Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Poly[[diaquabis[μ_4-5-nitroisophthalato-κ^4O^1:O^1:O^3:$O^{3'}$]bis[μ_3-pyridine-4-carboxylato-κ^3O:O':N]tricobalt(II)] tetrahydrate]

Xia Yin, Jun Fan,* Jingling Xin, Shengrun Zheng and Weiguang Zhang

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China
Correspondence e-mail: fanj@scnu.edu.cn

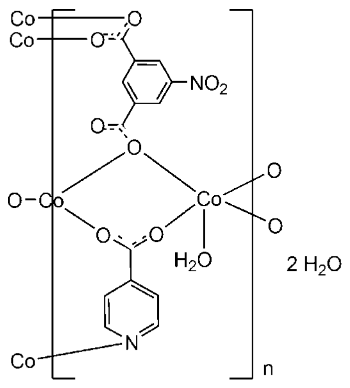
Received 5 March 2012; accepted 14 March 2012

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.027; wR factor = 0.071; data-to-parameter ratio = 11.0.

The title compound, {[$Co_3(C_6H_4NO_2)_2(C_8H_3NO_6)_2(H_2O)_2$]·$4H_2O$}$_n$, exhibits a two-dimensional layer-like structure in which the Co^{II} ions exhibit two kinds of coordination geometries. One nearly octahedral Co^{II} ion with crystallographic inversion symmetry is coordinated to six carboxylate O atoms from four bridging 5-nitroisophthalate (NIPH) ligands and two isonicotinate (IN) anions, while the other type of Co^{II} ion binds with one N atom and one carboxylate O atom from two IN anions, two carboxylate O atoms from two different NIPH anions and one ligated water molecule, displaying a distorted square-pyramidal coordination geometry. Three adjacent Co^{II} ions are bridged by six carboxylate groups from four NIPH ligands and two IN anions to form a linear trinuclear secondary building unit (SBU). Every trinuclear SBU is linked to its nearest neighbours in the ab plane, resulting in a two-dimensional layer-like structure perpendicular to the c axis. Along the a-axis direction neighbouring molecules are connected through carboxylate and pyridyl units of the IN anions, along the b axis through carboxylate groups of the NIPH ligands. The H atoms of one free water molecule are disordered in the crystal in a 1:1 ratio. Typical O—H···O hydrogen bonds are observed in the lattice, which include the following contacts: (a) between coordinated water molecules and carboxylate O atoms of the NIPH anions, (b) between lattice water molecules and carboxylate O atoms of the NIPH anions, and (c) between coordinated and lattice water molecules. These intermolecular hydrogen bonds connect the two-dimensional layers to form a three-dimensional supramolecular structure.

Related literature

For general background to the design and synthesis of coordination polymers, see: Jiang *et al.* (2010); Ma *et al.* (2009); Natarajan & Mahata (2009); Zang *et al.* (2006). For complexes with isonicotinate, see: Amo-Ochoa *et al.* (2010). For complexes with 5-nitroisophthalate, see: Chen *et al.* (2006, 2010); Sun *et al.* (2010). For related compounds, see: Du *et al.* (2008); Luo *et al.* (2003); Wang *et al.* (2009).



Experimental

Crystal data

[$Co_3(C_6H_4NO_2)_2(C_8H_3NO_6)_2$-($H_2O$)$_2$]·$4H_2O$
M_r = 947.32
Triclinic, $P\overline{1}$
a = 9.1890 (18) Å
b = 9.3548 (19) Å
c = 10.390 (2) Å
α = 78.74 (3)°
β = 88.64 (3)°
γ = 73.68 (3)°
V = 840.2 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.57 mm^{-1}
T = 298 K
0.35 × 0.28 × 0.16 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.610, T_{max} = 0.788
4357 measured reflections
2976 independent reflections
2667 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.071
S = 1.02
2976 reflections
271 parameters
10 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O3^{i}	0.84	2.05	2.861 (3)	160
O1W—H2W···O2W^{ii}	0.85	1.93	2.773 (3)	173
O3W—H5W···O2^{iii}	0.82	2.01	2.820 (2)	168
O3W—H6W···O1W^{iv}	0.83	1.83	2.648 (3)	167
O2W—H4WA···O2^{v}	0.85 (2)	2.27 (2)	3.098 (4)	165 (8)
O2W—H3WA···O6^{vi}	0.83 (2)	2.38 (6)	3.055 (3)	138 (8)
O2W—H3WB···O2W^{ii}	0.87 (2)	2.49 (3)	3.297 (6)	154 (6)
O2W—H4WB···O6^{vi}	0.89 (5)	2.54 (5)	3.055 (4)	118 (3)
O2W—H4WB···O2^{v}	0.89 (5)	2.54 (5)	3.098 (3)	121 (4)

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported financially by the National Natural Science Foundation of China (grant Nos. 21171059 and 21003053) and Guangdong Science and Technology Department (grant Nos. 2010B090300031 and 2011B010400023).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2461).

References

Amo-Ochoa, P., Welte, L., Gonzalez-Prieto, R., Sanz Miguel, P. J., Gomez-Garcia, C. J., Mateo-Marti, E., Delgado, S., Gomez-Herrero, J. & Zamora, F. (2010). *Chem. Commun.* **46**, 3262–3264.

Bruker (2002). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, S. P., Ren, Y. X., Wang, W. T. & Gao, S. L. (2010). *Dalton Trans.* **39**, 1552–1557.

Chen, H. J., Zhang, J., Feng, W. L. & Fu, M. (2006). *Inorg. Chem. Commun.* **9**, 300–303.

Du, M., Zhang, Z. H., You, Y. P. & Zhao, X. J. (2008). *CrystEngComm*, **10**, 306–321.

Jiang, H. L., Tatsu, Y., Lu, Z. H. & Xu, Q. (2010). *J. Am. Chem. Soc.* **132**, 5586–5587.

