

Bis(3,5-dinitrobenzoato- κO^1)tetra-methanolcobalt(II)

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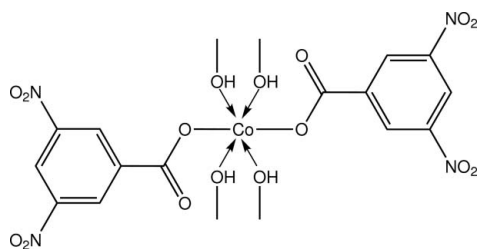
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.043; wR factor = 0.110; data-to-parameter ratio = 16.0.

The Co^{II} atom (site symmetry $\bar{1}$) in the title complex, $[Co(C_7H_3N_2O_6)_2(CH_3OH)_4]$, exists within an octahedral O_6 donor set defined by two O -monodentate 3,5-dinitrobenzoate anions and four methanol O atoms. An intramolecular $O_m-H \cdots O_c$ ($m =$ methanol and $c =$ carbonyl) hydrogen bond leads to the formation of an $S(6)$ ring. In the crystal, centrosymmetrically related molecules associate *via* further $O_m-H \cdots O_c$ hydrogen bonds, leading to linear supramolecular chains propagating along the a -axis direction.

Related literature

For the structures of related complexes, see: Tahir *et al.* (1996); Yang *et al.* (2000); Jin *et al.* (2008). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

 $[Co(C_7H_3N_2O_6)_2(CH_3O)_4]$
 $M_r = 609.33$

 Triclinic, $P\bar{1}$
 $a = 6.4068$ (8) Å

 $b = 8.7660$ (11) Å

 $c = 12.1603$ (16) Å

 $\alpha = 90.411$ (2)°

 $\beta = 100.407$ (2)°

 $\gamma = 102.214$ (2)°

 $V = 655.77$ (14) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 0.74$ mm⁻¹
 $T = 293$ K

 $0.35 \times 0.30 \times 0.05$ mm

Data collection

 Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.669$, $T_{max} = 0.746$

 6372 measured reflections
 2999 independent reflections
 2388 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.110$
 $S = 1.03$
 2999 reflections
 188 parameters
 2 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.38$ e Å⁻³
 $\Delta\rho_{min} = -0.30$ e Å⁻³
Table 1

Selected bond lengths (Å).

Co—O8	2.0645 (18)	Co—O7	2.1094 (16)
Co—O1	2.0666 (17)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O7—H7o \cdots O2 ⁱ	0.85 (3)	1.84 (2)	2.645 (2)	158 (3)
O8—H8o \cdots O2 ⁱⁱ	0.85 (3)	1.82 (1)	2.662 (2)	179 (3)

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5347).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Jin, Y., Che, Y. X. & Zheng, J. M. (2008). *Inorg. Chim. Acta*, **361**, 2799–2803.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Tahir, M. N., Ülku, D. & Mövsümov, E. M. (1996). *Acta Cryst.* **C52**, 1392–1394.
 Westrip, S. P. (2010). *publCIF*. In preparation.
 Yang, G., Zhu, H.-G., Zhang, L.-Z., Cai, Z.-G. & Chen, X.-M. (2000). *Aust. J. Chem.* **53**, 601–605.

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supporting information

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Bis(3,5-dinitrobenzoato- κ O¹)tetramethanolcobalt(II)**Bipasa Sarkar, Abhijit Roy, Seik Weng Ng and Edward R. T. Tiekink****S1. Comment**

The Co(II) atom in (I), Fig. 1, is located on a crystallographic centre of inversion and exists within an octahedral O₆ donor set defined by two carboxylate-O1 atoms and four methanol-O atoms. The Co–O1 bond distance [Co–O1 = 2.0666 (17) Å] is comparable to those, *i.e.* 2.0525 (20) and 2.0587 (19) Å, found in the related tetra-aqua-bis(3,5-dinitrobenzoato-O)cobalt(II) tetrahydrate structure (Tahir *et al.*, 1996; Yang *et al.*, 2000; Jin *et al.*, 2008). A small disparity in the Co–O_{methanol} bond distances in (I) [Co–O7 = 2.1094 (16) and Co–O8 = 2.0645 (18) Å] is noted. The methanol-O7–H hydrogen forms an intramolecular O–H \cdots O hydrogen bond with the carbonyl-O2 atom to close an almost planar {Co–O–C–O \cdots H–O} S(6) ring, Table 1. The methanol-O8–H also forms a hydrogen bond to the carbonyl-O2 atom on a centrosymmetrically related complex, Table 1. This results in the formation of 12-membered {Co–O–H \cdots O–C–O}₂ synthons and linear supramolecular chains along the *a* axis, Fig. 2. It is noted that the packing of molecules brings into close proximity two nitro-O atoms, *i.e.* O4 \cdots O4ⁱⁱ = 2.756 (3) Å for 3-*x*, -*y*, 2-*z*. While the nature of this interaction is not obvious, there are approximately 50 precedents for such O_{nitro} \cdots O_{nitro} contacts < 2.70 Å in the crystallographic literature (Allen, 2002).

