

catena-Poly[[[triaquacobalt(II)]- μ -10-methylphenothiazine-3,7-dicarboxylato] monohydrate]

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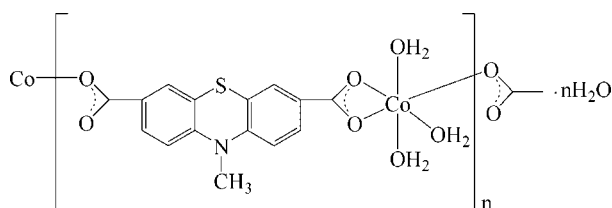
Received 24 February 2012; accepted 5 March 2012

Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.043; wR factor = 0.104; data-to-parameter ratio = 13.7.

The polymeric title compound, $[\text{Co}(\text{C}_{15}\text{H}_9\text{NO}_4\text{S})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, consists of chains along $[001]$ made up from Co^{2+} ions bridged by 10-methylphenothiazine-3,7-dicarboxylate anions. The Co^{2+} ion, coordinated by three O atoms from two different carboxylate groups and three water molecules, displays a distorted octahedral environment. In the crystal, π - π interchain interactions, with centroid-centroid distances of 3.656 (2) and 3.669 (2) Å between the benzene rings of the ligands, assemble the chains into sheets parallel to (100). O-H...O hydrogen-bonding interactions between the coordinating water molecules and carboxylate O atoms link the sheets into a three-dimensional network.

Related literature

For background to phenothiazine as a pharmacophore, see: Albery *et al.* (1979); Tsakovska & Pajeva (2006). For compounds with organic framework structures and with electro-optic or electronic properties, see: Chakraborty *et al.* (2005); Cho *et al.* (2006); Park *et al.* (2008); Krämer *et al.* (2001); Zhang *et al.* (2007). For structure elucidation, see: Spek (2009).



Experimental

Crystal data

$[\text{Co}(\text{C}_{15}\text{H}_9\text{NO}_4\text{S})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$
 $M_r = 430.30$
 Orthorhombic, $Pbca$
 $a = 15.3105$ (8) Å
 $b = 7.2983$ (4) Å
 $c = 29.5679$ (15) Å
 $V = 3303.9$ (3) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 1.21$ mm⁻¹
 $T = 291$ K
 $0.30 \times 0.26 \times 0.24$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
 $T_{\min} = 0.703$, $T_{\max} = 0.759$
 16812 measured reflections
 3236 independent reflections
 2650 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.104$
 $S = 1.08$
 3236 reflections
 236 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.62$ e Å⁻³
 $\Delta\rho_{\min} = -0.52$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O4 ⁱ	2.0523 (19)	Co1—O6	2.114 (2)
Co1—O5	2.074 (2)	Co1—O2	2.1581 (19)
Co1—O7	2.087 (2)	Co1—O1	2.1661 (19)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H5X...O8 ⁱⁱ	0.85	1.83	2.678 (4)	180
O5—H5Y...O4 ⁱⁱⁱ	0.85	2.16	2.879 (3)	142
O6—H6X...O1 ^{iv}	0.85	1.91	2.748 (3)	169
O6—H6Y...O8	0.85	2.43	3.149 (4)	143
O7—H7X...O2 ^v	0.85	2.00	2.826 (3)	163
O7—H7Y...O3 ⁱ	0.85	1.88	2.615 (3)	144
O8—H8X...O3 ⁱ	0.85	2.01	2.808 (4)	156
O8—H8Y...O2 ^{vi}	0.85	2.09	2.760 (3)	135

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, z$; (v) $-x + 1, -y, -z + 1$; (vi) $-x + 1, -y + 1, -z + 1$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge financial support from the Natural Science Foundation of China, the Opening Project of Xinjiang Laboratory of Phase Transitions and Microstructures of Condensed Matter (XJDX0912-2011-01) and the Foundation of Yili Normal University (2011YNYB034).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2597).

