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cis-Cyclohexane-1,3-dicarboxylic acid–*N*,*N*′-(pentane-1,5-diyl)bis(pyridine-4-carboxamide)–water (1/1/2)

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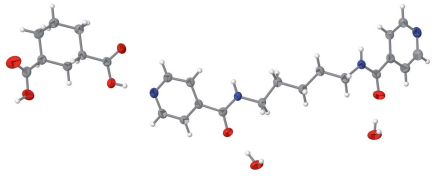
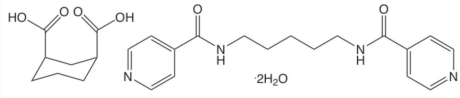
The title cocrystal, $C_8H_{12}O_4{\cdot}C_{17}H_{20}N_4O_2{\cdot}2H_2O$, shows O—H···N hydrogen bonded supramolecular chain motifs of *cis*-1,3-cyclohexanedicarboxylic acid (H_2cdc) molecules alternating with *N*,*N*′-(pentane-1,5-diyl)bis(pyridine-4-carboxamide)pentane (bpcpe) molecules. These chain motifs are aggregated by C—H···O interactions into supramolecular layers and slabs, which are stacked into the three-dimensional crystal structure by means of O—H···O interactions mediated by the water molecules of crystallization.

3D view



Chemical scheme



Structure description

The title compound was isolated during an exploratory synthetic effort aiming to produce divalent cadmium coordination polymers containing both *cis*-cyclohexane-1,3-dicarboxylate (cdc) and *N*,*N*′-(pentane-1,5-diyl)bis(pyridine-4-carboxamide) (bpcpe) ligands. Reports of cadmium coordination polymers containing cdc ligands have been seldom to date, with $\{[Cd(L)(cdc)]\cdot H_2O\}_n$ [*L* = 1,3-di(1*H*-imidazol-4-yl)benzene] representing one of the few known examples (Chen *et al.*, 2014). The bpcpe ligand has also rarely been used in coordination polymer chemistry to this point, with $\{[Cu(bpcpe)_2(H_2O)_2)(ClO_4)_2]\cdot 2H_2O\cdot 4CH_3OH\}_n$ being one of the very few reported examples (Mukherjee & Biradha, 2013).

The asymmetric unit of the title cocrystal contains a *cis*-cyclohexane-1,3-dicarboxylic acid (H_2cdc) molecule, a bpcpe molecule, and two water molecules of crystallization (Fig. 1). Adjacent H_2cdc and bpcpe molecules form supramolecular chain motifs (Fig. 2) by means of O—H···N hydrogen-bonding interactions (Table 1) between protonated H_2cdc carboxylate groups and the pyridyl ring N atoms in the bpcpe molecules. Nonclassical C—H···O interactions (C9—H9···O2^{iv} and C21—H21···O4^{v}; Table 1) between bpcpe pyridyl rings and unprotonated H_2cdc O atoms construct supramolecular layer motifs oriented parallel to the *ab* crystal planes (Fig. 3). Additional C—H···O

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.84	1.79	2.6251 (18)	178
O3—H3A···N4^{i}	0.84	1.79	2.6300 (19)	173
N2—H2···O1W^{ii}	0.88	2.03	2.8868 (19)	165
N3—H3···O2W^{ii}	0.88	2.01	2.849 (2)	159
O2W—H2WA···O2^{iii}	0.87	1.94	2.809 (2)	177
O2W—H2WB···O6	0.87	1.90	2.7684 (19)	173
O1W—H1WA···O5	0.87	1.88	2.7365 (18)	168
O1W—H1WB···O4^{iii}	0.87	1.99	2.863 (2)	178
C9—H9···O2^{iv}	0.95	2.51	3.143 (2)	124
C21—H21···O4^{v}	0.95	2.46	3.238 (2)	139
C6—H6···O6^{vi}	1.00	2.50	3.478 (2)	167

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

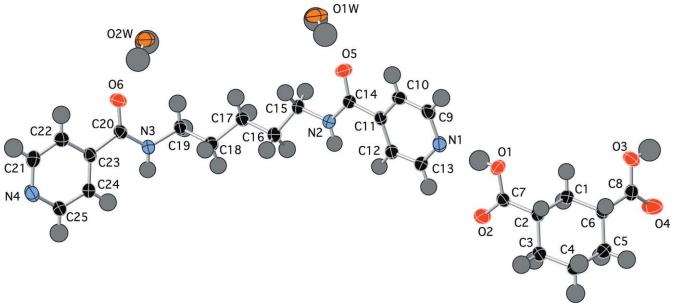


Figure 1
The asymmetric unit of the title cocrystal. Displacement ellipsoids are drawn at the 50% probability level. The H-atom positions are denoted by gray sticks. Color code: N blue, O red, C black, and H grey.

interactions (C6—H6···O6^{vi}; Table 1) between the tertiary C atoms of the H_2cdc molecules and bpcpe C═O carbonyl O atoms result in bilayer slab motifs (Fig. 4). Supramolecular O—H···O hydrogen-bonding interactions (Table 1) mediated by the water molecules of crystallization aggregate the supramolecular slabs into the full three-dimensional crystal structure of the title cocrystal (Fig. 5).

