Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetraaquabis(3,5-di-4-pyridyl-1,2,4-triazolato-κN)nickel(II) dihydrate

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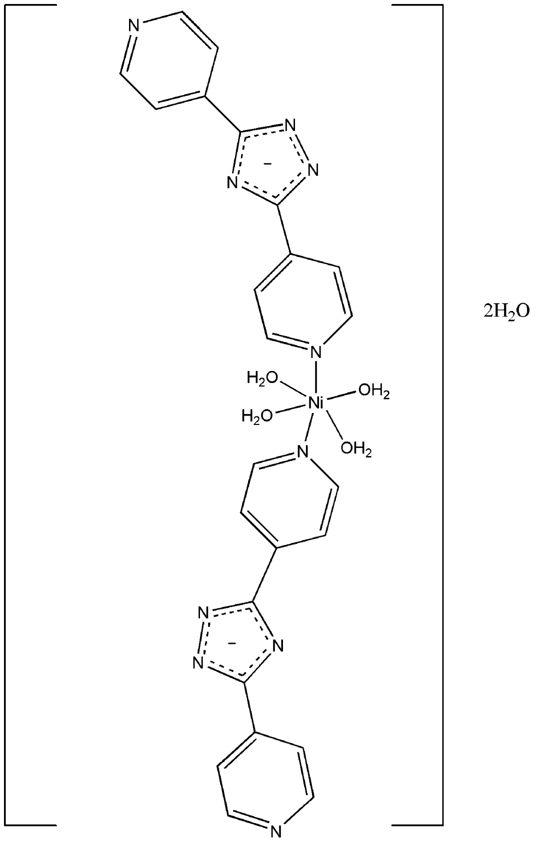
Received 28 June 2009; accepted 14 July 2009

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.078; data-to-parameter ratio = 11.1.

The Ni^{II} atom in the title compound, $[Ni(C_{12}H_8N_5)_2(H_2O)_4]\cdot 2H_2O$, lies on a center of inversion and is coordinated by the N atoms of two 3,5-di-4-pyridine-1,2,4-triazolate ligands and by four water O atoms in a slightly distorted octahedral geometry. The coordinated and uncoordinated water molecules interact with the *N*-heterocycles through O—H⋯N and O—H⋯O hydrogen bonds, generating a three-dimensional supramolecular architecture.

Related literature

For magnetic studies of transition metal complexes with 1,2,4-triazole derivatives, see: Haasnoot (2000). For 3,5-di-4-pyridine-1,2,4-triazole, see: Zhang *et al.* (2005, 2006). For the synthesis, see: Basu & Dutta (1964).



Experimental

Crystal data

$[Ni(C_{12}H_8N_5)_2(H_2O)_4]\cdot 2H_2O$
M_r = 611.27
Monoclinic, $P2_1/c$
a = 7.3390 (15) Å
b = 15.653 (3) Å
c = 11.829 (2) Å
β = 107.20 (3)°
V = 1298.1 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 293 K
0.43 × 0.27 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.722, T_{max} = 0.848
10883 measured reflections
2344 independent reflections
2131 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.078
S = 1.14
2344 reflections
211 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O3^{i}	0.82 (3)	2.03 (3)	2.818 (3)	160 (3)
O3—H3A···N4^{ii}	0.85 (3)	2.09 (3)	2.939 (3)	172 (3)
O3—H3B···N5^{iii}	0.86 (4)	1.94 (4)	2.789 (3)	173 (3)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2531).

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supporting information

Acta Cryst. (2009). E**65**, m962–m963   [doi:10.1107/S1600536809027688]

Tetraaquabis(3,5-di-4-pyridyl-1,2,4-triazolato-*κN*)nickel(II) dihydrate

Lin Yi Dong

S1. Comment

Transition metal complexes with 1,2,4-triazole derivatives as ligands are of great interest as they are the subject of magnetic studies (Haasnoot, 2000). The ligand 3,5-di(4-pyridine)-1,2,4-triazole is of special interest as it contains multi-dentate donor atoms and shows diverse coordination modes. Especially only a few examples about the coordinaiton chemistry of *L* are reported. Some unusual coordination modes of *L* also have been reported forming interesting supramolecular isomerism systems (Zhang *et al.*, 2006).