References

- Albery, W. J., Foulds, A. W., Hall, K. J., Hillman, A. R., Edgell, R. G. & Orchard, A. F. (1979). *Nature (London)*, **282**, 793–797.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2000). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chakraborty, S., Wadas, T. J., Hester, H., Schmehl, R. & Eisenberg, R. (2005). *Inorg. Chem.* **44**, 6865–6878.
- Cho, N. S., Park, J.-H., Lee, S.-K., Lee, J., Shim, H.-K., Park, M.-J., Hwang, D.-H. & Jung, B.-J. (2006). *Macromolecules*, **39**, 177–183.
- Krämer, C. S., Zeitler, K. & Müller, T. J. J. (2001). *Tetrahedron Lett.* **42**, 8619–8624.
- Park, M.-J., Lee, J., Park, J.-H., Lee, S. K., Lee, J.-I., Chu, H.-Y., Hwang, D.-H. & Shim, H.-K. (2008). *Macromolecules*, **41**, 3063–3070.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tsakovska, I. & Pajeva, I. (2006). *Curr. Drug Targets*, **7**, 1123–1134.
- Zhang, W.-W., Yu, Y.-G., Lu, Z.-D., Mao, W.-L., Li, Y.-Z. & Meng, Q.-J. (2007). *Organometallics*, **26**, 865–873.

supplementary materials

Acta Cryst. (2012). E68, m402–m403 [doi:10.1107/S1600536812009580]

catena-Poly[[[triaquacobalt(II)]- μ -10-methylphenothiazine-3,7-dicarboxylato] monohydrate]**Yun-Xia Hu, Yan Zhou, Fang-Ming Wang and Wen-Wei Zhang****Comment**

Phenothiazine, an intriguing type of biologically and pharmaceutically active heterocyclic compound well known as a pharmacophore in tranquilizers, antituberculosis agents, anti-tumor agents, bactericides, *etc.* (Albery *et al.*, 1979; Tsakovska & Pajeva, 2006), is now widely studied as an electron donor component and electrically conducting charge-transfer composite on account of its unique electro-optic properties in materials science (Chakraborty *et al.*, 2005; Cho *et al.*, 2006; Park *et al.*, 2008). Previous studies involving this compound had more emphasis on the large π -electron conjugated system (Krämer *et al.*, 2001; Zhang *et al.*, 2007); however, less work is reported on the construction of metal-organic frameworks using it as a building block. Here we employed the 10-methyl-10*H*-phenothiazine-3,7-dicarboxylate (MPTD) anion as a ligand to crystallize the title complex.

The title compound, $\{[\text{Co}(\text{C}_{15}\text{H}_9\text{NO}_4\text{S})(\text{H}_2\text{O})_3]\text{H}_2\text{O}\}$, consists of a three-dimensional supramolecular network built up from coordination bonds, hydrogen bonds, and π – π interactions. As shown in Fig. 1, the Co^{2+} ion has a slightly distorted octahedral coordination environment formed by three O atoms from two different carboxylate ligands and three O atoms from three coordinated water molecules. Each MPTD ligand bridges two Co atoms *via* two carboxylate groups in a monodentate and a bidentate coordination mode into a one-dimensional zigzag chain parallel to [001]. These chains are assembled in an antiparallel manner into two-dimensional sheets parallel (100) based on strong interchain π – π interactions between the ligands [centroid-centroid distance = 3.656, 3.669 Å]. The sheets are further connected to form a three-dimensional supramolecular network (Fig. 2) *via* interlayer O—H \cdots O hydrogen bond interactions. A *PLATON* calculation (Spek, 2009) shows that the structure has 13.6% solvent accessible voids when the coordinated and lattice water molecules are neglected. The resulting framework structure contains channels with approximate dimensions of 2.9 \times 4.9 Å² and 1.9 \times 1.9 Å² along [010] and [001], respectively. All the lattice water molecules and the coordinating water molecules are situated in these channels and are involved in the above extensive interlayer and intralayer H-bonding.