Luo, J. H., Hong, M. C., Wang, R. H., Cao, R., Han, L., Yuan, D. Q., Lin, Z. Z. & Zhou, Y. F. (2003). *Inorg. Chem.* **42**, 4486–4488.

Ma, S. Q., Sun, D. F., Yuan, D. Q., Wang, X. S. & Zhou, H. C. (2009). *J. Am. Chem. Soc.* **131**, 6445–6451.

Natarajan, S. & Mahata, P. (2009). *Chem. Soc. Rev.* **38**, 2304–2318.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sun, D., Luo, G. G., Zhang, N., Wei, Z. H., Yang, C. F., Xu, Q. J., Huang, R. B. & Zheng, L. S. (2010). *J. Mol. Struct.* **967**, 147–152.

Wang, H.-D., Li, M.-M. & He, H.-Y. (2009). *Acta Cryst.* E**65**, m510.

Zang, S. Q., Su, Y., Li, Y. Z., Ni, Z. P. & Meng, Q. J. (2006). *Inorg. Chem.* **45**, 174–180.

supplementary materials

Acta Cryst. (2012). E**68**, m451–m452   [doi:10.1107/S1600536812011269]

Poly[[diaquabis[μ_4-5-nitroisophthalato-$\kappa^4O^1:O^1:O^3:O^{3\prime}$]bis[$\mu_3$-pyridine-4-carboxylato-$\kappa^3O:O^\prime:N$]tricobalt(II)] tetrahydrate]

Xia Yin, Jun Fan, Jingling Xin, Shengrun Zheng and Weiguang Zhang

Comment

Over the past decades, rational design and construction of metal coordination polymers with aromatic carboxylates have become an attractive area in coordination and supramolecular chemistry, due to the fascinating network topologies they exhibit (Natarajan & Mahata, 2009) and due to industrially focused applications in gas storage, adsorption and separation (Ma *et al.*, 2009), nonlinear optical devices (Zang *et al.*, 2006), and fluorescence (Jiang *et al.*, 2010), *etc*. Due to versatile coordination modes and easy formation of secondary building units, 5-nitroisophthalate (NIPH) has been widely employed to construct coordination polymers (Chen *et al.*, 2010; Du *et al.*, 2008; Sun *et al.*, 2010).

Most cobalt complexes with 5-nitroisophthalate (NIPH) and aromatic N-donor coligands (pyridine, bipyridine, and imidazole) possess low-dimensional structure characteristics, namely, ladder, loop-like chain, zigzag chain, layer, and grid, *etc* (Chen *et al.*, 2006; Du *et al.*, 2008; Luo *et al.*, 2003). Cobalt complexes based on NIPH ligand and other carboxylates have been less developed (Wang *et al.*, 2009). In this work, we selected isonicotinic acid (HIN) as the coligand based on the following considerations: (1) it possesses the bifunctional bridging groups with both oxygen and nitrogen donors as a potential linkers and (2) it can adopt various coordination modes in high-dimensional heterometallic frameworks (Amo-Ochoa *et al.*, 2010). Herein, synthesis and crystal structure of a new cobalt compound is presented, which was prepared by hydrothermal reaction of $Co(CH_3COO)_2.4\ H_2O$ with 5-nitroisophthalic acid and isonicotinic acid.

The title compound exhibits a two-dimensional layer-like framework. As illustrated in Fig.1, each asymmetric unit contains one and a half Co^{II} ions, one 5-nitroisophthalate (NIPH) anion, an isonicotinate (IN) anion, one ligated and two lattice water molecules, as the $Co1^{II}$ ion lies on a crystallographic inversion centre. In the structure, the $Co1^{II}$ ion is six-coordinated in an O_6 donor set with the coordination geometry of a slightly distorted octahedron by four carboxylate oxygen atoms [O1, $O1^i$, $O4^{ii}$, $O4^{iii}$, symmetry codes: (i) -*x*, 1 - *y*, 1 - *z*; (ii) *x*, -1 + *y*, *z*; (iii) -*x*, 2 - *y*, 1 - *z*] from four bridging NIPH ligands in the equatorial plane, and the others [O8 and $O8^i$, symmetry code: (i) -*x*, 1 - *y*, 1 - *z*] from two IN anions at the axial sites; the $Co2^{II}$ ion coordinates with one $N2^{iv}$ atom [symmetry code: (iv) -1 + *x*, *y*, *z*] and one carboxylate O7 atom from two IN anions, two carboxylate oxygen atoms [$O3^{ii}$ and O7, symmetry code: (ii) *x*, -1 + *y*, *z*] from two different NIPH anions and one ligated water molecules, displaying a distorted square pyramidal coordination geometry. If the weak Co—O interaction between Co2 and O2 (2.4908 (6) Å) was considered, the coordination configuration of the Co2 ion could also be described as a severely distorted octahedron. The Co—O bond distances are in the range of 2.0206 (18)–2.1624 (16) Å, and the Co—N bond length is equal to 2.1465 (19) Å, all of which are in the normal ranges (Du *et al.*, 2008).

The NIPH ligand acts as μ_4-bridge to link four different Co^{II} ions through two carboxylate groups and the IN anion adopts a tridentate-bridging mode to connect three Co^{II} ions. Thus, one $Co1^{II}$ and two $Co2^{II}$ ions are bridged by six carboxylate groups from four NIPH ligands (two carboxylate groups in bis-monodentate mode and two in monodentate bridged mode) and two IN anions (the carboxylate groups in bis-monodentate mode) to form a linear trinuclear secondary building unit (SBU), $[Co_3(NIPH)_2(IN)_2(H_2O)_2]$ with a Co···Co separation of 3.5086 (10) Å. Every trinuclear SBU is in turn linked to its nearest neighbors in the *ab* plane, resulting in a two-dimensional layer like structure perpendicular to the *c*-axis (Fig. 2). Along the *a*-axis direction neighboring molecules are connected through carboxylate and pyridyl units of the IN anions, along the *b*-axis through carboxylate groups of the NIPH ligands. Topologically, the trinuclear Co^{II} units can be seen as four-connected nodes and the organic ligands (the NIPH and IN anions) act as two-connected rods. On the basis of this simplification, this two-dimensional structure can be described as a (4,4)-topological network.