In this work, we synthesized a new compound $[Ni(L)_2(H_2O)_4](H_2O)_2$ (*L* = 3,5-di(4-pyridine)-1,2,4-triazolate anions), which is composed of one nickel(II) cation, two *L* ligand, four coordinated and two lattice water molecules. The nickel(II) cation is six-coordinated in the octahedral geometry. The equatorial site of nickel cation is occupied by four aqua molecules while the axial site is occupied by two nitrogen atoms of two mono-dentate *L* ligands. The mono-dentate coordination mode of *L* is different from previously reported di-, tri- or tetra-dentate coordination modes of *L* (Zhang *et al.*, 2005; Zhang *et al.*, 2006).

O3 acts as both a hydrogen bond donor and a hydrogen bond acceptor. Strong O—H···N and O—H···O hydrogen bonds generated from water molecules and nitrogen atoms of pyridine or triazole groups are also observed resulting in the three-dimensional supramolecular network.

S2. Experimental

The ligand was prepared according to the previous literature (Basu & Dutta, (1964)). $[Ni(L)_2(H_2O)_4](H_2O)$ (I) (*L* = 3,5-di(4-pyridine)-1,2,4-triazole) was prepared under the hydrothermal conditions. $[Ni(ClO_4)_2].6H_2O$ (0.2 mmol), *L* (0.2 mmol) and 18 ml water was added to a 25 ml reaction vessel. The reaction vessel was then sealed and subsequently placed in an oven for 140 h at 160°C well shaped green block crystals were obtained and washed with ethanol.

S3. Refinement

All H atoms were found on difference maps. The water H atoms were refined freely, giving an O–H = 0.82–0.86 Å. The remaining H atoms were placed in calculated positions, with C–H = 0.93 Å, and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$

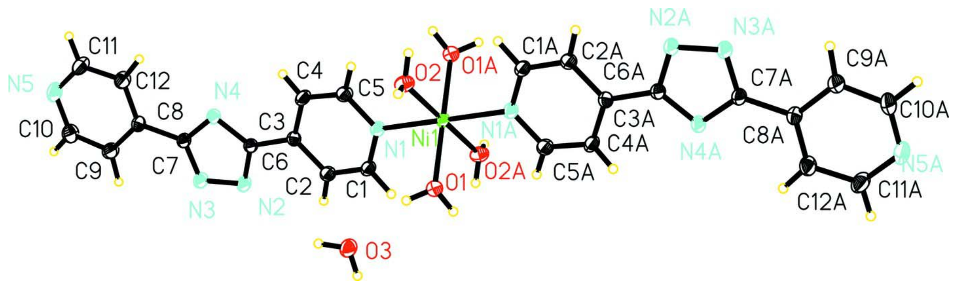

Figure 1

View of the title compound, with displacement ellipsoids drawn at the 40% probability level.