S2. Experimental

All chemicals purchased from commercial sources (AR/GR grade) were used without further purification. The crystalline sodium salt of 3,5-dinitrobenzoic acid was prepared by neutralising 3,5-dinitrobenzoic acid (1.00 g, 4.70 mmol) by NaOH (1.88 g, 4.70 mmol) in water. On concentration the solution yielded the sodium salt (1). To a purple solution of CoCl₂·6H₂O (0.50 g, 2.10 mmol) in water (15 ml) was added, with stirring, a solution of (1) (0.98 g, 4.20 mmol) in a mixture of water (3 ml) and methanol (140 ml) when the colour of the mixture turned pink. The solution was then heated under reflux for 6 h. Pink prisms of (I) were obtained from the filtrate after 25 days on slow evaporation.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C–H 0.93 to 0.96 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to 1.2 to 1.5 $U_{\text{equiv}}(\text{C})$. The methanol H-atoms were located in a difference Fourier map, and were refined with a distance restraint of O–H 0.85±0.01 Å; their U_{iso} values were freely refined

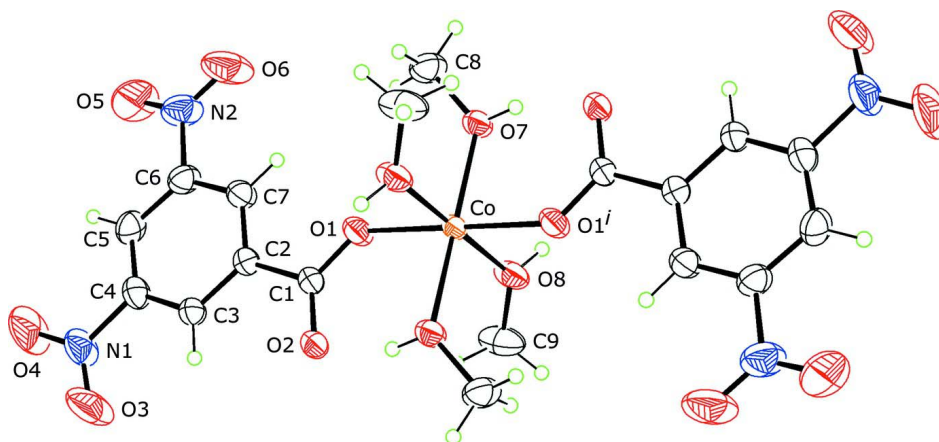


Figure 1

The molecular structure of (I) extended to show the coordination geometry for the Co(II) atom, showing displacement ellipsoids at the 50% probability level. Symmetry operation *i*: 1-*x*, 1-*y*, 1-*z*.