Experimental

The educt 10-methyl-10*H*-phenothiazine-3,7-dicarboxylic acid used to construct the title compound $\{[\text{Co}(\text{C}_{15}\text{H}_9\text{NO}_4\text{S})(\text{H}_2\text{O})_3]\text{H}_2\text{O}\}$ was prepared by oxidation of 10-methyl-10*H*-phenothiazine-3,7-dicarbaldehyde using silver nitrate as oxidant in an alkaline medium. 10-Methyl-10*H*-phenothiazine-3,7-dicarbaldehyde (0.6417 g, 2.38 mmol) (Cho *et al.*, 2006) was dissolved in 35 ml solution of KOH (10.0 g, 0.178 mol), then a 5 ml solution of AgNO₃ (1.3 g, 7.65 mmol) was added slowly. The mixture was filtered after heating at 103 K overnight, then HCl (2 *M*) was added to the filtrate until the pH value reached 1–2, during which a large amount of precipitate formed. The precipitate was filtered off, washed with distilled water, re-dissolved in KOH solution, and again acidified to pH 1–2. The final acidification product was obtained by filtration and dried *in vacuo* (yield 0.4323 g, 60.3%). ¹H NMR (300 MHz; DMSO-*d*⁶): δ_{H} 3.31 (3 H, s, CH₃), 7.03 (2 H, s, ArH), 7.22 (2 H, d, ArH), 7.70 (2 H, d, ArH), 12.70 (2H, br, COOH). ¹³C NMR (300 MHz; DMSO-*d*⁶):

δ_c 40.13 (CH₃), 115.41 (Ar), 122.24 (Ar), 126.10 (Ar), 128.86 (Ar), 130.52 (Ar), 148.80 (Ar), 167.23 (COOH). MS: m/z 300.01 [$M-1$]⁻ (Calcd 300.03).

Single crystals of {[Co(C₁₅H₉NO₄S)(H₂O)₃]}H₂O were obtained by solvothermal reaction of Co(NO₃)₂·6H₂O (58.2 mg, 0.2 mmol) and 10-methyl-10*H*-phenothiazine-3,7-dicarboxylic acid (15.6 mg, 0.05 mmol) in a mixed solvent of ethanol and H₂O (8 ml, volume ratio 1:4) at 393 K for 86 h and finally cooled to room temperature. The resulting products were filtered off, washed thoroughly with distilled water and dried in air at room temperature. The yield was 38.7 mg (45%).

Refinement

All the H atoms were fixed geometrically and treated as riding with C—H = 0.96 Å, O—H = 0.85 Å and with U_{iso} (H) = 1.2 U_{eq} (C) or 1.5 U_{eq} (C, O) for methyl and water H atoms.

Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

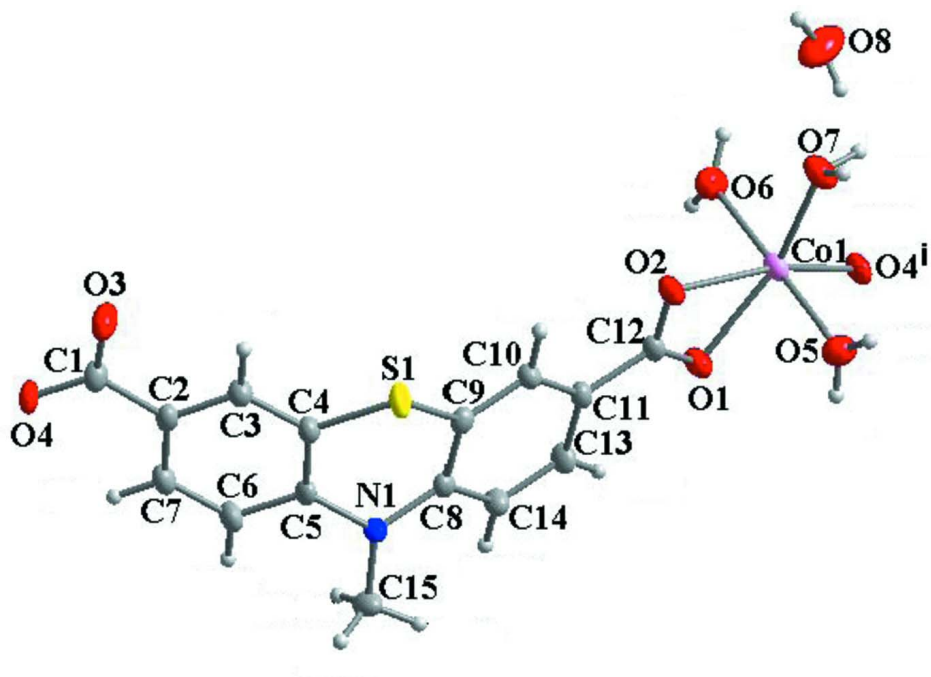
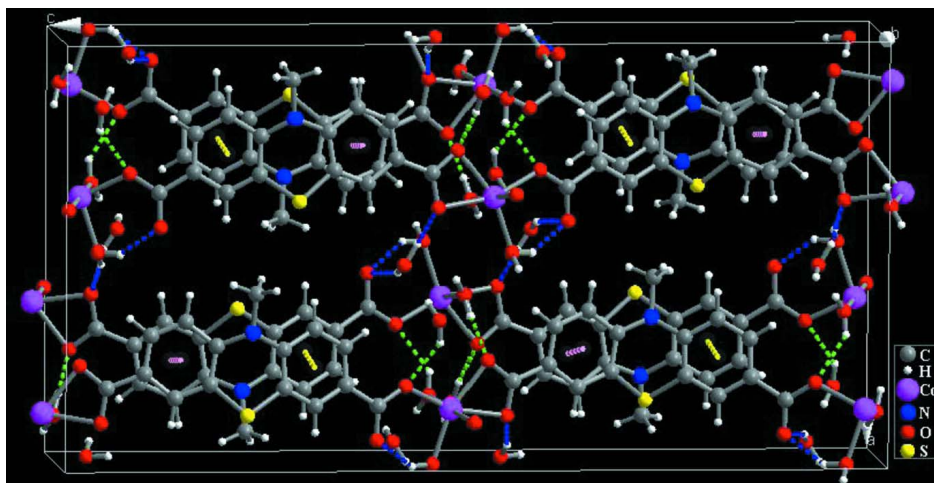