Synthesis and crystallization

$Cd(NO_3)_2{\cdot}4H_2O$ (114 mg, 0.37 mmol), *cis*-cyclohexane-1,3-dicarboxylic acid (64 mg, 0.37 mmol), bpcpe (115 mg, 0.37 mmol) and 0.75 ml of a 1.0 *M* NaOH solution were placed into 10 ml distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 393 K for 2 d, and then cooled slowly to 273 K. Colorless crystals of the title cocrystal (74 mg, 38% yield, based on *cis*-cyclohexane-1,3-dicarboxylic acid) were isolated after washing with distilled water and acetone, and drying in air.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{12}O_4{\cdot}C_{17}H_{20}N_4O_2{\cdot}2H_2O$
M_r	520.58
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	6.8931 (9), 25.486 (3), 15.2828 (19)
β (°)	96.739 (2)
V (Å^3)	2666.3 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.38 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.677, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21494, 4904, 3656
R_{int}	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.136, 1.04
No. of reflections	4904
No. of parameters	342
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.22

Computer programs: *COSMO* (Bruker, 2009), *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *CrystalMaker* (Palmer, 2013) and *OLEX2* (Dolomanov *et al.*, 2009).

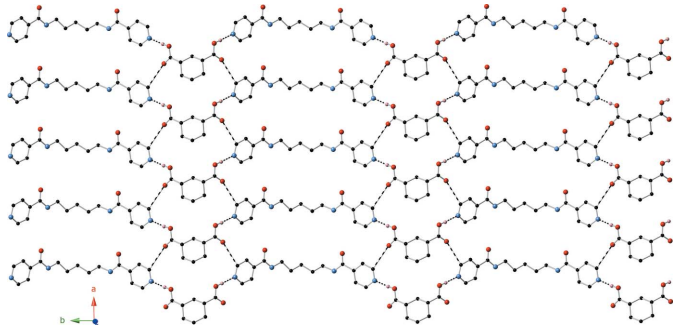


Figure 3
Supramolecular layer motif parallel to the *ab* crystal planes formed by nonclassical C—H···O interactions (shown as dashed lines) between neighboring chain motifs.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

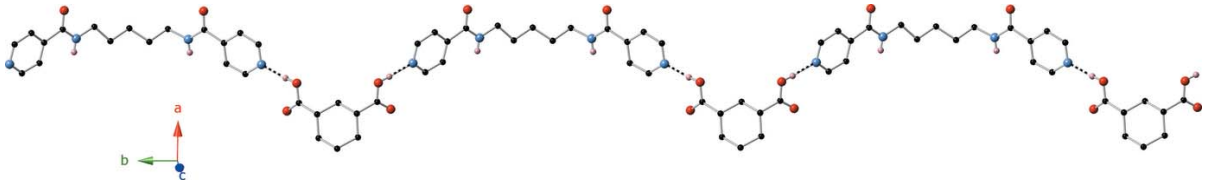


Figure 2
A hydrogen-bonded chain in the title cocrystal, oriented parallel to [010]. O—H···N hydrogen bonds are shown as dashed lines.

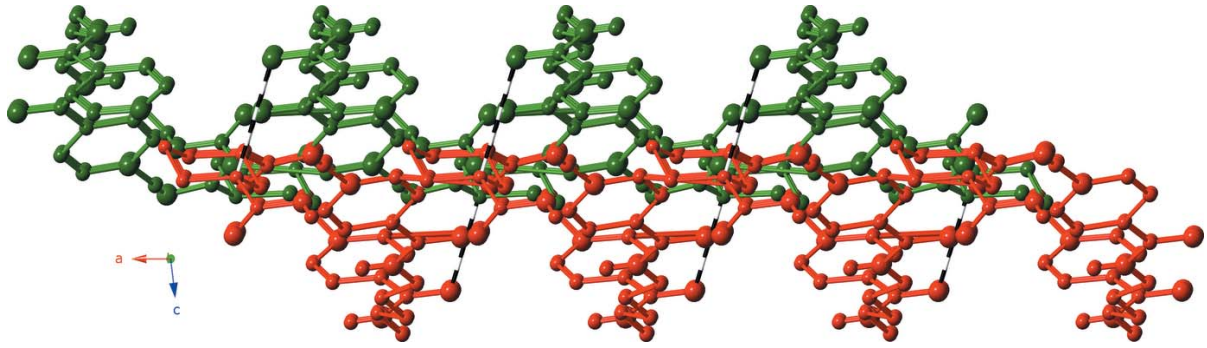


Figure 4
Aggregation of supramolecular layers into bilayer slabs by additional. C—H···O hydrogen-bonding interactions (shown as dashed lines).