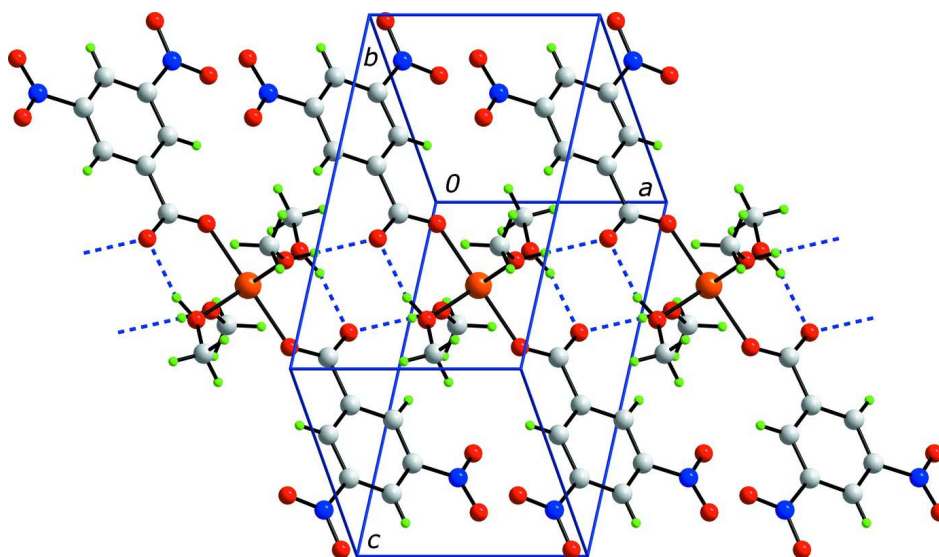


Figure 2

Linear supramolecular chain along the *a* axis in (I) mediated by O—H...O hydrogen bonding. These and the intramolecular O—H...O hydrogen bonds are shown as blue dashed lines.

Bis(3,5-dinitrobenzoato- κO^1)tetramethanolicobalt(II)

Crystal data

[Co(C₇H₃N₂O₆)₂(CH₄O)₄]

M_r = 609.33

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 6.4068 (8) Å

b = 8.7660 (11) Å

c = 12.1603 (16) Å

α = 90.411 (2)°

β = 100.407 (2)°

γ = 102.214 (2)°

V = 655.77 (14) Å³

Z = 1

F(000) = 313

D_x = 1.543 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 1592 reflections

θ = 2.4–22.8°

μ = 0.74 mm⁻¹

$T = 293$ K
Prism, pink

$0.35 \times 0.30 \times 0.05$ mm

Data collection

Bruker SMART APEX
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
 $T_{\min} = 0.669$, $T_{\max} = 0.746$

6372 measured reflections
2999 independent reflections
2388 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 1.7^\circ$
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.110$
 $S = 1.03$
2999 reflections
188 parameters
2 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.1427P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co	0.5000	0.5000	0.5000	0.03530 (16)
O1	0.6891 (3)	0.3924 (2)	0.61732 (14)	0.0514 (5)
O2	0.8795 (3)	0.2811 (2)	0.51696 (14)	0.0471 (4)
O3	1.4087 (5)	0.0083 (4)	0.7142 (2)	0.1213 (12)
O4	1.4957 (5)	0.0210 (4)	0.8875 (2)	0.1234 (12)
O5	1.0327 (5)	0.2304 (4)	1.1038 (2)	0.1159 (11)
O6	0.8093 (6)	0.3608 (4)	1.0193 (2)	0.1090 (10)
O7	0.3342 (3)	0.5533 (2)	0.62522 (14)	0.0458 (4)
H7O	0.255 (4)	0.614 (3)	0.595 (2)	0.075 (11)*
O8	0.2673 (3)	0.2953 (2)	0.46261 (18)	0.0550 (5)
H8O	0.145 (3)	0.291 (4)	0.481 (3)	0.075 (10)*
N1	1.3845 (5)	0.0471 (3)	0.8033 (2)	0.0710 (8)
N2	0.9450 (5)	0.2836 (4)	1.0197 (2)	0.0775 (8)