Tetraaquabis(3,5-di-4-pyridyl-1,2,4-triazolato-κ*N*)nickel(II) dihydrate

Crystal data

$[Ni(C_{12}H_8N_5)_2(H_2O)_4]\cdot 2H_2O$
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$b = 15.653$ (3) Å
$c = 11.829$ (2) Å
$\beta = 107.20$ (3)°
$V = 1298.1$ (5) Å^3
$Z = 2$
$F(000) = 636$
$D_x = 1.564$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 467 reflections
$\theta = 1.5$–25.3°
$\mu = 0.81$ mm^{-1}
$T = 293$ K
Block, green
0.43 × 0.27 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.722$, $T_{max} = 0.848$
10883 measured reflections
2344 independent reflections
2131 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.2°$, $\theta_{min} = 3.2°$
$h = -8\rightarrow 8$
$k = -18\rightarrow 18$
$l = -14\rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.078$
$S = 1.14$
2344 reflections
211 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 1.0454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ 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	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.4927 (3)	0.33129 (14)	0.6238 (2)	0.0265 (5)
H1C	0.5402	0.3645	0.6914	0.032*
C2	0.4672 (3)	0.24522 (14)	0.6376 (2)	0.0272 (5)
H2C	0.4983	0.2216	0.7131	0.033*
C3	0.3951 (3)	0.19348 (13)	0.53900 (19)	0.0218 (5)
C4	0.3570 (4)	0.23293 (14)	0.4292 (2)	0.0287 (5)
H4A	0.3117	0.2010	0.3603	0.034*
C5	0.3864 (4)	0.31953 (14)	0.4228 (2)	0.0283 (5)
H5A	0.3590	0.3446	0.3483	0.034*
C6	0.3545 (3)	0.10302 (13)	0.55253 (19)	0.0217 (5)
C7	0.2505 (3)	−0.02231 (13)	0.52360 (19)	0.0224 (5)
C8	0.1688 (3)	−0.10334 (14)	0.46845 (19)	0.0232 (5)
C9	0.1536 (4)	−0.17397 (16)	0.5368 (2)	0.0370 (6)
H9A	0.1892	−0.1697	0.6189	0.044*
C10	0.0858 (4)	−0.24977 (16)	0.4823 (2)	0.0411 (7)
H10A	0.0794	−0.2962	0.5301	0.049*
C11	0.0428 (4)	−0.19348 (16)	0.3005 (2)	0.0359 (6)
H11A	0.0042	−0.1995	0.2186	0.043*
C12	0.1111 (4)	−0.11487 (15)	0.3471 (2)	0.0312 (6)
H12A	0.1184	−0.0699	0.2971	0.037*
H1A	0.413 (5)	0.550 (2)	0.686 (3)	0.051 (9)*
H2A	0.149 (5)	0.527 (2)	0.358 (3)	0.051 (10)*
H3A	0.163 (5)	0.426 (2)	0.782 (3)	0.054 (10)*
H1B	0.283 (5)	0.493 (2)	0.633 (3)	0.055 (10)*
H2B	0.257 (4)	0.5122 (18)	0.292 (3)	0.048 (9)*
H3B	0.077 (5)	0.372 (2)	0.691 (3)	0.062 (10)*
N1	0.4525 (3)	0.36961 (11)	0.51811 (16)	0.0237 (4)
N2	0.3943 (3)	0.06670 (12)	0.65942 (16)	0.0279 (5)
N3	0.3259 (3)	−0.01470 (12)	0.64046 (17)	0.0290 (5)
N4	0.2645 (3)	0.04985 (11)	0.46332 (16)	0.0226 (4)
N5	0.0286 (3)	−0.26126 (13)	0.3656 (2)	0.0360 (5)
Ni1	0.5000	0.5000	0.5000	0.01983 (13)
O1	0.3476 (3)	0.53202 (12)	0.61834 (15)	0.0275 (4)
O2	0.2507 (3)	0.50476 (11)	0.35989 (15)	0.0287 (4)
O3	0.1179 (3)	0.42339 (11)	0.70636 (17)	0.0314 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0368 (14)	0.0208 (12)	0.0204 (12)	−0.0048 (10)	0.0062 (10)	−0.0025 (9)
C2	0.0390 (14)	0.0215 (12)	0.0197 (12)	−0.0036 (10)	0.0066 (10)	0.0023 (9)
C3	0.0249 (12)	0.0178 (11)	0.0234 (12)	−0.0009 (9)	0.0083 (9)	−0.0001 (9)
C4	0.0434 (15)	0.0199 (12)	0.0204 (12)	−0.0063 (11)	0.0057 (10)	−0.0029 (9)
C5	0.0416 (15)	0.0216 (12)	0.0199 (12)	−0.0021 (10)	0.0062 (10)	0.0026 (9)
C6	0.0269 (12)	0.0174 (11)	0.0209 (11)	−0.0006 (9)	0.0073 (9)	0.0001 (9)
C7	0.0281 (12)	0.0162 (11)	0.0224 (11)	−0.0009 (9)	0.0068 (9)	−0.0005 (8)
C8	0.0239 (12)	0.0188 (11)	0.0254 (12)	−0.0003 (9)	0.0051 (9)	−0.0010 (9)
C9	0.0588 (18)	0.0260 (13)	0.0251 (13)	−0.0116 (12)	0.0108 (12)	0.0001 (10)
C10	0.0624 (19)	0.0225 (13)	0.0392 (16)	−0.0129 (13)	0.0161 (13)	0.0020 (11)
C11	0.0424 (15)	0.0314 (14)	0.0280 (13)	−0.0042 (11)	0.0014 (11)	−0.0060 (11)
C12	0.0400 (15)	0.0221 (12)	0.0269 (13)	−0.0029 (10)	0.0031 (11)	0.0039 (10)
N1	0.0310 (11)	0.0168 (9)	0.0223 (10)	−0.0024 (8)	0.0067 (8)	−0.0006 (7)
N2	0.0413 (12)	0.0175 (10)	0.0232 (10)	−0.0064 (9)	0.0070 (9)	0.0002 (8)
N3	0.0429 (12)	0.0189 (10)	0.0232 (10)	−0.0071 (9)	0.0067 (9)	0.0009 (8)
N4	0.0281 (10)	0.0161 (9)	0.0222 (10)	−0.0016 (8)	0.0053 (8)	0.0011 (7)
N5	0.0408 (13)	0.0244 (11)	0.0416 (13)	−0.0077 (10)	0.0102 (10)	−0.0075 (9)
Ni1	0.0263 (2)	0.0140 (2)	0.0186 (2)	−0.00180 (17)	0.00564 (16)	−0.00025 (16)
O1	0.0322 (10)	0.0267 (9)	0.0246 (9)	−0.0036 (8)	0.0101 (8)	−0.0021 (7)
O2	0.0288 (10)	0.0329 (10)	0.0228 (9)	0.0044 (8)	0.0054 (7)	−0.0001 (7)
O3	0.0420 (11)	0.0222 (9)	0.0288 (10)	−0.0034 (8)	0.0088 (8)	−0.0015 (7)

