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Crystal structure of tetraaquabis(1,3-dimethyl-2,6-dioxo-3,7-dihydro-1*H*-purin-9-ido)magnesium

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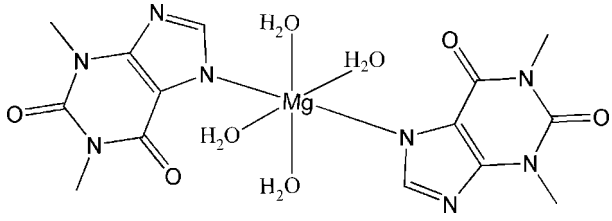
The title complex, $[Mg(C_7H_7N_4O_2)_2(H_2O)_4]$, lies across an inversion centre and the Mg^{II} atom is coordinated in a slightly distorted octahedral environment by four aqua ligands in the equatorial sites and two 1,3-dimethyl-2,6-dioxo-3,7-dihydro-1*H*-purin-9-ide ligands, through imidazole ring N atoms, in the axial sites. An intramolecular O—H···O hydrogen bond forms an *S*(7) graph-set motif. In the crystal, O—H···O and O—H···N hydrogen bonds link complex molecules forming a three-dimensional network incorporating $R_4^2(8)$ and $R_2^2(18)$ graph-set motifs.

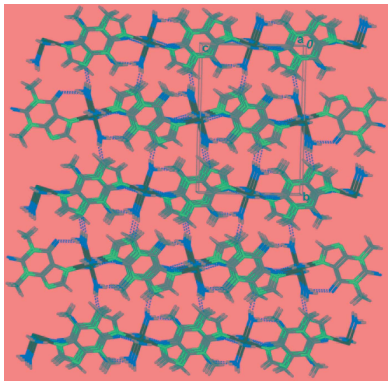
1. Chemical context

Co-crystallization represents a crystal engineering approach for modifying properties of active pharmaceutical ingredients (APIs) (Sun, 2013). Metal coordination is an alternative strategy without changing chemical structures of APIs (Ma & Moulton, 2007). Theophylline is a methylxanthine drug in the treatment of asthma and chronic obstructive pulmonary disease (Barnes, 2003). In this study, we reacted theophylline with the Mg^{II} ion in a basic solution to give rise to a tetraaqua mononuclear Mg^{II} complex, (I).



2. Structural commentary

The molecular structure of (I) is shown in Fig. 1. The complex lies across an inversion centre and the Mg^{II} atom is coordinated in a slightly distorted octahedral environment (Table 1) by four aqua ligands in the equatorial sites and two 1,3-dimethyl-2,6-dioxo-3,7-dihydro-1*H*-purin-9-ide ligands, through imidazole ring N atoms [N1 and N1($-x$ + 1, $-y$, $-z$ + 1)], in the axial sites. The symmetry-unique purine ring system is essentially planar, with a maximum deviation of 0.030 (2) Å for N3 and the bonded methyl C atoms C4 and C5 deviate from this mean plane by −0.118 (3) and 0.136 (2) Å, respectively.



3. Supramolecular features

In the crystal, the coordinating water molecules are involved in various hydrogen-bonding interactions (Table 2). A $R_4^2(8)$

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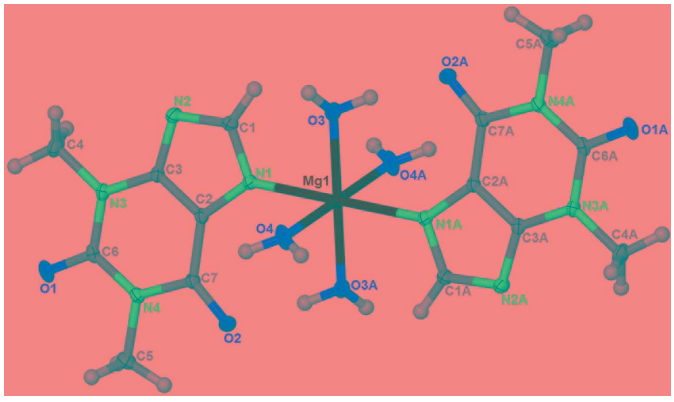

Figure 1
The molecular structure of the title complex, shown with 30% probability displacement ellipsoids [symmetry code: (A) $x, -y, -z + 1$).