C1	0.8312 (4)	0.3181 (3)	0.60687 (19)	0.0379 (5)
C2	0.9496 (4)	0.2659 (3)	0.7142 (2)	0.0383 (5)
C3	1.1103 (4)	0.1830 (3)	0.7114 (2)	0.0420 (6)
H3	1.1468	0.1592	0.6436	0.050*
C4	1.2149 (4)	0.1366 (3)	0.8100 (2)	0.0498 (6)
C5	1.1687 (5)	0.1679 (3)	0.9125 (2)	0.0547 (7)
H5	1.2420	0.1356	0.9783	0.066*
C6	1.0075 (5)	0.2500 (3)	0.9125 (2)	0.0525 (7)
C7	0.8985 (4)	0.2998 (3)	0.8158 (2)	0.0468 (6)
H7	0.7914	0.3558	0.8191	0.056*
C8	0.4162 (5)	0.5914 (4)	0.7407 (2)	0.0604 (8)
H8A	0.3034	0.6156	0.7755	0.091*
H8B	0.5356	0.6803	0.7491	0.091*
H8C	0.4652	0.5041	0.7755	0.091*
C9	0.2797 (6)	0.1460 (3)	0.4244 (3)	0.0787 (11)
H9A	0.2018	0.1255	0.3487	0.118*
H9B	0.2166	0.0686	0.4712	0.118*
H9C	0.4292	0.1422	0.4271	0.118*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.0357 (3)	0.0419 (3)	0.0339 (3)	0.01829 (19)	0.00943 (18)	0.00124 (18)
O1	0.0558 (11)	0.0699 (12)	0.0409 (10)	0.0385 (10)	0.0118 (8)	0.0069 (8)
O2	0.0428 (9)	0.0662 (12)	0.0387 (9)	0.0257 (8)	0.0080 (7)	0.0001 (8)
O3	0.151 (3)	0.177 (3)	0.083 (2)	0.133 (3)	0.0311 (18)	0.0207 (19)
O4	0.125 (2)	0.193 (3)	0.086 (2)	0.117 (2)	0.0082 (17)	0.044 (2)
O5	0.157 (3)	0.168 (3)	0.0389 (14)	0.074 (2)	0.0149 (15)	0.0175 (16)
O6	0.167 (3)	0.132 (2)	0.0629 (16)	0.085 (2)	0.0510 (17)	0.0109 (15)
O7	0.0501 (11)	0.0574 (11)	0.0379 (9)	0.0259 (9)	0.0125 (8)	0.0023 (8)
O8	0.0428 (11)	0.0497 (11)	0.0767 (13)	0.0086 (9)	0.0242 (10)	-0.0125 (9)
N1	0.0722 (17)	0.088 (2)	0.0672 (18)	0.0498 (16)	0.0113 (14)	0.0207 (15)
N2	0.109 (2)	0.086 (2)	0.0466 (16)	0.0382 (18)	0.0211 (15)	0.0030 (14)
C1	0.0346 (12)	0.0411 (13)	0.0400 (13)	0.0133 (10)	0.0064 (10)	0.0019 (10)
C2	0.0375 (12)	0.0384 (12)	0.0398 (13)	0.0105 (10)	0.0064 (10)	0.0032 (10)
C3	0.0429 (13)	0.0482 (14)	0.0377 (13)	0.0173 (11)	0.0060 (10)	0.0027 (10)
C4	0.0463 (14)	0.0495 (15)	0.0560 (16)	0.0200 (12)	0.0046 (12)	0.0081 (12)
C5	0.0603 (17)	0.0605 (17)	0.0422 (15)	0.0184 (14)	-0.0003 (12)	0.0095 (12)
C6	0.0645 (17)	0.0566 (16)	0.0380 (14)	0.0176 (14)	0.0080 (12)	0.0011 (12)
C7	0.0509 (15)	0.0488 (14)	0.0458 (14)	0.0205 (12)	0.0107 (11)	0.0031 (11)
C8	0.078 (2)	0.0658 (19)	0.0409 (15)	0.0215 (16)	0.0146 (14)	-0.0014 (13)
C9	0.084 (2)	0.0532 (18)	0.104 (3)	0.0050 (17)	0.044 (2)	-0.0217 (18)

Geometric parameters (Å, °)

Co—O8	2.0645 (18)	N2—C6	1.476 (4)
Co—O8 ⁱ	2.0645 (18)	C1—C2	1.511 (3)
Co—O1	2.0666 (17)	C2—C7	1.380 (3)