There are multiple O–H···O hydrogen bonds in the complex, which include the following types of contacts: (*a*) between coordinated water molecule and carboxylate oxygen atoms of the NIPH anions [O···O, 2.820 (3) Å], (*b*) between lattice water molecule and carboxylate oxygen atoms of the NIPH anions [O···O, 2.861 (3) – 3.098 (4) Å] and (*c*) between coordinated and lattice water molecules [O···O, 2.648 (3) – 3.297 (6) Å]. Thus, these two-dimensional layers are further extended to a three-dimensional supramolecular network (Fig. 3).

The IR spectrum shows characteristic absorptions for the carboxylate stretching vibrations and the coordination of organic carboxylate anions (NIPH and IN) to Co^{II} was confirmed by the absence of υ(COOH) absorption bands of the organic ligands at around 1700 cm^{-1}. The characteristic vibrations of the carboxylate groups are seen in the range 1607–1541 cm^{-1} for asymmetric stretching and 1461–1360 cm^{-1} for symmetric stretching. The broad absorption band observed at 3412 cm^{-1} can be assigned to the O–H stretching vibration, indicating the presence of water molecules.

In summary, a new (4, 4)–two-dimensional layer-like polynuclear Co^{II} coordination polymer was constructed by hydrothermal reaction between Co(II) ions and mixed carboxylate ligands, which is further extended to a three-dimensional supramolecular network through intermolecular hydrogen bonding.

Experimental

A mixture of $Co(CH_3COO)_2.4\,H_2O$ (0.1245 g, 0.50 mmol), 5-nitroisophthalic acid (0.0503 g, 0.25 mmol) and isonicotinic acid (0.0310 g, 0.25 mmol) in 8 ml H_2O were sealed in a 15 ml Teflon-lined stainless steel reactor and kept under autogenous pressure at 393 K for three days. After the sample was cooled to room temperature at a rate of 5 K/h, pink block-shaped crystals of the title compound were collected and washed with ethanol and water (yield, 45%). IR (KBr pellet, *v*, cm^{-1}): 3412 (*br*), 3102 (*s*), 1607 (*s*), 1587 (*s*), 1541 (*s*), 1461 (*m*), 1420 (*m*), 1403 (*s*), 1360 (*m*), 1342 (*m*), 1163 (*w*), 1088 (*m*), 1065 (*m*), 1024 (*m*), 933 (*m*), 921 (*w*), 862 (*m*), 792 (*m*), 781 (*m*), 724 (*m*), 714 (*s*), 691 (*m*), 592 (*w*), 562 (*w*).

Refinement

The disordered hydrogen atoms (H3W and H4W) of lattice water molecule O2W are, due to a close contact of O2W with one of its symmetry equivalent counterparts across an inversion center, disordered in a 1:1 mode in the crystal. In one of the alternative orientations O2W is hydrogen bonding via H3WB to $O2W^{ii}$ and via H4WB to both $O2^{v}$ and $O5^{vi}$. In the other orientation, with O2W acting as the acceptor of a hydrogen bond from $O2W^{ii}$, the water molecule hydrogen bonds via H3WA and H3WB to $O6^{vi}$ and $O2^{v}$ (see Table 1 for symmetry operators). All hydrogen atoms of water molecules were located in electron difference density Fourier maps. The disordered hydrogen atoms (H3W and H4W) of lattice water molecule O2W were refined in a 1:1 disordered mode with O—H distance restraints of 0.85 (2) Å, and H···H distance restraints of 1.37 (2) Å. The other hydrogen atoms were placed geometrically and refined as riding atoms [C—H = 0.93 Å (aromatic C—H), O–H = 0.83 Å (coordinated H_2O) and 0.85 Å (lattice water molecules)]. All H atoms were refined with isotropic thermal factors U_{iso} (H) = 1.2 U_{eq} (C), or U_{iso} (H) = 1.5 U_{eq}(O)].