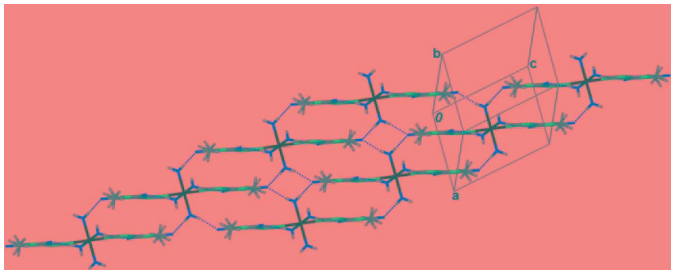

Figure 2
Part of the crystal structure, showing hydrogen bonds in two dimensions (dashed lines).

graph-set motif (Bernstein *et al.*, 1995) is formed through [O4···O1^{iii} = 2.829 (3) Å and O4···O1^{iv} = 2.780 (2) Å; symmetry codes: (iii) $-x, -y, -z$; (iv) $x, y, z + 1$] between a coordinating water molecule and a carbonyl group of a symmetry-related theophylline group. The mononuclear units

Table 1
Selected geometric parameters (Å, °).

Mg1—O3^{i}	2.0672 (17)	Mg1—N1^{i}	2.2255 (19)
Mg1—O4^{i}	2.081 (2)		
O3^{i}—Mg1—O3	180.00 (3)	O4—Mg1—N1^{i}	91.31 (6)
O3—Mg1—O4^{i}	87.98 (7)	O3—Mg1—N1	90.06 (6)
O3—Mg1—O4	92.02 (7)	O4—Mg1—N1	88.69 (6)
O4^{i}—Mg1—O4	180.0	N1^{i}—Mg1—N1	180.0
O3—Mg1—N1^{i}	89.94 (6)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···N2^{ii}	0.88 (1)	1.97 (1)	2.809 (3)	160 (3)
O3—H3B···O2^{i}	0.87 (1)	1.80 (1)	2.668 (2)	173 (3)
O4—H4E···O1^{iii}	0.87 (1)	1.93 (1)	2.780 (2)	168 (3)
O4—H4D···O1^{iv}	0.87 (1)	1.96 (1)	2.829 (3)	178 (3)

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

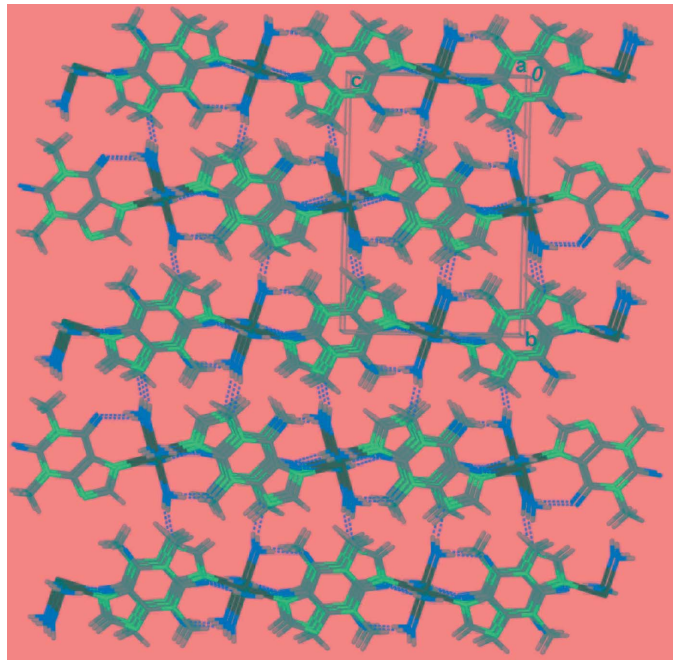

Figure 3
Part of the crystal structure, showing the overall three-dimensional hydrogen-bonded structure (dashed lines).

are connected into a layer parallel to (010) (Fig. 2), which is further connected into a three-dimensional structure (Fig. 3)

Table 3
Experimental details.