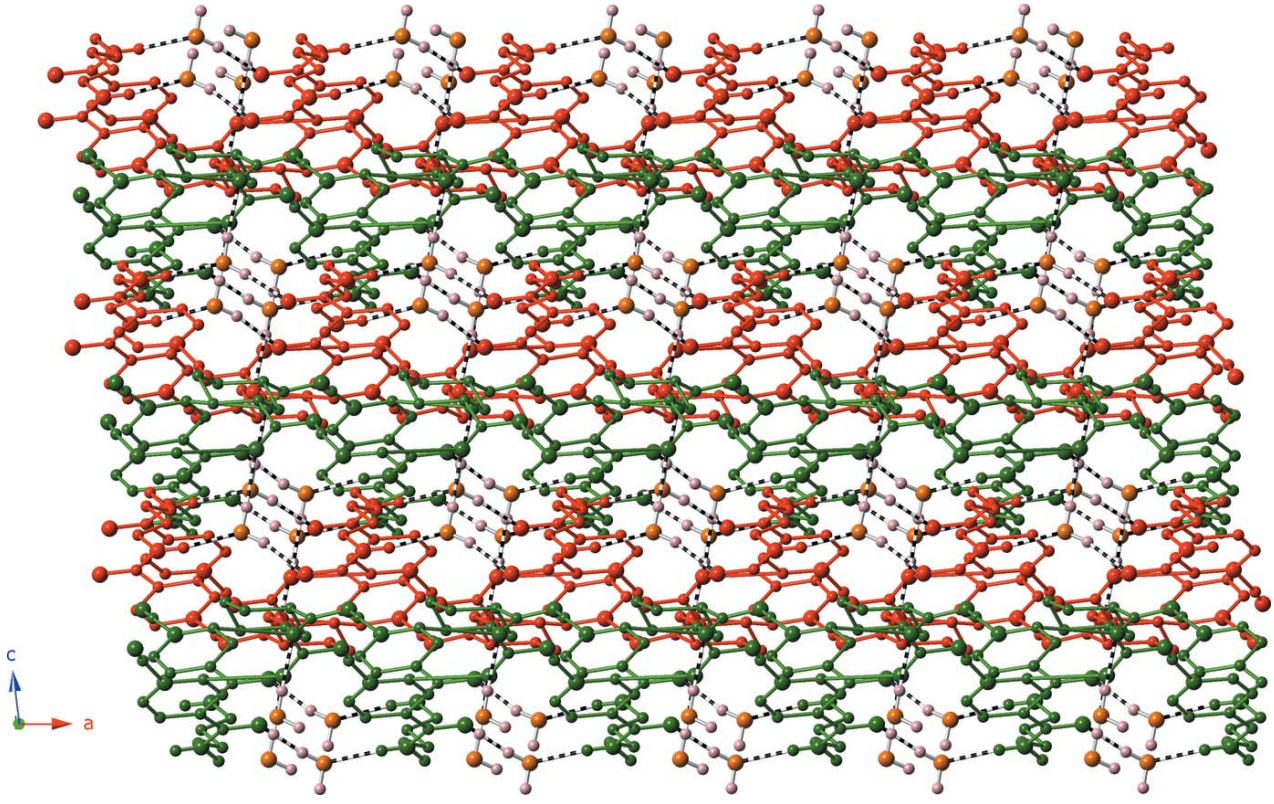


Figure 5
Stacking of supramolecular slab motifs in the title cocrystal, to afford the three-dimensional crystal structure, mediated by O—H···O hydrogen-bonding interactions (shown as dashed lines) involving the water molecules of crystallization.