Figure 1

ORTEP plot of the title compound showing the local coordination environment of Co²⁺ with displacement ellipsoids at the 50% probability levels and H atoms shown as small spheres of arbitrary radius. [Symmetry code: $i = x, 0.5 - y, 0.5 + z$.]


Figure 2

The crystal packing diagram showing the 3-dimensional network. Inter-chain (blue dotted lines), intra-chain (bright green dotted lines), hydrogen bonds and inter-chain π — π interactions (yellow and rose dashed lines) are displayed.

catena-Poly[[[triaquacobalt(II)]- μ -10-methylphenothiazine-3,7-dicarboxylato] monohydrate]
Crystal data

 $M_r = 430.30$

 Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

 $a = 15.3105 (8) \text{ \AA}$
 $b = 7.2983 (4) \text{ \AA}$
 $c = 29.5679 (15) \text{ \AA}$
 $V = 3303.9 (3) \text{ \AA}^3$
 $Z = 8$
 $F(000) = 1768$
 $D_x = 1.730 \text{ Mg m}^{-3}$

 Mo *K* α radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8389 reflections

 $\theta = 2.7\text{--}28.1^\circ$
 $\mu = 1.21 \text{ mm}^{-1}$
 $T = 291 \text{ K}$

Block, dark blue

 $0.30 \times 0.26 \times 0.24 \text{ mm}$
Data collection

Bruker SMART CCD

diffractometer

Radiation source: sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

 (*SADABS*; Bruker, 2000)

 $T_{\min} = 0.703$, $T_{\max} = 0.759$

16812 measured reflections

3236 independent reflections

 2650 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 1.9^\circ$
 $h = -18 \rightarrow 18$
 $k = -8 \rightarrow 9$
 $l = -36 \rightarrow 25$
Refinement

 Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.104$
 $S = 1.08$

3236 reflections

236 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$

 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.62 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e \AA}^{-3}$

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.