Co—O1 ⁱ	2.0666 (16)	C2—C3	1.385 (3)
Co—O7	2.1094 (16)	C3—C4	1.373 (3)
Co—O7 ⁱ	2.1094 (16)	C3—H3	0.9300
O1—C1	1.250 (3)	C4—C5	1.371 (4)
O2—C1	1.247 (3)	C5—C6	1.378 (4)
O3—N1	1.179 (4)	C5—H5	0.9300
O4—N1	1.190 (3)	C6—C7	1.379 (4)
O5—N2	1.220 (4)	C7—H7	0.9300
O6—N2	1.209 (4)	C8—H8A	0.9600
O7—C8	1.418 (3)	C8—H8B	0.9600
O7—H7O	0.85 (3)	C8—H8C	0.9600
O8—C9	1.408 (3)	C9—H9A	0.9600
O8—H8O	0.85 (3)	C9—H9B	0.9600
N1—C4	1.482 (3)	C9—H9C	0.9600
O8—Co—O1	91.36 (8)	C7—C2—C3	119.3 (2)
O8 ⁱ —Co—O1	88.64 (8)	C7—C2—C1	120.5 (2)
O8—Co—O1 ⁱ	88.64 (8)	C3—C2—C1	120.2 (2)
O8 ⁱ —Co—O1 ⁱ	91.36 (8)	C4—C3—C2	119.1 (2)
O8—Co—O7	88.14 (7)	C4—C3—H3	120.5
O8 ⁱ —Co—O7	91.86 (7)	C2—C3—H3	120.5
O1—Co—O7	89.22 (7)	C5—C4—C3	123.3 (2)
O1 ⁱ —Co—O7	90.78 (7)	C5—C4—N1	119.3 (2)
O8—Co—O7 ⁱ	91.86 (7)	C3—C4—N1	117.4 (2)
O8 ⁱ —Co—O7 ⁱ	88.14 (7)	C4—C5—C6	116.3 (2)
O1—Co—O7 ⁱ	90.78 (7)	C4—C5—H5	121.9
O1 ⁱ —Co—O7 ⁱ	89.22 (7)	C6—C5—H5	121.9
O1—Co—O1 ⁱ	180.0	C5—C6—C7	122.6 (2)
O7—Co—O7 ⁱ	180.0	C5—C6—N2	119.1 (3)
O8—Co—O8 ⁱ	180.0	C7—C6—N2	118.3 (3)
C1—O1—Co	130.70 (16)	C6—C7—C2	119.4 (2)
C8—O7—Co	128.82 (16)	C6—C7—H7	120.3
C8—O7—H7O	113 (2)	C2—C7—H7	120.3
Co—O7—H7O	105 (2)	O7—C8—H8A	109.5
C9—O8—Co	131.57 (18)	O7—C8—H8B	109.5
C9—O8—H8O	110 (2)	H8A—C8—H8B	109.5
Co—O8—H8O	118 (2)	O7—C8—H8C	109.5
O3—N1—O4	122.3 (3)	H8A—C8—H8C	109.5
O3—N1—C4	118.6 (3)	H8B—C8—H8C	109.5
O4—N1—C4	119.1 (3)	O8—C9—H9A	109.5
O6—N2—O5	123.7 (3)	O8—C9—H9B	109.5
O6—N2—C6	118.5 (3)	H9A—C9—H9B	109.5
O5—N2—C6	117.8 (3)	O8—C9—H9C	109.5
O2—C1—O1	126.1 (2)	H9A—C9—H9C	109.5
O2—C1—C2	118.0 (2)	H9B—C9—H9C	109.5
O1—C1—C2	115.9 (2)		
O8—Co—O1—C1	87.5 (2)	C1—C2—C3—C4	-179.8 (2)

O8 ⁱ —Co—O1—C1	-92.5 (2)	C2—C3—C4—C5	0.0 (4)
O7—Co—O1—C1	175.6 (2)	C2—C3—C4—N1	179.5 (2)
O7 ⁱ —Co—O1—C1	-4.4 (2)	O3—N1—C4—C5	173.0 (3)
O8—Co—O7—C8	125.9 (2)	O4—N1—C4—C5	-9.2 (5)
O8 ⁱ —Co—O7—C8	-54.1 (2)	O3—N1—C4—C3	-6.5 (5)
O1—Co—O7—C8	34.5 (2)	O4—N1—C4—C3	171.2 (3)
O1 ⁱ —Co—O7—C8	-145.5 (2)	C3—C4—C5—C6	0.2 (4)
O1—Co—O8—C9	-58.0 (3)	N1—C4—C5—C6	-179.3 (3)
O1 ⁱ —Co—O8—C9	122.0 (3)	C4—C5—C6—C7	-0.5 (4)
O7—Co—O8—C9	-147.1 (3)	C4—C5—C6—N2	178.2 (3)
O7 ⁱ —Co—O8—C9	32.9 (3)	O6—N2—C6—C5	177.2 (3)
Co—O1—C1—O2	-6.2 (4)	O5—N2—C6—C5	-3.4 (5)
Co—O1—C1—C2	175.42 (15)	O6—N2—C6—C7	-4.0 (5)
O2—C1—C2—C7	-178.2 (2)	O5—N2—C6—C7	175.4 (3)
O1—C1—C2—C7	0.3 (4)	C5—C6—C7—C2	0.6 (4)
O2—C1—C2—C3	1.6 (4)	N2—C6—C7—C2	-178.1 (3)
O1—C1—C2—C3	-179.9 (2)	C3—C2—C7—C6	-0.3 (4)
C7—C2—C3—C4	0.0 (4)	C1—C2—C7—C6	179.5 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7 _o ...O2 ⁱ	0.85 (3)	1.84 (2)	2.645 (2)	158 (3)
O8—H8 _o ...O2 ⁱⁱ	0.85 (3)	1.82 (1)	2.662 (2)	179 (3)

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