Acknowledgements

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Funding information

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full crystallographic data

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cis-Cyclohexane-1,3-dicarboxylic acid–*N*,*N*′-(pentane-1,5-diyl)bis(pyridine-4-carboxamide)–water (1/1/2)

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Crystal data

$C_8H_{12}O_4·C_{17}H_{20}N_4O_2·2H_2O$
M_r = 520.58
Monoclinic, $P2_1/c$
a = 6.8931 (9) Å
b = 25.486 (3) Å
c = 15.2828 (19) Å
β = 96.739 (2)°
V = 2666.3 (6) Å^3
Z = 4
$F(000)$ = 1112
D_x = 1.297 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7916 reflections
θ = 2.7–25.3°
μ = 0.10 mm^{-1}
T = 173 K
Chunk, yellow
0.38 × 0.20 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.677, T_{max} = 0.745
21494 measured reflections
4904 independent reflections
3656 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.4°, θ_{min} = 1.6°
h = −8→8
k = −30→30
l = −17→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.136
S = 1.04
4904 reflections
342 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.4255P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Experimental. Data was collected using a BRUKER CCD (charge coupled device) based diffractometer equipped with an Oxford low-temperature apparatus operating at 173 K. A suitable crystal was chosen and mounted on a nylon loop using Paratone oil. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images were based on results from the program COSMO where redundancy was expected to be 4 and completeness to 0.83Å to 100%. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections.Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS6 multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F2, SHELXL-97, incorporated in OLEX2.

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

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H) groups, All C(H,H) groups, All N(H) groups At 1.5 times of: All O(H) groups, All O(H,H) groups 2.a Free rotating group: O2W(H2WA,H2WB), O1W(H1WA,H1WB) 2.b Ternary CH refined with riding coordinates: C2(H2A), C6(H6) 2.c Secondary CH2 refined with riding coordinates: C1(H1A,H1B), C3(H3B,H3C), C4(H4A,H4B), C5(H5A,H5B), C15(H15A,H15B), C16(H16A, H16B), C17(H17A,H17B), C18(H18A,H18B), C19(H19A,H19B) 2.d Aromatic/amide H refined with riding coordinates: N2(H2), N3(H3), C9(H9), C10(H10), C12(H12), C13(H13), C21(H21), C22(H22), C24(H24), C25(H25) 2.e Idealised tetrahedral OH refined as rotating group: O1(H1), O3(H3A)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.69221 (18)	0.70893 (5)	0.46245 (9)	0.0415 (3)
H1	0.6489	0.6807	0.4807	0.062*
O2	0.97352 (19)	0.67403 (5)	0.51706 (11)	0.0566 (4)
O3	0.75087 (19)	0.90622 (5)	0.54822 (10)	0.0494 (4)
H3A	0.7214	0.9334	0.5747	0.074*
O4	1.0488 (2)	0.92646 (6)	0.60909 (10)	0.0647 (5)
O5	0.12014 (17)	0.48185 (5)	0.61568 (9)	0.0429 (3)
O6	0.19314 (17)	0.13036 (5)	0.71696 (9)	0.0437 (3)
N1	0.5492 (2)	0.62099 (5)	0.51727 (9)	0.0341 (3)
N2	0.4134 (2)	0.44849 (5)	0.66705 (9)	0.0309 (3)
H2	0.5411	0.4526	0.6738	0.037*
N3	0.4875 (2)	0.16526 (5)	0.76547 (9)	0.0333 (3)
H3	0.6145	0.1600	0.7734	0.040*
N4	0.6284 (2)	−0.00909 (5)	0.62335 (10)	0.0405 (4)
C1	0.9160 (2)	0.80455 (6)	0.52173 (11)	0.0330 (4)
H1A	0.9587	0.7945	0.5836	0.040*
H1B	0.7720	0.8082	0.5146	0.040*
C2	0.9750 (2)	0.76158 (6)	0.45969 (11)	0.0316 (4)
H2A	0.9226	0.7714	0.3981	0.038*
C3	1.1964 (3)	0.75739 (7)	0.46439 (13)	0.0402 (4)
H3B	1.2502	0.7449	0.5237	0.048*
H3C	1.2305	0.7313	0.4207	0.048*
C4	1.2881 (3)	0.81000 (7)	0.44617 (13)	0.0431 (5)
H4A	1.2456	0.8206	0.3846	0.052*
H4B	1.4321	0.8064	0.4531	0.052*

