**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···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$A$···O5$^{i}$ | 0.90 | 2.07 | 2.956 (3) | 167 |
| N2—H2$B$···O3$^{i}$ | 0.90 | 2.11 | 2.996 (3) | 168 |
| N3—H3$A$···O4$^{i}$ | 0.90 | 2.03 | 2.898 (4) | 160 |
| N3—H3$B$···O2$W^{ii}$ | 0.90 | 2.14 | 3.026 (3) | 166 |
| N1—H1$B$···O5$^{i}$ | 0.90 | 2.09 | 2.967 (4) | 166 |
| N4—H4$A$···O2$W^{ii}$ | 0.90 | 2.15 | 2.974 (2) | 152 |
| N4—H4$B$···O2$^{ii}$ | 0.90 | 2.18 | 3.024 (2) | 157 |
| O2$W$—H21$W$···O4$^{iii}$ | 0.851 (16) | 1.854 (19) | 2.695 (4) | 169.7 (18) |
| O2$W$—H22$W$···O1$W$ | 0.853 (17) | 1.96 (2) | 2.754 (4) | 154 (2) |
| O1$W$—H11$W$···O3 | 0.851 (17) | 1.907 (17) | 2.751 (3) | 171 (2) |
| O1$W$—H12$W$···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) = 1.2$U_{eq}$(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: *SHELXS*97 (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997) in *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999).

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# supporting information

*Acta Cryst.* (2004). E**60**, m381–m383 [https://doi.org/10.1107/S1600536804005070]

## Tetra-*n*-butylamine(carbonato-$\kappa^2O,O'$)cobalt(III) *n*-butylcarbamate dihydrate

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

**(I)**

*Crystal data*

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Triclinic, $P\overline{1}$
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) Å$^3$
$Z = 2$
$F(000) = 616$
$D_x = 1.22$ 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 × 0.14 × 0.08 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ 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 $I > 2\sigma(I)$
$R_{int} = 0.092$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.9°$
$h = -11\rightarrow11$
$k = -16\rightarrow16$
$l = -17\rightarrow18$

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, º)*

| | | | |
|---|---|---|---|
| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*A*···O5$^{i}$ | 0.90 | 2.07 | 2.956 (3) | 167 |
| N2—H2*B*···O3$^{i}$ | 0.90 | 2.11 | 2.996 (3) | 168 |
| N3—H3*A*···O4$^{i}$ | 0.90 | 2.03 | 2.898 (4) | 160 |
| N3—H3*B*···O2*W*$^{ii}$ | 0.90 | 2.14 | 3.026 (3) | 166 |
| N1—H1*B*···O5$^{i}$ | 0.90 | 2.09 | 2.967 (4) | 166 |
| N4—H4*A*···O2*W*$^{ii}$ | 0.90 | 2.15 | 2.974 (2) | 152 |
| N4—H4*B*···O2$^{ii}$ | 0.90 | 2.18 | 3.024 (2) | 157 |
| O2*W*—H21*W*···O4$^{iii}$ | 0.85 (2) | 1.85 (2) | 2.695 (4) | 170 (2) |
| O2*W*—H22*W*···O1*W* | 0.85 (2) | 1.96 (2) | 2.754 (4) | 154 (2) |

| | | | | |
|---|---|---|---|---|
| O1*W*—H11*W*···O3 | 0.85 (2) | 1.91 (2) | 2.751 (3) | 171 (2) |
| O1*W*—H12*W*···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.