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

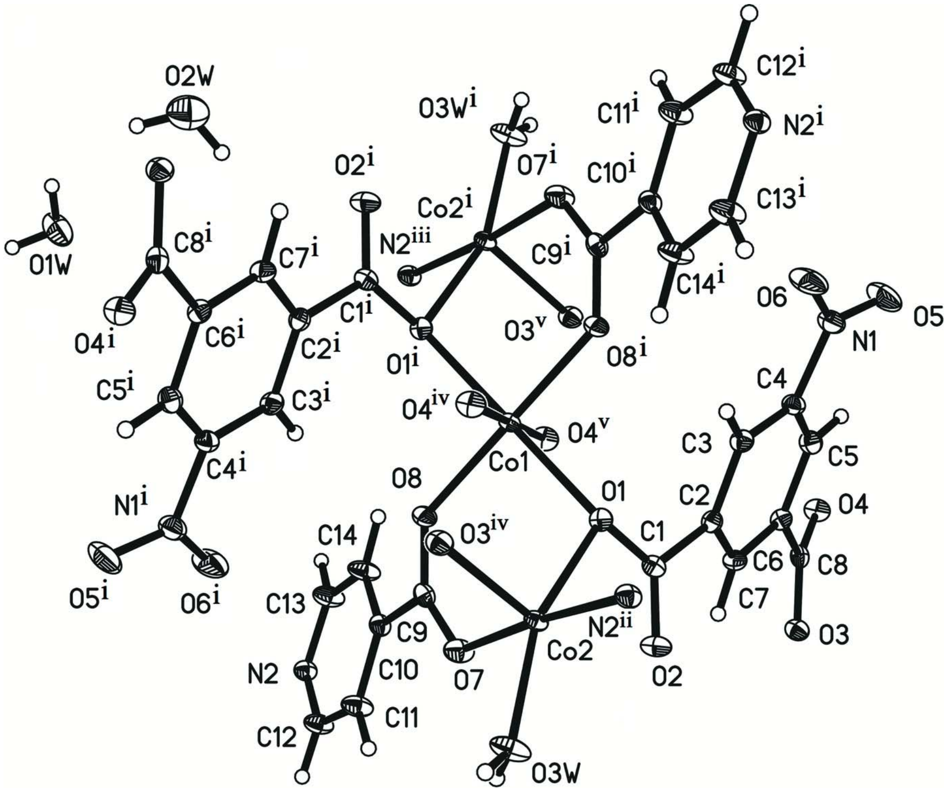


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. All H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i): -*x*, -*y* + 1, -*z* + 1; (ii): *x* - 1, *y*, *z*; (iii): -*x* + 1, -*y* + 1, -*z* + 1; (iv): *x*, *y* - 1, *z*; (v): -*x*, -*y* + 2, -*z* - 1]. Disorder of H atoms of O2W is omitted for clarity.

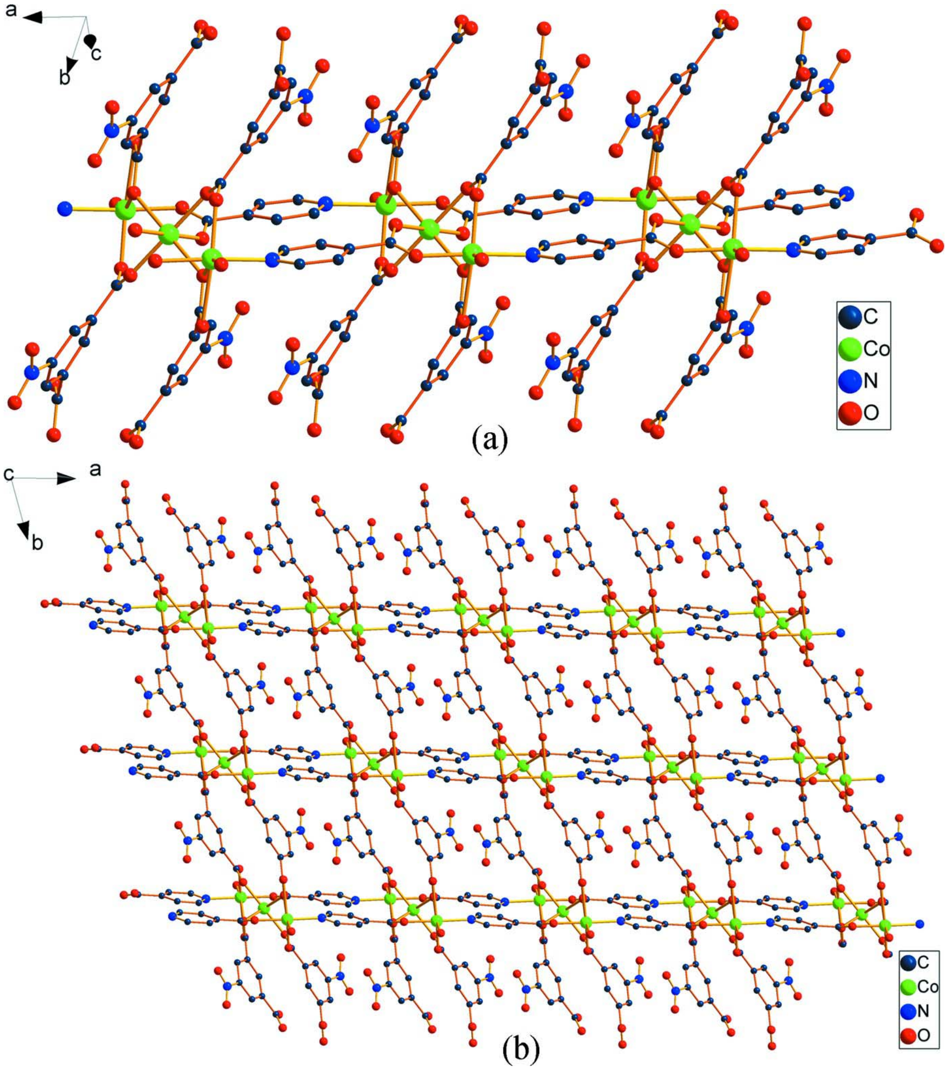


Figure 2

(*a*) A packing diagram along the *a*-axial direction. (*b*) A packing diagram, showing the two-dimensional layer-like structure in the *ab* plane. H atoms are omitted for clarity.