Crystal data	
Chemical formula	[Mg($C_7H_7N_4O_2$)$_2$(H_2O)$_4$]
M_r	454.71
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	7.694 (4), 13.399 (7), 9.739 (5)
β (°)	105.169 (9)
V (Å^3)	969.0 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.16
Crystal size (mm)	0.2 × 0.2 × 0.2
Data collection	
Diffractometer	Rigaku CCD
Absorption correction	Multi-scan (*CrystalClear*; Rigaku, 2000)
T_{min}, T_{max}	0.949, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7442, 2153, 1738
R_{int}	0.032
(sin θ/λ)$_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.123, 1.09
No. of reflections	2153
No. of parameters	160
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.25

Computer programs: *CrystalClear* (Rigaku, 2000), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *X-SEED* (Barbour, 2001).

by hydrogen-bonding interactions between coordinating water molecules and symmetry-related imidazole groups [O3···N2^{ii} = 2.809 (3) Å; symmetry code: (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$].

4. Database survey

A search of the Cambridge Structural Database (Version 5.36, November 2014; Groom & Allen, 2014) revealed 16 metal complexes of theophylline, including ternary, polynuclear complexes and coordination polymers but only five are mononuclear complexes. The most closely related compound to the title complex, in terms of the ligand types is triaqua-bis(theophylline)copper(II) dihydrate (WEZYIJ; Begum & Manohar, 1994). The title compound is the first crystal structure reported to date of a complex of theophylline with an alkaline-earth metal.

5. Synthesis and crystallization

Theophylline (180 mg, 1 mmol) was dissolved in water (20 ml). An aqueous solution (15 ml) of NaOH (40 mg, 1 mmol) was added slowly. $MgCl_2{\cdot}6H_2O$ (102 mg, 0.5 mmol) in water (15 ml) was then added. The resulting solution was kept in air and, after several days, colourless block-shaped crystals were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms bonded to C atoms were positioned geometrically (C—H = 0.95–0.98 Å) with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$. H atoms bonded to O atoms were located in difference Fourier maps and were refined with a distance restraint of O—H = 0.87 (1) Å. The isotropic displacement parameters were refined freely.

Acknowledgements

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supporting information

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Crystal structure of tetraaquabis(1,3-dimethyl-2,6-dioxo-3,7-dihydro-1*H*-purin-9-ido)magnesium

Yabin Shi and Benyong Lou

Computing details

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear* (Rigaku, 2000); data reduction: *CrystalClear* (Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

tetraaquabis(1,3-dimethyl-2,6-dioxo-3,7-dihydro-1*H*-purin-9-ido)magnesium(II)

Crystal data

$[Mg(C_7H_7N_4O_2)_2(H_2O)_4]$
M_r = 454.71
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 7.694 (4) Å
b = 13.399 (7) Å
c = 9.739 (5) Å
β = 105.169 (9)°
V = 969.0 (9) Å^3
Z = 2
$F(000)$ = 476
D_x = 1.558 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2170 reflections
θ = 2.7–27.5°
μ = 0.16 mm^{-1}
T = 295 K
Prism, colorless
0.2 × 0.2 × 0.2 mm

Data collection

Rigaku CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 14.6306 pixels mm^{-1}
CCD_Profile_fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
T_{min} = 0.949, T_{max} = 1.000
7442 measured reflections
2153 independent reflections
1738 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°, θ_{min} = 2.7°
$h = -8 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.123
S = 1.09
2153 reflections
160 parameters
4 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

$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.4099P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ 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.