C5	1.2305 (3)	0.85243 (7)	0.50838 (13)	0.0396 (4)
H5A	1.2829	0.8435	0.5697	0.048*
H5B	1.2875	0.8864	0.4932	0.048*
C6	1.0094 (2)	0.85722 (6)	0.50142 (12)	0.0337 (4)
H6	0.9619	0.8663	0.4389	0.040*
C7	0.8812 (3)	0.71042 (6)	0.48201 (11)	0.0324 (4)
C8	0.9407 (3)	0.90007 (7)	0.55893 (12)	0.0375 (4)
C9	0.3591 (3)	0.61025 (7)	0.50323 (12)	0.0376 (4)
H9	0.2761	0.6340	0.4685	0.045*
C10	0.2769 (3)	0.56648 (7)	0.53651 (12)	0.0355 (4)
H10	0.1405	0.5601	0.5246	0.043*
C11	0.3962 (2)	0.53176 (6)	0.58778 (10)	0.0289 (4)
C12	0.5942 (2)	0.54227 (6)	0.60169 (11)	0.0320 (4)
H12	0.6806	0.5190	0.6357	0.038*
C13	0.6644 (3)	0.58703 (6)	0.56543 (11)	0.0336 (4)
H13	0.8007	0.5940	0.5752	0.040*
C14	0.3000 (2)	0.48484 (6)	0.62487 (11)	0.0304 (4)
C15	0.3270 (2)	0.40181 (6)	0.70226 (12)	0.0339 (4)
H15A	0.2251	0.3876	0.6574	0.041*
H15B	0.2634	0.4117	0.7547	0.041*
C16	0.4771 (3)	0.35976 (6)	0.72765 (12)	0.0358 (4)
H16A	0.5803	0.3740	0.7718	0.043*
H16B	0.5390	0.3493	0.6751	0.043*
C17	0.3854 (3)	0.31174 (6)	0.76581 (12)	0.0358 (4)
H17A	0.3756	0.3179	0.8291	0.043*
H17B	0.2513	0.3071	0.7357	0.043*
C18	0.5013 (3)	0.26172 (6)	0.75602 (12)	0.0346 (4)
H18A	0.5089	0.2551	0.6927	0.042*
H18B	0.6361	0.2665	0.7852	0.042*
C19	0.4099 (3)	0.21464 (6)	0.79581 (12)	0.0373 (4)
H19A	0.4357	0.2165	0.8608	0.045*
H19B	0.2667	0.2155	0.7795	0.045*
C20	0.3735 (2)	0.12807 (6)	0.72641 (11)	0.0310 (4)
C21	0.4367 (3)	−0.00126 (7)	0.61656 (13)	0.0438 (5)
H21	0.3530	−0.0271	0.5875	0.053*
C22	0.3537 (3)	0.04258 (7)	0.64964 (12)	0.0393 (4)
H22	0.2157	0.0466	0.6433	0.047*
C23	0.4720 (2)	0.08057 (6)	0.69197 (11)	0.0308 (4)
C24	0.6715 (3)	0.07249 (6)	0.70014 (12)	0.0374 (4)
H24	0.7583	0.0976	0.7293	0.045*
C25	0.7427 (3)	0.02756 (7)	0.66535 (13)	0.0414 (4)
H25	0.8801	0.0224	0.6715	0.050*
O2W	−0.09932 (19)	0.17555 (6)	0.80134 (11)	0.0575 (4)
H2WA	−0.0639	0.1741	0.8578	0.086*
H2WB	−0.0003	0.1628	0.7779	0.086*
O1W	−0.16723 (18)	0.44347 (6)	0.70724 (10)	0.0574 (4)
H1WA	−0.0646	0.4553	0.6854	0.086*
H1WB	−0.1281	0.4386	0.7628	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0357 (7)	0.0325 (7)	0.0549 (8)	−0.0046 (5)	−0.0003 (6)	0.0107 (6)
O2	0.0408 (8)	0.0367 (7)	0.0918 (11)	0.0044 (6)	0.0066 (7)	0.0236 (7)
O3	0.0443 (8)	0.0385 (8)	0.0652 (9)	0.0075 (6)	0.0050 (7)	−0.0188 (7)
O4	0.0515 (9)	0.0694 (10)	0.0731 (11)	−0.0112 (8)	0.0071 (8)	−0.0408 (8)