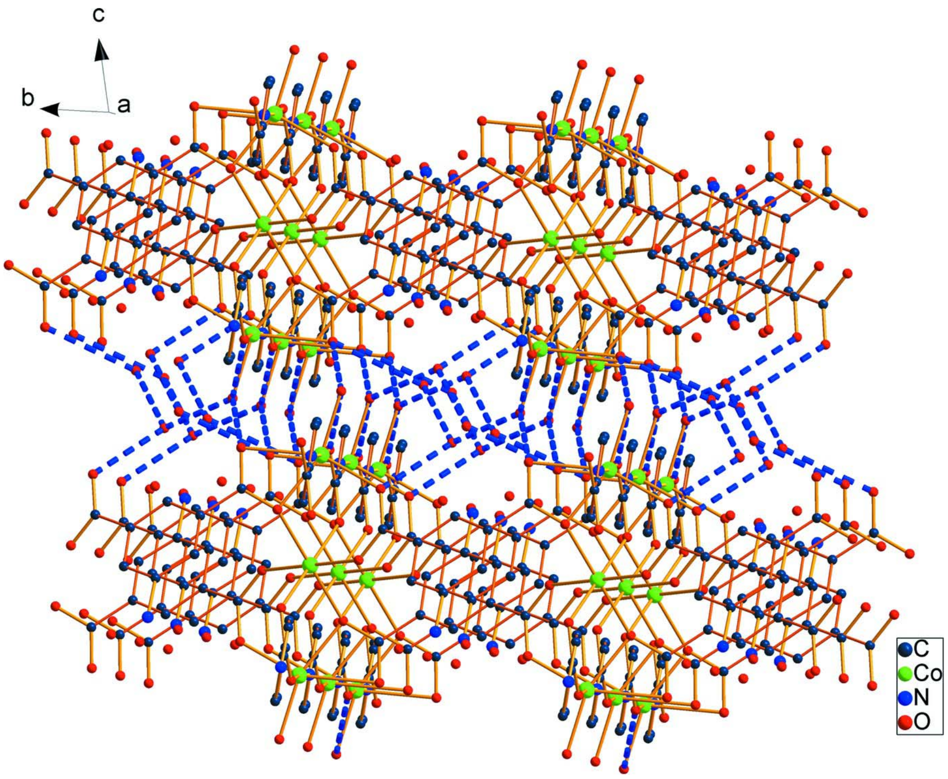


Figure 3

A packing diagram of the title compound, showing the three-dimensional supramolecular network driven by intermolecular hydrogen bonds (dashed lines). H atoms are omitted for clarity.

Poly[[diaquabis[μ_4-5-nitroisophthalato- $\kappa^4O^1:O^{1\prime}:O^3:O^{3\prime}$]bis[$\mu_3$-pyridine-4- carboxylato-$\kappa^3O:O':N$]tricobalt(II)] tetrahydrate]

Crystal data

$[Co_3(C_6H_4NO_2)_2(C_8H_3NO_6)_2(H_2O)_2]\cdot 4H_2O$	$Z = 1$
$M_r = 947.32$	$F(000) = 479$
Triclinic, $P\overline{1}$	$D_x = 1.872$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.1890$ (18) Å	Cell parameters from 3665 reflections
$b = 9.3548$ (19) Å	$\theta = 2.0$–27.9°
$c = 10.390$ (2) Å	$\mu = 1.57$ mm^{-1}
$\alpha = 78.74$ (3)°	$T = 298$ K
$\beta = 88.64$ (3)°	Block, pink
$\gamma = 73.68$ (3)°	0.35 × 0.28 × 0.16 mm
$V = 840.2$ (3) Å^3	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	4357 measured reflections
Radiation source: fine-focus sealed tube	2976 independent reflections
Graphite monochromator	2667 reflections with $I > 2\sigma(I)$
φ and ω scan	$R_{int} = 0.012$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$\theta_{max} = 25.3°$, $\theta_{min} = 2.0°$
	$h = -9\rightarrow 11$
	$k = -11\rightarrow 11$
$T_{min} = 0.610$, $T_{max} = 0.788$	$l = -12\rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.585P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\max} = 0.001$
2976 reflections	$\Delta\rho_{\max} = 0.40$ e Å^{-3}
271 parameters	$\Delta\rho_{\min} = -0.40$ e Å^{-3}
10 restraints	
Primary atom site location: structure-invariant direct methods	

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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
C1	−0.1582 (2)	0.6886 (2)	0.7129 (2)	0.0192 (5)	
C2	−0.1920 (3)	0.8433 (2)	0.6267 (2)	0.0193 (5)	
C3	−0.2761 (3)	0.8738 (2)	0.5103 (2)	0.0215 (5)	
H3	−0.3109	0.7991	0.4846	0.026*	
C4	−0.3067 (3)	1.0182 (3)	0.4336 (2)	0.0226 (5)	
C5	−0.2494 (3)	1.1290 (3)	0.4646 (2)	0.0241 (5)	
H5	−0.2671	1.2232	0.4086	0.029*	
C6	−0.1647 (3)	1.0974 (2)	0.5811 (2)	0.0194 (5)	
C7	−0.1408 (3)	0.9561 (2)	0.6638 (2)	0.0212 (5)	
H7	−0.0902	0.9370	0.7445	0.025*	
C9	0.2058 (2)	0.3927 (2)	0.7504 (2)	0.0201 (5)	
C10	0.3646 (2)	0.3974 (2)	0.7775 (2)	0.0201 (5)	
C11	0.4307 (3)	0.3616 (3)	0.9022 (2)	0.0302 (6)	
H11	0.3769	0.3339	0.9753	0.036*	
C12	0.5780 (3)	0.3674 (3)	0.9166 (2)	0.0291 (5)	
H12	0.6227	0.3388	1.0005	0.035*	
C13	0.5920 (3)	0.4501 (3)	0.6972 (2)	0.0320 (6)	
H13	0.6454	0.4836	0.6259	0.038*	
C14	0.4490 (3)	0.4422 (3)	0.6743 (2)	0.0313 (6)	
H14	0.4085	0.4672	0.5889	0.038*	
C8	−0.1022 (2)	1.2189 (2)	0.6151 (2)	0.0202 (5)	
Co1	0.0000	0.5000	0.5000	0.01527 (11)	
Co2	−0.10352 (3)	0.39808 (3)	0.82492 (3)	0.01738 (10)	
N2	0.6596 (2)	0.4120 (2)	0.81683 (18)	0.0218 (4)	
N1	−0.4063 (2)	1.0548 (2)	0.3153 (2)	0.0297 (5)	