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_{iso}*/U_{eq}
Mg1	0.5000	0.0000	0.5000	0.0220 (2)
O1	0.0856 (2)	−0.02565 (12)	−0.27579 (14)	0.0366 (4)
O2	0.2118 (2)	−0.14692 (11)	0.17770 (15)	0.0396 (4)
O3	0.5654 (2)	0.14587 (11)	0.56135 (16)	0.0361 (4)
O4	0.2306 (2)	0.02272 (14)	0.49391 (16)	0.0419 (4)
N1	0.4375 (2)	0.04557 (11)	0.27257 (16)	0.0253 (4)
N2	0.4425 (2)	0.16133 (12)	0.09955 (17)	0.0295 (4)
N3	0.2518 (2)	0.07368 (12)	−0.10112 (17)	0.0277 (4)
N4	0.1533 (2)	−0.08355 (12)	−0.04781 (17)	0.0260 (4)
C1	0.4967 (3)	0.13335 (14)	0.2386 (2)	0.0285 (4)
H1	0.5733	0.1745	0.3083	0.034*
C2	0.3344 (2)	0.01127 (14)	0.14086 (19)	0.0231 (4)
C3	0.3417 (3)	0.08329 (14)	0.0411 (2)	0.0241 (4)
C4	0.2540 (4)	0.15494 (17)	−0.2003 (2)	0.0426 (6)
H4A	0.3623	0.1497	−0.2350	0.064*
H4B	0.2543	0.2190	−0.1517	0.064*
H4C	0.1468	0.1507	−0.2809	0.064*
C5	0.0602 (3)	−0.17694 (16)	−0.1029 (2)	0.0379 (5)
H5A	−0.0695	−0.1645	−0.1367	0.057*
H5B	0.0827	−0.2270	−0.0269	0.057*
H5C	0.1054	−0.2016	−0.1819	0.057*
C6	0.1602 (2)	−0.01192 (15)	−0.1483 (2)	0.0263 (4)
C7	0.2344 (3)	−0.07757 (14)	0.1001 (2)	0.0256 (4)
H3A	0.505 (3)	0.2015 (13)	0.557 (3)	0.058 (8)*
H3B	0.644 (3)	0.149 (2)	0.6439 (17)	0.059 (9)*
H4D	0.188 (4)	0.007 (2)	0.566 (2)	0.072 (10)*
H4E	0.142 (3)	0.023 (2)	0.4175 (19)	0.055 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0247 (5)	0.0223 (4)	0.0169 (5)	0.0003 (3)	0.0018 (3)	0.0002 (3)

O1	0.0312 (8)	0.0563 (10)	0.0181 (7)	−0.0009 (7)	−0.0013 (6)	−0.0023 (6)
O2	0.0501 (9)	0.0329 (8)	0.0287 (8)	−0.0141 (7)	−0.0021 (7)	0.0066 (6)
O3	0.0495 (10)	0.0243 (7)	0.0278 (8)	0.0015 (7)	−0.0020 (7)	−0.0018 (6)
O4	0.0278 (8)	0.0722 (12)	0.0239 (9)	0.0027 (8)	0.0034 (7)	0.0008 (8)
N1	0.0292 (9)	0.0234 (8)	0.0207 (8)	−0.0013 (6)	0.0022 (7)	−0.0005 (6)
N2	0.0375 (9)	0.0255 (8)	0.0238 (9)	−0.0042 (7)	0.0052 (7)	0.0021 (6)
N3	0.0311 (9)	0.0309 (9)	0.0189 (8)	0.0003 (7)	0.0026 (7)	0.0055 (6)
N4	0.0252 (8)	0.0274 (8)	0.0225 (8)	−0.0018 (6)	0.0010 (7)	−0.0027 (6)
C1	0.0323 (10)	0.0253 (10)	0.0257 (10)	−0.0041 (8)	0.0037 (8)	−0.0012 (8)
C2	0.0242 (9)	0.0244 (9)	0.0193 (9)	0.0017 (7)	0.0035 (7)	0.0005 (7)
C3	0.0248 (9)	0.0253 (9)	0.0211 (9)	0.0040 (7)	0.0042 (7)	0.0007 (7)
C4	0.0566 (15)	0.0412 (13)	0.0274 (12)	0.0027 (11)	0.0064 (10)	0.0114 (9)
C5	0.0399 (12)	0.0357 (11)	0.0332 (12)	−0.0078 (9)	0.0011 (10)	−0.0100 (9)
C6	0.0202 (9)	0.0367 (11)	0.0205 (10)	0.0047 (8)	0.0029 (7)	−0.0006 (8)
C7	0.0257 (10)	0.0274 (9)	0.0223 (10)	0.0003 (7)	0.0039 (8)	0.0000 (7)

Geometric parameters (Å, º)