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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.64689 (18)	0.1531 (4)	0.11609 (9)	0.0251 (6)
C2	0.69797 (18)	0.0972 (4)	0.15690 (8)	0.0226 (6)
C3	0.65262 (17)	0.0449 (4)	0.19532 (9)	0.0231 (6)
H3A	0.5899	0.0458	0.1951	0.028*
C4	0.69635 (17)	−0.0086 (4)	0.23421 (8)	0.0208 (5)
C5	0.78763 (17)	−0.0105 (4)	0.23556 (8)	0.0186 (5)
C6	0.83264 (19)	0.0454 (4)	0.19657 (9)	0.0250 (6)
H6A	0.8953	0.0471	0.1969	0.030*
C7	0.78842 (19)	0.0987 (4)	0.15843 (9)	0.0256 (6)
H7A	0.8207	0.1367	0.1323	0.031*
C8	0.79744 (17)	−0.0200 (4)	0.31735 (8)	0.0193 (5)
C9	0.70693 (17)	−0.0173 (4)	0.32467 (8)	0.0197 (5)
C10	0.67305 (17)	0.0274 (4)	0.36651 (9)	0.0211 (5)
H10A	0.6109	0.0300	0.3708	0.025*
C11	0.72820 (17)	0.0696 (3)	0.40252 (8)	0.0210 (5)
C12	0.69238 (17)	0.1164 (4)	0.44740 (8)	0.0208 (5)
C13	0.81794 (18)	0.0699 (4)	0.39510 (9)	0.0234 (6)
H13A	0.8563	0.1008	0.4196	0.028*
C14	0.85212 (17)	0.0271 (4)	0.35350 (9)	0.0230 (6)
H14A	0.9142	0.0295	0.3491	0.028*
C15	0.92396 (18)	−0.1018 (4)	0.27125 (10)	0.0302 (6)
H15A	0.9461	−0.1404	0.3001	0.045*
H15B	0.9348	−0.1955	0.2492	0.045*
H15C	0.9527	0.0093	0.2622	0.045*
Co1	0.63098 (2)	0.19466 (5)	0.523713 (12)	0.02238 (13)
N1	0.83090 (14)	−0.0684 (3)	0.27475 (7)	0.0212 (5)
O1	0.74252 (13)	0.1653 (3)	0.47923 (6)	0.0267 (4)
O2	0.61043 (12)	0.1094 (3)	0.45464 (6)	0.0266 (4)
O3	0.56576 (13)	0.1431 (3)	0.11768 (7)	0.0363 (5)
O4	0.68927 (13)	0.2090 (3)	0.08152 (6)	0.0285 (5)
O5	0.64958 (14)	−0.0747 (3)	0.54390 (8)	0.0359 (5)
H5X	0.6117	−0.1448	0.5558	0.043*
H5Y	0.7035	−0.1014	0.5420	0.043*
O6	0.61132 (15)	0.4686 (3)	0.50278 (7)	0.0356 (5)
H6X	0.6603	0.5165	0.4962	0.043*
H6Y	0.5731	0.5414	0.5134	0.043*
O7	0.50146 (14)	0.1985 (3)	0.54566 (7)	0.0333 (5)