O5	0.0284 (7)	0.0435 (7)	0.0563 (8)	−0.0029 (5)	0.0036 (6)	0.0149 (6)
O6	0.0312 (7)	0.0466 (8)	0.0521 (8)	0.0071 (6)	0.0003 (6)	−0.0113 (6)
N1	0.0387 (9)	0.0276 (7)	0.0371 (8)	−0.0005 (6)	0.0093 (6)	−0.0003 (6)
N2	0.0281 (7)	0.0247 (7)	0.0401 (8)	−0.0019 (6)	0.0054 (6)	0.0025 (6)
N3	0.0317 (8)	0.0242 (7)	0.0452 (9)	0.0011 (6)	0.0098 (6)	−0.0004 (6)
N4	0.0476 (10)	0.0294 (8)	0.0465 (9)	0.0036 (7)	0.0142 (7)	−0.0020 (7)
C1	0.0301 (9)	0.0310 (9)	0.0384 (10)	0.0001 (7)	0.0058 (7)	−0.0032 (7)
C2	0.0334 (9)	0.0267 (8)	0.0348 (9)	0.0019 (7)	0.0047 (7)	0.0010 (7)
C3	0.0368 (10)	0.0331 (9)	0.0524 (12)	0.0037 (8)	0.0131 (9)	0.0007 (8)
C4	0.0363 (10)	0.0403 (10)	0.0551 (12)	−0.0018 (8)	0.0148 (9)	−0.0003 (9)
C5	0.0352 (10)	0.0380 (10)	0.0460 (11)	−0.0053 (8)	0.0062 (8)	−0.0031 (8)
C6	0.0358 (9)	0.0301 (9)	0.0352 (9)	−0.0024 (7)	0.0042 (7)	−0.0039 (7)
C7	0.0357 (10)	0.0278 (9)	0.0346 (9)	0.0026 (7)	0.0080 (7)	−0.0014 (7)
C8	0.0422 (11)	0.0307 (9)	0.0397 (10)	−0.0046 (8)	0.0057 (8)	−0.0041 (8)
C9	0.0378 (10)	0.0326 (9)	0.0435 (11)	0.0070 (8)	0.0097 (8)	0.0096 (8)
C10	0.0291 (9)	0.0348 (9)	0.0436 (10)	0.0027 (7)	0.0084 (8)	0.0044 (8)
C11	0.0338 (9)	0.0243 (8)	0.0296 (9)	0.0015 (7)	0.0077 (7)	0.0006 (7)
C12	0.0338 (9)	0.0280 (9)	0.0339 (9)	0.0005 (7)	0.0024 (7)	−0.0006 (7)
C13	0.0336 (9)	0.0297 (9)	0.0377 (10)	−0.0029 (7)	0.0048 (8)	−0.0020 (7)
C14	0.0297 (9)	0.0282 (9)	0.0337 (9)	−0.0014 (7)	0.0048 (7)	−0.0012 (7)
C15	0.0338 (9)	0.0256 (8)	0.0431 (10)	−0.0028 (7)	0.0077 (8)	0.0031 (7)
C16	0.0359 (10)	0.0302 (9)	0.0415 (10)	−0.0004 (7)	0.0057 (8)	0.0038 (7)
C17	0.0365 (10)	0.0284 (9)	0.0440 (10)	0.0014 (7)	0.0111 (8)	0.0033 (7)
C18	0.0355 (9)	0.0277 (9)	0.0418 (10)	0.0024 (7)	0.0092 (8)	0.0036 (7)
C19	0.0420 (10)	0.0259 (9)	0.0461 (11)	0.0025 (7)	0.0143 (8)	−0.0007 (8)
C20	0.0321 (10)	0.0301 (9)	0.0309 (9)	0.0044 (7)	0.0043 (7)	0.0042 (7)
C21	0.0474 (12)	0.0344 (10)	0.0494 (12)	−0.0026 (8)	0.0047 (9)	−0.0098 (8)
C22	0.0350 (10)	0.0367 (10)	0.0455 (11)	0.0002 (8)	0.0022 (8)	−0.0044 (8)
C23	0.0363 (9)	0.0269 (8)	0.0303 (9)	0.0019 (7)	0.0078 (7)	0.0032 (7)
C24	0.0345 (10)	0.0273 (9)	0.0506 (11)	−0.0009 (7)	0.0063 (8)	−0.0013 (8)
C25	0.0370 (10)	0.0309 (9)	0.0580 (12)	0.0033 (8)	0.0125 (9)	−0.0012 (9)
O2W	0.0338 (7)	0.0620 (9)	0.0771 (11)	0.0019 (7)	0.0084 (7)	−0.0228 (9)
O1W	0.0286 (7)	0.0764 (10)	0.0675 (10)	−0.0011 (7)	0.0075 (7)	0.0284 (8)