Mg1—O3^{i}	2.0672 (17)	N3—C6	1.361 (3)
Mg1—O3	2.0672 (17)	N3—C3	1.383 (2)
Mg1—O4^{i}	2.081 (2)	N3—C4	1.459 (3)
Mg1—O4	2.081 (2)	N4—C6	1.382 (3)
Mg1—N1^{i}	2.2255 (19)	N4—C7	1.414 (3)
Mg1—N1	2.2255 (19)	N4—C5	1.472 (3)
O1—C6	1.238 (2)	C1—H1	0.9500
O2—C7	1.238 (2)	C2—C3	1.381 (3)
O3—H3A	0.875 (10)	C2—C7	1.416 (3)
O3—H3B	0.872 (10)	C4—H4A	0.9800
O4—H4D	0.873 (10)	C4—H4B	0.9800
O4—H4E	0.867 (10)	C4—H4C	0.9800
N1—C1	1.334 (3)	C5—H5A	0.9800
N1—C2	1.398 (2)	C5—H5B	0.9800
N2—C3	1.337 (2)	C5—H5C	0.9800
N2—C1	1.361 (3)		
O3^{i}—Mg1—O3	180.00 (3)	C6—N4—C5	115.94 (16)
O3^{i}—Mg1—O4^{i}	92.02 (7)	C7—N4—C5	117.55 (16)
O3—Mg1—O4^{i}	87.98 (7)	N1—C1—N2	116.97 (17)
O3^{i}—Mg1—O4	87.98 (7)	N1—C1—H1	121.5
O3—Mg1—O4	92.02 (7)	N2—C1—H1	121.5
O4^{i}—Mg1—O4	180.0	C3—C2—N1	107.34 (17)
O3^{i}—Mg1—N1^{i}	90.06 (6)	C3—C2—C7	120.60 (17)
O3—Mg1—N1^{i}	89.94 (6)	N1—C2—C7	132.06 (17)
O4^{i}—Mg1—N1^{i}	88.69 (6)	N2—C3—C2	111.89 (17)
O4—Mg1—N1^{i}	91.31 (6)	N2—C3—N3	125.57 (17)
O3^{i}—Mg1—N1	89.94 (6)	C2—C3—N3	122.53 (17)
O3—Mg1—N1	90.06 (6)	N3—C4—H4A	109.5
O4^{i}—Mg1—N1	91.31 (6)	N3—C4—H4B	109.5

O4—Mg1—N1	88.69 (6)	H4A—C4—H4B	109.5
N1^{i}—Mg1—N1	180.0	N3—C4—H4C	109.5
Mg1—O3—H3A	135.0 (19)	H4A—C4—H4C	109.5
Mg1—O3—H3B	111.8 (19)	H4B—C4—H4C	109.5
H3A—O3—H3B	103 (3)	N4—C5—H5A	109.5
Mg1—O4—H4D	122 (2)	N4—C5—H5B	109.5
Mg1—O4—H4E	125.3 (19)	H5A—C5—H5B	109.5
H4D—O4—H4E	108 (3)	N4—C5—H5C	109.5
C1—N1—C2	102.20 (16)	H5A—C5—H5C	109.5
C1—N1—Mg1	119.32 (12)	H5B—C5—H5C	109.5
C2—N1—Mg1	138.26 (13)	O1—C6—N3	121.81 (19)
C3—N2—C1	101.59 (16)	O1—C6—N4	120.91 (19)
C6—N3—C3	119.72 (16)	N3—C6—N4	117.28 (17)
C6—N3—C4	120.00 (17)	O2—C7—N4	118.96 (17)
C3—N3—C4	120.28 (17)	O2—C7—C2	127.74 (18)
C6—N4—C7	126.42 (16)	N4—C7—C2	113.31 (17)

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···N2^{ii}	0.88 (1)	1.97 (1)	2.809 (3)	160 (3)
O3—H3*B*···O2^{i}	0.87 (1)	1.80 (1)	2.668 (2)	173 (3)
O4—H4*E*···O1^{iii}	0.87 (1)	1.93 (1)	2.780 (2)	168 (3)
O4—H4*D*···O1^{iv}	0.87 (1)	1.96 (1)	2.829 (3)	178 (3)

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