H7X	0.4691	0.1071	0.5516	0.040*
H7Y	0.4990	0.2478	0.5717	0.040*
O8	0.53016 (16)	0.7045 (4)	0.58142 (10)	0.0592 (8)
H8X	0.5528	0.6002	0.5865	0.071*
H8Y	0.4840	0.7002	0.5655	0.071*
S1	0.63643 (4)	−0.08955 (10)	0.28101 (2)	0.02552 (18)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0279 (14)	0.0268 (15)	0.0205 (13)	−0.0044 (11)	−0.0003 (11)	0.0048 (11)
C2	0.0303 (14)	0.0213 (13)	0.0163 (13)	0.0022 (11)	0.0007 (10)	0.0014 (10)
C3	0.0219 (13)	0.0276 (14)	0.0199 (14)	−0.0005 (10)	−0.0005 (10)	0.0009 (10)
C4	0.0221 (13)	0.0243 (14)	0.0158 (12)	−0.0015 (10)	0.0014 (9)	0.0006 (10)
C5	0.0233 (13)	0.0200 (13)	0.0126 (12)	0.0005 (10)	−0.0016 (9)	−0.0027 (10)
C6	0.0250 (13)	0.0341 (15)	0.0160 (14)	−0.0021 (11)	0.0010 (10)	−0.0019 (11)
C7	0.0288 (14)	0.0294 (15)	0.0186 (13)	−0.0013 (12)	0.0050 (10)	0.0015 (11)
C8	0.0237 (13)	0.0192 (13)	0.0151 (12)	0.0016 (10)	0.0011 (10)	0.0031 (9)
C9	0.0229 (13)	0.0180 (13)	0.0182 (12)	−0.0023 (10)	−0.0015 (10)	0.0019 (9)
C10	0.0206 (12)	0.0253 (14)	0.0176 (13)	0.0011 (11)	0.0017 (10)	−0.0001 (10)
C11	0.0261 (14)	0.0212 (14)	0.0156 (12)	−0.0004 (10)	0.0016 (10)	0.0009 (10)
C12	0.0271 (13)	0.0194 (13)	0.0160 (12)	0.0010 (10)	0.0018 (10)	−0.0015 (10)
C13	0.0239 (13)	0.0296 (14)	0.0168 (13)	−0.0050 (11)	−0.0028 (10)	−0.0035 (10)
C14	0.0181 (12)	0.0320 (15)	0.0188 (13)	0.0001 (10)	−0.0017 (10)	−0.0007 (11)
C15	0.0241 (14)	0.0416 (18)	0.0250 (14)	0.0104 (12)	−0.0048 (11)	−0.0042 (12)
Co1	0.0213 (2)	0.0297 (2)	0.0162 (2)	−0.00106 (14)	0.00060 (14)	−0.00571 (14)
N1	0.0172 (10)	0.0312 (13)	0.0151 (11)	0.0037 (9)	−0.0023 (8)	−0.0009 (9)
O1	0.0220 (10)	0.0381 (12)	0.0201 (9)	−0.0026 (8)	0.0000 (8)	−0.0081 (8)
O2	0.0229 (9)	0.0386 (12)	0.0183 (10)	0.0004 (8)	0.0013 (7)	−0.0063 (8)
O3	0.0260 (11)	0.0556 (14)	0.0273 (11)	−0.0009 (10)	−0.0025 (9)	0.0148 (10)
O4	0.0304 (11)	0.0395 (13)	0.0156 (9)	−0.0006 (9)	0.0002 (8)	0.0092 (8)
O5	0.0358 (12)	0.0328 (12)	0.0392 (13)	0.0047 (9)	−0.0013 (9)	0.0018 (9)
O6	0.0328 (11)	0.0358 (12)	0.0382 (13)	0.0003 (10)	0.0049 (9)	0.0062 (10)
O7	0.0272 (11)	0.0420 (12)	0.0308 (12)	−0.0065 (9)	0.0057 (9)	−0.0104 (9)
O8	0.0315 (13)	0.0651 (19)	0.081 (2)	−0.0039 (12)	−0.0143 (13)	0.0253 (14)
S1	0.0230 (3)	0.0396 (4)	0.0139 (3)	−0.0101 (3)	−0.0013 (2)	0.0024 (3)

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

C1—O3	1.245 (3)	C12—O2	1.274 (3)
C1—O4	1.278 (3)	C12—Co1	2.510 (2)
C1—C2	1.495 (4)	C13—C14	1.373 (4)
C2—C3	1.385 (4)	C13—H13A	0.9601
C2—C7	1.386 (4)	C14—H14A	0.9600
C3—C4	1.387 (4)	C15—N1	1.449 (3)
C3—H3A	0.9600	C15—H15A	0.9601
C4—C5	1.398 (4)	C15—H15B	0.9599
C4—S1	1.762 (3)	C15—H15C	0.9600
C5—N1	1.400 (3)	Co1—O4 ⁱ	2.0523 (19)
C5—C6	1.404 (4)	Co1—O5	2.074 (2)