Geometric parameters (Å, º)

O1—H1	0.8400	C9—H9	0.9500
O1—C7	1.302 (2)	C9—C10	1.376 (2)
O2—C7	1.213 (2)	C10—H10	0.9500
O3—H3A	0.8400	C10—C11	1.387 (2)
O3—C8	1.309 (2)	C11—C12	1.382 (2)

O4—C8	1.209 (2)	C11—C14	1.510 (2)
O5—C14	1.233 (2)	C12—H12	0.9500
O6—C20	1.236 (2)	C12—C13	1.381 (2)
N1—C9	1.331 (2)	C13—H13	0.9500
N1—C13	1.336 (2)	C15—H15A	0.9900
N2—H2	0.8800	C15—H15B	0.9900
N2—C14	1.329 (2)	C15—C16	1.508 (2)
N2—C15	1.461 (2)	C16—H16A	0.9900
N3—H3	0.8800	C16—H16B	0.9900
N3—C19	1.464 (2)	C16—C17	1.524 (2)
N3—C20	1.327 (2)	C17—H17A	0.9900
N4—C21	1.328 (2)	C17—H17B	0.9900
N4—C25	1.337 (2)	C17—C18	1.521 (2)
C1—H1A	0.9900	C18—H18A	0.9900
C1—H1B	0.9900	C18—H18B	0.9900
C1—C2	1.534 (2)	C18—C19	1.515 (2)
C1—C6	1.536 (2)	C19—H19A	0.9900
C2—H2A	1.0000	C19—H19B	0.9900
C2—C3	1.523 (2)	C20—C23	1.512 (2)
C2—C7	1.512 (2)	C21—H21	0.9500
C3—H3B	0.9900	C21—C22	1.378 (3)
C3—H3C	0.9900	C22—H22	0.9500
C3—C4	1.522 (2)	C22—C23	1.377 (2)
C4—H4A	0.9900	C23—C24	1.382 (2)
C4—H4B	0.9900	C24—H24	0.9500
C4—C5	1.523 (3)	C24—C25	1.377 (2)
C5—H5A	0.9900	C25—H25	0.9500
C5—H5B	0.9900	O2W—H2WA	0.8696
C5—C6	1.521 (2)	O2W—H2WB	0.8702
C6—H6	1.0000	O1W—H1WA	0.8703
C6—C8	1.512 (2)	O1W—H1WB	0.8696

C7—O1—H1	109.5	C12—C11—C14	124.41 (14)
C8—O3—H3A	109.5	C11—C12—H12	120.5
C9—N1—C13	117.79 (14)	C13—C12—C11	118.99 (15)
C14—N2—H2	119.9	C13—C12—H12	120.5
C14—N2—C15	120.28 (14)	N1—C13—C12	122.85 (16)
C15—N2—H2	119.9	N1—C13—H13	118.6
C19—N3—H3	118.7	C12—C13—H13	118.6
C20—N3—H3	118.7	O5—C14—N2	122.56 (15)
C20—N3—C19	122.52 (15)	O5—C14—C11	119.11 (15)
C21—N4—C25	117.23 (15)	N2—C14—C11	118.33 (14)
H1A—C1—H1B	108.1	N2—C15—H15A	109.2
C2—C1—H1A	109.5	N2—C15—H15B	109.2
C2—C1—H1B	109.5	N2—C15—C16	112.12 (14)
C2—C1—C6	110.55 (14)	H15A—C15—H15B	107.9
C6—C1—H1A	109.5	C16—C15—H15A	109.2
C6—C1—H1B	109.5	C16—C15—H15B	109.2

C1—C2—H2A	108.1	C15—C16—H16A	109.3
C3—C2—C1	110.97 (14)	C15—C16—H16B	109.3
C3—C2—H2A	108.1	C15—C16—C17	111.48 (14)
C7—C2—C1	108.93 (13)	H16A—C16—H16B	108.0
C7—C2—H2A	108.1	C17—C16—H16A	109.3
C7—C2—C3	112.43 (14)	C17—C16—H16B	109.3
C2—C3—H3B	109.3	C16—C17—H17A	109.0
C2—C3—H3C	109.3	C16—C17—H17B	109.0
H3B—C3—H3C	108.0	H17A—C17—H17B	107.8
C4—C3—C2	111.40 (14)	C18—C17—C16	112.91 (14)
C4—C3—H3B	109.3	C18—C17—H17A	109.0
C4—C3—H3C	109.3	C18—C17—H17B	109.0
C3—C4—H4A	109.3	C17—C18—H18A	109.2
C3—C4—H4B	109.3	C17—C18—H18B	109.2
C3—C4—C5	111.53 (15)	H18A—C18—H18B	107.9
H4A—C4—H4B	108.0	C19—C18—C17	112.11 (14)
C5—C4—H4A	109.3	C19—C18—H18A	109.2
C5—C4—H4B	109.3	C19—C18—H18B	109.2
C4—C5—H5A	109.6	N3—C19—C18	111.67 (14)
C4—C5—H5B	109.6	N3—C19—H19A	109.3
H5A—C5—H5B	108.1	N3—C19—H19B	109.3
C6—C5—C4	110.24 (15)	C18—C19—H19A	109.3
C6—C5—H5A	109.6	C18—C19—H19B	109.3
C6—C5—H5B	109.6	H19A—C19—H19B	107.9
C1—C6—H6	107.3	O6—C20—N3	123.57 (15)
C5—C6—C1	110.87 (14)	O6—C20—C23	118.90 (15)
C5—C6—H6	107.3	N3—C20—C23	117.53 (14)
C8—C6—C1	110.28 (14)	N4—C21—H21	118.5
C8—C6—C5	113.38 (14)	N4—C21—C22	123.05 (17)
C8—C6—H6	107.3	C22—C21—H21	118.5
O1—C7—C2	114.58 (14)	C21—C22—H22	120.2
O2—C7—O1	122.53 (16)	C23—C22—C21	119.58 (17)
O2—C7—C2	122.87 (16)	C23—C22—H22	120.2
O3—C8—C6	112.97 (15)	C22—C23—C20	117.45 (15)
O4—C8—O3	123.05 (17)	C22—C23—C24	117.77 (15)
O4—C8—C6	123.98 (17)	C24—C23—C20	124.78 (15)
N1—C9—H9	118.4	C23—C24—H24	120.5
N1—C9—C10	123.21 (16)	C25—C24—C23	119.03 (17)
C10—C9—H9	118.4	C25—C24—H24	120.5
C9—C10—H10	120.5	N4—C25—C24	123.34 (17)
C9—C10—C11	118.92 (16)	N4—C25—H25	118.3
C11—C10—H10	120.5	C24—C25—H25	118.3
C10—C11—C14	117.37 (14)	H2WA—O2W—H2WB	104.5
C12—C11—C10	118.23 (15)	H1WA—O1W—H1WB	104.5