O2	−0.1492 (2)	0.67118 (19)	0.83422 (16)	0.0285 (4)	
O1	−0.14157 (17)	0.57462 (16)	0.65704 (15)	0.0192 (3)	
O6	−0.4433 (3)	0.9517 (2)	0.2817 (2)	0.0474 (5)	
O5	−0.4506 (3)	1.1871 (2)	0.2580 (2)	0.0484 (5)	
O7	0.11919 (18)	0.3888 (2)	0.84536 (16)	0.0285 (4)	
O3	−0.07060 (19)	1.21068 (17)	0.73447 (16)	0.0247 (4)	
O4	−0.08995 (18)	1.31976 (17)	0.52098 (16)	0.0250 (4)	
O8	0.17412 (17)	0.39430 (18)	0.63366 (15)	0.0231 (3)	
O1W	0.8479 (2)	0.0405 (2)	0.1145 (2)	0.0498 (5)	
H1W	0.9262	−0.0299	0.1429	0.075*	
H2W	0.8017	0.0109	0.0599	0.075*	
O3W	−0.0897 (2)	0.2994 (2)	1.01711 (16)	0.0356 (4)	
H5W	−0.0190	0.3181	1.0515	0.053*	
H6W	−0.1021	0.2183	1.0577	0.053*	
O2W	0.3255 (3)	0.0491 (3)	0.0522 (3)	0.0676 (7)	
H4WA	0.271 (8)	0.114 (6)	0.094 (7)	0.101*	0.50
H3WA	0.386 (8)	−0.021 (7)	0.103 (6)	0.101*	0.50
H3WB	0.415 (3)	−0.006 (6)	0.038 (6)	0.101*	0.50
H4WB	0.344 (5)	0.096 (5)	0.114 (5)	0.101*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0180 (11)	0.0210 (11)	0.0200 (12)	−0.0090 (9)	−0.0018 (9)	−0.0017 (9)
C2	0.0203 (11)	0.0170 (11)	0.0211 (12)	−0.0057 (9)	0.0012 (9)	−0.0046 (9)
C3	0.0245 (12)	0.0198 (11)	0.0226 (12)	−0.0085 (9)	0.0000 (9)	−0.0067 (9)
C4	0.0246 (12)	0.0229 (12)	0.0205 (12)	−0.0059 (9)	−0.0043 (9)	−0.0050 (9)
C5	0.0285 (13)	0.0181 (11)	0.0244 (13)	−0.0068 (9)	0.0002 (10)	−0.0009 (9)
C6	0.0226 (11)	0.0168 (10)	0.0212 (11)	−0.0087 (9)	0.0018 (9)	−0.0049 (9)
C7	0.0244 (12)	0.0227 (11)	0.0185 (11)	−0.0095 (9)	−0.0006 (9)	−0.0044 (9)
C9	0.0164 (11)	0.0186 (11)	0.0247 (13)	−0.0058 (9)	−0.0022 (9)	−0.0012 (9)
C10	0.0165 (11)	0.0222 (11)	0.0224 (12)	−0.0059 (9)	−0.0030 (9)	−0.0047 (9)
C11	0.0256 (13)	0.0474 (15)	0.0193 (12)	−0.0183 (11)	−0.0009 (10)	0.0010 (11)
C12	0.0247 (13)	0.0447 (15)	0.0191 (12)	−0.0142 (11)	−0.0049 (10)	−0.0017 (11)
C13	0.0258 (13)	0.0518 (16)	0.0201 (13)	−0.0196 (12)	0.0000 (10)	0.0016 (11)
C14	0.0237 (13)	0.0541 (17)	0.0186 (13)	−0.0191 (12)	−0.0043 (10)	−0.0003 (11)
C8	0.0164 (11)	0.0173 (11)	0.0274 (13)	−0.0048 (9)	−0.0008 (9)	−0.0053 (9)
Co1	0.0164 (2)	0.0163 (2)	0.0144 (2)	−0.00812 (16)	−0.00199 (16)	−0.00068 (16)
Co2	0.01635 (17)	0.02053 (17)	0.01603 (17)	−0.00834 (12)	−0.00217 (11)	−0.00047 (12)
N2	0.0185 (10)	0.0277 (10)	0.0205 (10)	−0.0088 (8)	−0.0011 (8)	−0.0042 (8)
N1	0.0334 (12)	0.0289 (11)	0.0256 (11)	−0.0078 (9)	−0.0075 (9)	−0.0031 (9)
O2	0.0386 (10)	0.0315 (9)	0.0176 (9)	−0.0147 (8)	−0.0028 (7)	−0.0024 (7)
O1	0.0226 (8)	0.0158 (7)	0.0209 (8)	−0.0086 (6)	0.0011 (6)	−0.0028 (6)
O6	0.0637 (14)	0.0393 (11)	0.0429 (12)	−0.0196 (10)	−0.0279 (10)	−0.0057 (9)
O5	0.0636 (14)	0.0314 (11)	0.0423 (12)	−0.0081 (10)	−0.0262 (10)	0.0072 (9)
O7	0.0183 (8)	0.0470 (10)	0.0226 (9)	−0.0141 (7)	−0.0003 (7)	−0.0050 (8)
O3	0.0308 (9)	0.0209 (8)	0.0242 (9)	−0.0095 (7)	−0.0051 (7)	−0.0048 (7)
O4	0.0319 (9)	0.0219 (8)	0.0254 (9)	−0.0163 (7)	−0.0005 (7)	−0.0013 (7)
O8	0.0211 (8)	0.0282 (8)	0.0200 (9)	−0.0062 (7)	−0.0051 (6)	−0.0051 (7)

O1W	0.0499 (13)	0.0354 (11)	0.0605 (14)	−0.0130 (10)	−0.0197 (11)	0.0029 (10)
O3W	0.0370 (11)	0.0510 (11)	0.0227 (9)	−0.0284 (9)	−0.0097 (8)	0.0079 (8)
O2W	0.0697 (18)	0.0779 (19)	0.0591 (16)	−0.0224 (14)	−0.0130 (14)	−0.0186 (14)