C6—C7	1.371 (4)	Co1—O7	2.087 (2)
C6—H6A	0.9601	Co1—O6	2.114 (2)
C7—H7A	0.9594	Co1—O2	2.1581 (19)
C8—C14	1.400 (4)	Co1—O1	2.1661 (19)
C8—C9	1.403 (4)	O4—Co1 ⁱⁱ	2.0523 (19)
C8—N1	1.405 (3)	O5—H5X	0.8497
C9—C10	1.381 (4)	O5—H5Y	0.8500
C9—S1	1.763 (3)	O6—H6X	0.8499
C10—C11	1.393 (4)	O6—H6Y	0.8500
C10—H10A	0.9601	O7—H7X	0.8500
C11—C13	1.391 (4)	O7—H7Y	0.8500
C11—C12	1.476 (3)	O8—H8X	0.8500
C12—O1	1.266 (3)	O8—H8Y	0.8499
O3—C1—O4	123.7 (3)	N1—C15—H15A	109.5
O3—C1—C2	118.4 (2)	N1—C15—H15B	109.8
O4—C1—C2	117.9 (2)	H15A—C15—H15B	109.5
C3—C2—C7	118.5 (2)	N1—C15—H15C	109.2
C3—C2—C1	118.4 (2)	H15A—C15—H15C	109.5
C7—C2—C1	123.2 (2)	H15B—C15—H15C	109.5
C2—C3—C4	121.0 (2)	O4 ⁱ —Co1—O5	91.44 (9)
C2—C3—H3A	119.7	O4 ⁱ —Co1—O7	98.60 (8)
C4—C3—H3A	119.3	O5—Co1—O7	93.09 (9)
C3—C4—C5	120.6 (2)	O4 ⁱ —Co1—O6	88.96 (9)
C3—C4—S1	119.6 (2)	O5—Co1—O6	179.58 (10)
C5—C4—S1	119.6 (2)	O7—Co1—O6	86.73 (9)
C4—C5—N1	120.0 (2)	O4 ⁱ —Co1—O2	161.86 (8)
C4—C5—C6	117.7 (2)	O5—Co1—O2	91.09 (9)
N1—C5—C6	122.4 (2)	O7—Co1—O2	99.19 (8)
C7—C6—C5	121.0 (3)	O6—Co1—O2	88.56 (8)
C7—C6—H6A	119.9	O4 ⁱ —Co1—O1	101.35 (8)
C5—C6—H6A	119.1	O5—Co1—O1	88.44 (8)
C6—C7—C2	121.2 (3)	O7—Co1—O1	159.95 (8)
C6—C7—H7A	119.4	O6—Co1—O1	91.61 (8)
C2—C7—H7A	119.4	O2—Co1—O1	60.78 (7)
C14—C8—C9	118.0 (2)	O4 ⁱ —Co1—C12	131.59 (8)
C14—C8—N1	121.9 (2)	O5—Co1—C12	89.52 (9)
C9—C8—N1	120.1 (2)	O7—Co1—C12	129.68 (9)
C10—C9—C8	120.8 (2)	O6—Co1—C12	90.31 (9)
C10—C9—S1	119.8 (2)	O2—Co1—C12	30.49 (8)
C8—C9—S1	119.19 (19)	O1—Co1—C12	30.29 (8)
C9—C10—C11	120.6 (2)	C5—N1—C8	119.6 (2)
C9—C10—H10A	119.7	C5—N1—C15	117.2 (2)
C11—C10—H10A	119.6	C8—N1—C15	117.7 (2)
C13—C11—C10	118.6 (2)	C12—O1—Co1	90.08 (16)
C13—C11—C12	120.6 (2)	C12—O2—Co1	90.23 (15)
C10—C11—C12	120.9 (2)	C1—O4—Co1 ⁱⁱ	123.71 (18)
O1—C12—O2	118.9 (2)	Co1—O5—H5X	126.6
O1—C12—C11	120.6 (2)	Co1—O5—H5Y	109.4