O6—C20—C23—C22	1.5 (2)	C9—C10—C11—C12	−1.3 (2)
O6—C20—C23—C24	−178.30 (16)	C9—C10—C11—C14	178.60 (15)
N1—C9—C10—C11	0.5 (3)	C10—C11—C12—C13	1.0 (2)

N2—C15—C16—C17	178.96 (14)	C10—C11—C14—O5	−6.9 (2)
N3—C20—C23—C22	−178.53 (15)	C10—C11—C14—N2	173.68 (15)
N3—C20—C23—C24	1.7 (2)	C11—C12—C13—N1	0.1 (3)
N4—C21—C22—C23	0.0 (3)	C12—C11—C14—O5	172.95 (16)
C1—C2—C3—C4	−54.9 (2)	C12—C11—C14—N2	−6.4 (2)
C1—C2—C7—O1	69.37 (19)	C13—N1—C9—C10	0.6 (3)
C1—C2—C7—O2	−109.11 (19)	C14—N2—C15—C16	166.15 (15)
C1—C6—C8—O3	−59.2 (2)	C14—C11—C12—C13	−178.87 (15)
C1—C6—C8—O4	121.5 (2)	C15—N2—C14—O5	2.1 (2)
C2—C1—C6—C5	−57.09 (19)	C15—N2—C14—C11	−178.56 (14)
C2—C1—C6—C8	176.51 (14)	C15—C16—C17—C18	155.48 (16)
C2—C3—C4—C5	55.8 (2)	C16—C17—C18—C19	178.95 (15)
C3—C2—C7—O1	−167.20 (15)	C17—C18—C19—N3	164.15 (15)
C3—C2—C7—O2	14.3 (2)	C19—N3—C20—O6	−4.5 (3)
C3—C4—C5—C6	−56.8 (2)	C19—N3—C20—C23	175.56 (14)
C4—C5—C6—C1	57.5 (2)	C20—N3—C19—C18	−124.01 (17)
C4—C5—C6—C8	−177.86 (15)	C20—C23—C24—C25	−179.65 (16)
C5—C6—C8—O3	175.77 (15)	C21—N4—C25—C24	−0.8 (3)
C5—C6—C8—O4	−3.5 (3)	C21—C22—C23—C20	179.54 (16)
C6—C1—C2—C3	55.44 (18)	C21—C22—C23—C24	−0.7 (3)
C6—C1—C2—C7	179.73 (14)	C22—C23—C24—C25	0.6 (3)
C7—C2—C3—C4	−177.15 (15)	C23—C24—C25—N4	0.2 (3)
C9—N1—C13—C12	−0.9 (2)	C25—N4—C21—C22	0.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.84	1.79	2.6251 (18)	178
O3—H3*A*···N4^{i}	0.84	1.79	2.6300 (19)	173
N2—H2···O1*W*^{ii}	0.88	2.03	2.8868 (19)	165
N3—H3···O2*W*^{ii}	0.88	2.01	2.849 (2)	159
O2*W*—H2*WA*···O2^{iii}	0.87	1.94	2.809 (2)	177
O2*W*—H2*WB*···O6	0.87	1.90	2.7684 (19)	173
O1*W*—H1*WA*···O5	0.87	1.88	2.7365 (18)	168
O1*W*—H1*WB*···O4^{iii}	0.87	1.99	2.863 (2)	178
C9—H9···O2^{iv}	0.95	2.51	3.143 (2)	124
C21—H21···O4^{v}	0.95	2.46	3.238 (2)	139
C6—H6···O6^{vi}	1.00	2.50	3.478 (2)	167

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) −*x*+1, *y*−1/2, −*z*+3/2; (iv) *x*−1, *y*, *z*; (v) *x*−1, *y*−1, *z*; (vi) −*x*+1, −*y*+1, −*z*+1.