Geometric parameters (Å, º)

C1—O2	1.241 (3)	C8—O4	1.246 (3)
C1—O1	1.281 (3)	C8—O3	1.263 (3)
C1—C2	1.499 (3)	Co1—O8	2.0363 (17)
C2—C3	1.388 (3)	Co1—O8^{i}	2.0363 (17)
C2—C7	1.389 (3)	Co1—O4^{ii}	2.0506 (15)
C3—C4	1.384 (3)	Co1—O4^{iii}	2.0506 (15)
C3—H3	0.9300	Co1—O1	2.1623 (16)
C4—C5	1.379 (3)	Co1—O1^{i}	2.1623 (16)
C4—N1	1.477 (3)	Co2—O3W	2.0205 (18)
C5—C6	1.391 (3)	Co2—O7	2.0383 (16)
C5—H5	0.9300	Co2—O3^{ii}	2.0927 (16)
C6—C7	1.391 (3)	Co2—O1	2.1146 (17)
C6—C8	1.511 (3)	Co2—N2^{iv}	2.1468 (19)
C7—H7	0.9300	N2—Co2^{v}	2.1468 (19)
C9—O8	1.250 (3)	N1—O6	1.220 (3)
C9—O7	1.254 (3)	N1—O5	1.222 (3)
C9—C10	1.507 (3)	O3—Co2^{vi}	2.0927 (16)
C10—C14	1.376 (3)	O4—Co1^{vi}	2.0506 (15)
C10—C11	1.384 (3)	O1W—H1W	0.8406
C11—C12	1.383 (3)	O1W—H2W	0.8463
C11—H11	0.9300	O3W—H5W	0.8243
C12—N2	1.334 (3)	O3W—H6W	0.8285
C12—H12	0.9300	O2W—H4WA	0.854 (19)
C13—N2	1.341 (3)	O2W—H3WA	0.83 (2)
C13—C14	1.366 (3)	O2W—H3WB	0.868 (19)
C13—H13	0.9300	O2W—H4WB	0.886 (18)
C14—H14	0.9300		

O2—C1—O1	120.9 (2)	O8—Co1—O4^{iii}	84.51 (7)
O2—C1—C2	121.4 (2)	O8^{i}—Co1—O4^{iii}	95.49 (7)
O1—C1—C2	117.69 (19)	O4^{ii}—Co1—O4^{iii}	180.0
C3—C2—C7	120.2 (2)	O8—Co1—O1	89.18 (6)
C3—C2—C1	119.64 (19)	O8^{i}—Co1—O1	90.82 (6)
C7—C2—C1	120.2 (2)	O4^{ii}—Co1—O1	87.91 (6)
C4—C3—C2	118.2 (2)	O4^{iii}—Co1—O1	92.09 (6)
C4—C3—H3	120.9	O8—Co1—O1^{i}	90.82 (6)
C2—C3—H3	120.9	O8^{i}—Co1—O1^{i}	89.18 (6)
C5—C4—C3	122.5 (2)	O4^{ii}—Co1—O1^{i}	92.09 (6)
C5—C4—N1	119.0 (2)	O4^{iii}—Co1—O1^{i}	87.91 (6)
C3—C4—N1	118.4 (2)	O1—Co1—O1^{i}	180.0
C4—C5—C6	118.8 (2)	O3W—Co2—O7	86.46 (7)
C4—C5—H5	120.6	O3W—Co2—O3^{ii}	101.78 (7)
C6—C5—H5	120.6	O7—Co2—O3^{ii}	97.35 (7)
C5—C6—C7	119.6 (2)	O3W—Co2—O1	158.16 (7)

C5—C6—C8	118.8 (2)
C7—C6—C8	121.6 (2)
C2—C7—C6	120.5 (2)
C2—C7—H7	119.8
C6—C7—H7	119.8
O8—C9—O7	126.8 (2)
O8—C9—C10	115.7 (2)
O7—C9—C10	117.6 (2)
C14—C10—C11	117.4 (2)
C14—C10—C9	119.2 (2)
C11—C10—C9	123.4 (2)
C12—C11—C10	119.0 (2)
C12—C11—H11	120.5
C10—C11—H11	120.5
N2—C12—C11	123.7 (2)
N2—C12—H12	118.2
C11—C12—H12	118.2
N2—C13—C14	123.5 (2)
N2—C13—H13	118.3
C14—C13—H13	118.3
C13—C14—C10	120.1 (2)
C13—C14—H14	120.0
C10—C14—H14	120.0
O4—C8—O3	126.6 (2)
O4—C8—C6	115.6 (2)
O3—C8—C6	117.70 (19)
O8—Co1—O8^{i}	180.000 (1)
O8—Co1—O4^{ii}	95.49 (7)
O8^{i}—Co1—O4^{ii}	84.51 (7)
O7—Co2—O1	93.45 (7)
O3^{ii}—Co2—O1	99.89 (6)
O3W—Co2—N2^{iv}	90.42 (8)
O7—Co2—N2^{iv}	175.95 (7)
O3^{ii}—Co2—N2^{iv}	85.80 (7)
O1—Co2—N2^{iv}	88.50 (7)
C12—N2—C13	116.3 (2)
C12—N2—Co2^{v}	126.40 (16)
C13—N2—Co2^{v}	116.62 (15)
O6—N1—O5	123.4 (2)
O6—N1—C4	118.2 (2)
O5—N1—C4	118.4 (2)
C1—O1—Co2	99.61 (13)
C1—O1—Co1	132.30 (13)
Co2—O1—Co1	110.24 (7)
C9—O7—Co2	122.97 (15)
C8—O3—Co2^{vi}	124.57 (14)
C8—O4—Co1^{vi}	134.35 (15)
C9—O8—Co1	138.09 (15)
H1W—O1W—H2W	108.3
Co2—O3W—H5W	107.7
Co2—O3W—H6W	133.6
H5W—O3W—H6W	109.9
H4WA—O2W—H3WA	111 (4)
H4WA—O2W—H3WB	149 (7)
H3WA—O2W—H3WB	51 (7)
H4WA—O2W—H4WB	46 (6)
H3WA—O2W—H4WB	77 (6)
H3WB—O2W—H4WB	103 (3)