Geometric parameters (Å, º)

C1—N1	1.339 (3)	C10—N5	1.331 (3)
C1—C2	1.377 (3)	C10—H10A	0.9300
C1—H1C	0.9300	C11—N5	1.333 (3)
C2—C3	1.390 (3)	C11—C12	1.380 (3)
C2—H2C	0.9300	C11—H11A	0.9300
C3—C4	1.389 (3)	C12—H12A	0.9300
C3—C6	1.465 (3)	N1—Ni1	2.0921 (18)
C4—C5	1.378 (3)	N2—N3	1.364 (3)
C4—H4A	0.9300	Ni1—O2	2.0753 (19)
C5—N1	1.341 (3)	Ni1—O2$^{\mathrm{i}}$	2.0753 (19)
C5—H5A	0.9300	Ni1—N1$^{\mathrm{i}}$	2.0921 (18)
C6—N2	1.337 (3)	Ni1—O1	2.0945 (17)
C6—N4	1.353 (3)	Ni1—O1$^{\mathrm{i}}$	2.0945 (17)
C7—N3	1.334 (3)	O1—H1A	0.85 (3)
C7—N4	1.356 (3)	O1—H1B	0.82 (3)
C7—C8	1.471 (3)	O2—H2A	0.82 (3)
C8—C12	1.384 (3)	O2—H2B	0.82 (3)
C8—C9	1.393 (3)	O3—H3A	0.85 (3)
C9—C10	1.372 (3)	O3—H3B	0.86 (4)
C9—H9A	0.9300		