O2—C12—C11	120.5 (2)	H5X—O5—H5Y	123.5
O1—C12—Co1	59.64 (13)	Co1—O6—H6X	109.3
O2—C12—Co1	59.28 (13)	Co1—O6—H6Y	125.5
C11—C12—Co1	179.7 (2)	H6X—O6—H6Y	115.7
C14—C13—C11	121.2 (2)	Co1—O7—H7X	127.4
C14—C13—H13A	119.8	Co1—O7—H7Y	109.3
C11—C13—H13A	119.1	H7X—O7—H7Y	96.8
C13—C14—C8	120.8 (2)	H8X—O8—H8Y	113.8
C13—C14—H14A	119.7	C4—S1—C9	98.98 (12)
C8—C14—H14A	119.5		
O3—C1—C2—C3	-2.9 (4)	O1—C12—Co1—O5	-87.73 (16)
O4—C1—C2—C3	176.9 (3)	O2—C12—Co1—O5	92.97 (16)
O3—C1—C2—C7	178.4 (3)	O1—C12—Co1—O7	178.66 (15)
O4—C1—C2—C7	-1.8 (4)	O2—C12—Co1—O7	-0.6 (2)
C7—C2—C3—C4	-1.4 (4)	O1—C12—Co1—O6	92.65 (16)
C1—C2—C3—C4	179.9 (3)	O2—C12—Co1—O6	-86.64 (16)
C2—C3—C4—C5	0.2 (4)	O1—C12—Co1—O2	179.3 (3)
C2—C3—C4—S1	-175.5 (2)	O2—C12—Co1—O1	-179.3 (3)
C3—C4—C5—N1	-178.7 (2)	C4—C5—N1—C8	-38.7 (4)
S1—C4—C5—N1	-3.0 (3)	C6—C5—N1—C8	141.9 (3)
C3—C4—C5—C6	0.7 (4)	C4—C5—N1—C15	168.1 (2)
S1—C4—C5—C6	176.5 (2)	C6—C5—N1—C15	-11.3 (4)
C4—C5—C6—C7	-0.5 (4)	C14—C8—N1—C5	-141.7 (3)
N1—C5—C6—C7	178.9 (3)	C9—C8—N1—C5	38.1 (4)
C5—C6—C7—C2	-0.7 (4)	C14—C8—N1—C15	11.3 (4)
C3—C2—C7—C6	1.6 (4)	C9—C8—N1—C15	-168.9 (2)
C1—C2—C7—C6	-179.7 (3)	O2—C12—O1—Co1	0.7 (3)
C14—C8—C9—C10	-1.1 (4)	C11—C12—O1—Co1	-179.8 (2)
N1—C8—C9—C10	179.1 (2)	O4 ⁱ —Co1—O1—C12	-177.13 (16)
C14—C8—C9—S1	-176.1 (2)	O5—Co1—O1—C12	91.71 (17)
N1—C8—C9—S1	4.1 (3)	O7—Co1—O1—C12	-3.0 (3)
C8—C9—C10—C11	-0.5 (4)	O6—Co1—O1—C12	-87.87 (17)
S1—C9—C10—C11	174.5 (2)	O2—Co1—O1—C12	-0.41 (15)
C9—C10—C11—C13	1.5 (4)	O1—C12—O2—Co1	-0.7 (3)
C9—C10—C11—C12	-179.6 (2)	C11—C12—O2—Co1	179.8 (2)
C13—C11—C12—O1	3.2 (4)	O4 ⁱ —Co1—O2—C12	10.8 (4)
C10—C11—C12—O1	-175.7 (3)	O5—Co1—O2—C12	-87.19 (16)
C13—C11—C12—O2	-177.3 (3)	O7—Co1—O2—C12	179.51 (16)
C10—C11—C12—O2	3.8 (4)	O6—Co1—O2—C12	93.05 (16)
C10—C11—C13—C14	-0.9 (4)	O1—Co1—O2—C12	0.41 (15)
C12—C11—C13—C14	-179.9 (3)	O3—C1—O4—Co1 ⁱⁱ	3.4 (4)
C11—C13—C14—C8	-0.6 (4)	C2—C1—O4—Co1 ⁱⁱ	-176.40 (18)
C9—C8—C14—C13	1.7 (4)	C3—C4—S1—C9	-149.7 (2)
N1—C8—C14—C13	-178.5 (3)	C5—C4—S1—C9	34.6 (2)
O1—C12—Co1—O4 ⁱ	3.8 (2)	C10—C9—S1—C4	150.0 (2)
O2—C12—Co1—O4 ⁱ	-175.52 (15)	C8—C9—S1—C4	-35.0 (2)

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5X \cdots O8 ⁱⁱⁱ	0.85	1.83	2.678 (4)	180
O5—H5Y \cdots O4 ^{iv}	0.85	2.16	2.879 (3)	142
O6—H6X \cdots O1 ^v	0.85	1.91	2.748 (3)	169
O6—H6Y \cdots O8	0.85	2.43	3.149 (4)	143
O7—H7X \cdots O2 ^{vi}	0.85	2.00	2.826 (3)	163
O7—H7Y \cdots O3 ⁱ	0.85	1.88	2.615 (3)	144
O8—H8X \cdots O3 ⁱ	0.85	2.01	2.808 (4)	156
O8—H8Y \cdots O2 ^{vii}	0.85	2.09	2.760 (3)	135

Symmetry codes: (i) $x, -y+1/2, z+1/2$; (iii) $x, y-1, z$; (iv) $-x+3/2, -y, z+1/2$; (v) $-x+3/2, y+1/2, z$; (vi) $-x+1, -y, -z+1$; (vii) $-x+1, -y+1, -z+1$.