O2—C1—C2—C3	−146.5 (2)
O1—C1—C2—C3	32.3 (3)
O2—C1—C2—C7	32.7 (3)
O1—C1—C2—C7	−148.5 (2)
C7—C2—C3—C4	0.0 (3)
C1—C2—C3—C4	179.3 (2)
C2—C3—C4—C5	4.0 (3)
C2—C3—C4—N1	−175.2 (2)
C3—C4—C5—C6	−3.7 (4)
N1—C4—C5—C6	175.4 (2)
C4—C5—C6—C7	−0.5 (3)
C4—C5—C6—C8	−179.9 (2)
C3—C2—C7—C6	−4.1 (3)
C1—C2—C7—C6	176.6 (2)
C5—C6—C7—C2	4.4 (3)
C8—C6—C7—C2	−176.2 (2)
O8—C9—C10—C14	16.8 (3)
O7—C9—C10—C14	−162.7 (2)
O8—C9—C10—C11	−164.6 (2)
C3—C4—N1—O5	169.9 (2)
O2—C1—O1—Co2	0.1 (2)
C2—C1—O1—Co2	−178.70 (16)
O2—C1—O1—Co1	−128.83 (19)
C2—C1—O1—Co1	52.4 (3)
O3W—Co2—O1—C1	8.5 (2)
O7—Co2—O1—C1	−80.54 (13)
O3^{ii}—Co2—O1—C1	−178.62 (13)
N2^{iv}—Co2—O1—C1	95.91 (13)
O3W—Co2—O1—Co1	150.72 (15)
O7—Co2—O1—Co1	61.64 (8)
O3^{ii}—Co2—O1—Co1	−36.44 (8)
N2^{iv}—Co2—O1—Co1	−121.91 (8)
O8—Co1—O1—C1	84.14 (19)
O8^{i}—Co1—O1—C1	−95.86 (19)
O4^{ii}—Co1—O1—C1	179.66 (19)
O4^{iii}—Co1—O1—C1	−0.34 (19)
O8—Co1—O1—Co2	−41.04 (7)
O8^{i}—Co1—O1—Co2	138.96 (7)

O7—C9—C10—C11	16.0 (3)	O4^{ii}—Co1—O1—Co2	54.48 (8)
C14—C10—C11—C12	−2.2 (4)	O4^{iii}—Co1—O1—Co2	−125.52 (8)
C9—C10—C11—C12	179.2 (2)	O8—C9—O7—Co2	−4.1 (3)
C10—C11—C12—N2	2.8 (4)	C10—C9—O7—Co2	175.29 (14)
N2—C13—C14—C10	1.9 (4)	O3W—Co2—O7—C9	157.95 (19)
C11—C10—C14—C13	0.0 (4)	O3^{ii}—Co2—O7—C9	56.52 (18)
C9—C10—C14—C13	178.7 (2)	O1—Co2—O7—C9	−43.92 (18)
C5—C6—C8—O4	−21.3 (3)	O4—C8—O3—Co2^{vi}	35.3 (3)
C7—C6—C8—O4	159.2 (2)	C6—C8—O3—Co2^{vi}	−143.13 (16)
C5—C6—C8—O3	157.3 (2)	O3—C8—O4—Co1^{vi}	7.4 (4)
C7—C6—C8—O3	−22.2 (3)	C6—C8—O4—Co1^{vi}	−174.15 (14)
C11—C12—N2—C13	−1.0 (4)	O7—C9—O8—Co1	43.6 (4)
C11—C12—N2—Co2^{v}	−171.6 (2)	C10—C9—O8—Co1	−135.76 (18)
C14—C13—N2—C12	−1.3 (4)	O4^{ii}—Co1—O8—C9	−101.0 (2)
C14—C13—N2—Co2^{v}	170.1 (2)	O4^{iii}—Co1—O8—C9	79.0 (2)
C5—C4—N1—O6	172.6 (2)	O1—Co1—O8—C9	−13.2 (2)
C3—C4—N1—O6	−8.3 (3)	O1^{i}—Co1—O8—C9	166.8 (2)
C5—C4—N1—O5	−9.3 (3)		

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*, *y*−1, *z*; (iii) −*x*, −*y*+2, −*z*+1; (iv) *x*−1, *y*, *z*; (v) *x*+1, *y*, *z*; (vi) *x*, *y*+1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O3^{vii}	0.84	2.05	2.861 (3)	160
O1*W*—H2*W*···O2*W*^{viii}	0.85	1.93	2.773 (3)	173
O3*W*—H5*W*···O2^{ix}	0.82	2.01	2.820 (2)	168
O3*W*—H6*W*···O1*W*^{x}	0.83	1.83	2.648 (3)	167
O2*W*—H4*WA*···O2^{i}	0.85 (2)	2.27 (2)	3.098 (4)	165 (8)
O2*W*—H3*WA*···O6^{xi}	0.83 (2)	2.38 (6)	3.055 (3)	138 (8)
O2*W*—H3*WB*···O2*W*^{viii}	0.87 (2)	2.49 (3)	3.297 (6)	154 (6)
O2*W*—H4*WB*···O6^{xi}	0.89 (5)	2.54 (5)	3.055 (4)	118 (3)
O2*W*—H4*WB*···O2^{i}	0.89 (5)	2.54 (5)	3.098 (3)	121 (4)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*, −*z*; (ix) −*x*, −*y*+1, −*z*+2; (x) *x*−1, *y*, *z*+1; (xi) *x*+1, *y*−1, *z*.