N1—C1—C2	123.3 (2)	C11—C12—C8	119.6 (2)
N1—C1—H1C	118.3	C11—C12—H12A	120.2
C2—C1—H1C	118.3	C8—C12—H12A	120.2
C1—C2—C3	120.1 (2)	C1—N1—C5	116.65 (19)
C1—C2—H2C	119.9	C1—N1—Ni1	122.37 (14)
C3—C2—H2C	119.9	C5—N1—Ni1	120.94 (15)
C4—C3—C2	116.5 (2)	C6—N2—N3	105.95 (17)
C4—C3—C6	122.7 (2)	C7—N3—N2	105.88 (17)
C2—C3—C6	120.7 (2)	C6—N4—C7	101.41 (18)
C5—C4—C3	119.8 (2)	C10—N5—C11	115.9 (2)
C5—C4—H4A	120.1	O2—Ni1—O2^{i}	180.0
C3—C4—H4A	120.1	O2—Ni1—N1^{i}	90.99 (7)
N1—C5—C4	123.5 (2)	O2^{i}—Ni1—N1^{i}	89.01 (7)
N1—C5—H5A	118.2	O2—Ni1—N1	89.01 (7)
C4—C5—H5A	118.2	O2^{i}—Ni1—N1	90.99 (7)
N2—C6—N4	113.30 (19)	N1^{i}—Ni1—N1	180.0
N2—C6—C3	121.29 (19)	O2—Ni1—O1	90.36 (8)
N4—C6—C3	125.27 (19)	O2^{i}—Ni1—O1	89.64 (8)
N3—C7—N4	113.45 (19)	N1^{i}—Ni1—O1	88.45 (7)
N3—C7—C8	121.77 (19)	N1—Ni1—O1	91.55 (7)
N4—C7—C8	124.7 (2)	O2—Ni1—O1^{i}	89.64 (8)
C12—C8—C9	116.5 (2)	O2^{i}—Ni1—O1^{i}	90.36 (8)
C12—C8—C7	122.2 (2)	N1^{i}—Ni1—O1^{i}	91.55 (7)
C9—C8—C7	121.3 (2)	N1—Ni1—O1^{i}	88.45 (7)
C10—C9—C8	119.6 (2)	O1—Ni1—O1^{i}	180.0
C10—C9—H9A	120.2	Ni1—O1—H1A	117 (2)
C8—C9—H9A	120.2	Ni1—O1—H1B	115 (2)
N5—C10—C9	124.3 (2)	H1A—O1—H1B	104 (3)
N5—C10—H10A	117.8	Ni1—O2—H2A	128 (2)
C9—C10—H10A	117.8	Ni1—O2—H2B	119 (2)
N5—C11—C12	124.1 (2)	H2A—O2—H2B	103 (3)
N5—C11—H11A	118.0	H3A—O3—H3B	106 (3)
C12—C11—H11A	118.0		

N1—C1—C2—C3	−0.5 (4)	C4—C5—N1—Ni1	178.32 (19)
C1—C2—C3—C4	1.7 (3)	N4—C6—N2—N3	−0.5 (3)
C1—C2—C3—C6	−175.6 (2)	C3—C6—N2—N3	175.4 (2)
C2—C3—C4—C5	−1.7 (4)	N4—C7—N3—N2	−0.2 (3)
C6—C3—C4—C5	175.6 (2)	C8—C7—N3—N2	177.4 (2)
C3—C4—C5—N1	0.5 (4)	C6—N2—N3—C7	0.4 (2)
C4—C3—C6—N2	179.4 (2)	N2—C6—N4—C7	0.4 (3)
C2—C3—C6—N2	−3.4 (3)	C3—C6—N4—C7	−175.3 (2)
C4—C3—C6—N4	−5.2 (4)	N3—C7—N4—C6	−0.2 (3)
C2—C3—C6—N4	172.1 (2)	C8—C7—N4—C6	−177.6 (2)
N3—C7—C8—C12	−172.1 (2)	C9—C10—N5—C11	1.0 (4)
N4—C7—C8—C12	5.1 (4)	C12—C11—N5—C10	−0.2 (4)
N3—C7—C8—C9	4.9 (4)	C1—N1—Ni1—O2	−142.48 (19)
N4—C7—C8—C9	−177.8 (2)	C5—N1—Ni1—O2	40.10 (19)

C12—C8—C9—C10	0.6 (4)	C1—N1—Ni1—O2^{i}	37.52 (19)
C7—C8—C9—C10	−176.6 (2)	C5—N1—Ni1—O2^{i}	−139.90 (19)
C8—C9—C10—N5	−1.2 (5)	C1—N1—Ni1—N1^{i}	139 (100)
N5—C11—C12—C8	−0.4 (4)	C5—N1—Ni1—N1^{i}	−39 (100)
C9—C8—C12—C11	0.2 (4)	C1—N1—Ni1—O1	−52.15 (19)
C7—C8—C12—C11	177.3 (2)	C5—N1—Ni1—O1	130.43 (19)
C2—C1—N1—C5	−0.7 (4)	C1—N1—Ni1—O1^{i}	127.85 (19)
C2—C1—N1—Ni1	−178.26 (18)	C5—N1—Ni1—O1^{i}	−49.57 (19)
C4—C5—N1—C1	0.8 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O3^{ii}	0.82 (3)	2.03 (3)	2.818 (3)	160 (3)
O3—H3*A*···N4^{iii}	0.85 (3)	2.09 (3)	2.939 (3)	172 (3)
O3—H3*B*···N5^{iv}	0.86 (4)	1.94 (4)	2.789 (3)	173 (3)

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