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Ammonium diphosphitoindate(III)

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(In–O) = 0.002 Å; R factor = 0.017; wR factor = 0.041; data-to-parameter ratio = 32.1.

The crystal structure of the title compound, $NH_4[In(HPO_3)_2]$, is built up from In^{III} cations (site symmetry $3m.$) adopting an octahedral environment and two different phosphite anions (each with site symmetry $3m.$) exhibiting a triangular–pyramidal geometry. Each InO_6 octahedron shares its six apices with hydrogen phosphite groups. Reciprocally, each HPO_3 group shares all its O atoms with three different metal cations, leading to $[In(HPO_3)_2]^-$ layers which propagate in the ab plane. The ammonium cation likewise has site symmetry $3m.$. In the structure, the cations are located between the $[In(HPO_3)_2]^-$ layers of the host framework. The sheets are held together by hydrogen bonds formed between the NH_4^+ cations and the O atoms of the framework.

Related literature

For general background, see: Natarajan & Mandal (2008); Marcos *et al.* (1993). For related structures, see: Li *et al.* (2013); Hamchaoui *et al.* (2013); Giester (2000); Graeber & Rosenzweig (1971). For potential applications of open-framework transition metal phosphates, see: Cheetham *et al.* (1999). For the synthesis of the first organically templated vanadium phosphite with an open framework, see: Bonavia *et al.* (1995). Structures of purely inorganic phosphite compounds have been evidenced with magnetic and non-magnetic cations (Marcos *et al.*, 1993; Morris *et al.*, 1994; Orive *et al.*, 2011) while closely related structures can be obtained by replacing organic cations by inorganic ones as observed in the $A_xMn_3(HPO_3)_4$ system [A = en (Fernández *et al.*, 2000); A = K (Hamchaoui *et al.*, 2009)].

Experimental

Crystal data

$NH_4[In(HPO_3)_2]$
M_r = 292.82
Hexagonal, $P6_3mc$
a = 5.4705 (1) Å
c = 13.0895 (4) Å
V = 339.24 (1) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.93 mm^{-1}
T = 293 K
0.10 × 0.05 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.66, T_{max} = 0.92
7774 measured reflections
962 independent reflections
912 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.041
S = 1.26
962 reflections
30 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −1.39 e Å^{-3}
Absolute structure: Flack (1983), 459 Friedel pairs
Flack parameter: −0.01 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—HN1···O1	0.86 (2)	2.38 (2)	3.066 (2)	138 (2)
N1—HN1···O1^{i}	0.86 (2)	2.38 (2)	3.066 (2)	138 (2)
N1—HN2···O2^{ii}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)
N1—HN2···O2^{iii}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)
N1—HN2···O2^{iv}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)
N1—HN2···O2^{v}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2050).

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Acta Cryst. (2013). E**69**, i21–i22 [doi:10.1107/S160053681300771X]

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S1. Comment

After the discovery of microporous aluminophosphates, considerable efforts have been directed towards the synthesis of new open-framework transition metal phosphates because of their potential applications (Cheetham *et al.*, 1999). The replacement of phosphate by phosphite in transition metal phosphates has recently attracted effort, notably since the synthesis of the first organically templated vanadium phosphite with an open framework (Bonavia *et al.*, 1995). Consequently the literature is currently dominated by reports of organically template phosphite frame- works (Natarajan & Mandal, 2008). Purely inorganic phosphite structures have also been evidenced with magnetic and non-magnetic cations (Marcos *et al.*, 1993, Morris *et al.*, 1994, Orive *et al.*, 2011) while, interestingly, closely related structures can be obtained by replacing organic cations by inorganic ones as observed in the $A_xMn_3(HPO_3)_4$ system. (A = en: Fernández *et al.*, 2000, A = K: Hamchaoui *et al.*, 2009).

The structure of the title compound is built up from $In(HPO_3)_2$ layers separated by NH_4 cations. It is isostructural to $(H_3O)In(HPO_3)_2$ (Li *et al.*, 2013) and to the $A[M(HPO_3)_2]$ family (A = K, Rb, NH_4 and M = V, Fe) (Hamchaoui *et al.*, 2013). The structural model is also related to the yavapaiite aluns type (Graeber & Rosenzweig, 1971) and the mixed selenite-selenate $[(RbFe(SeO_4)(SeO_3)]$(Giester, 2000). As shown in Fig. 1, the asymmetric unit contains one crystallographic independant In^{III} cation and two ones for both phosphorus and oxygen atoms. Six oxygen atoms define an octahedral geometry around the metallic center while three oxygen atoms and one hydrogen atom define the triangular pyramidal environment of the phosphorus atom. The quaternary ammonium ions are displayed between the $[M(HPO_3)_2]^-$ layers of the host framework (Fig. 2). They exhibit N—H bond distances in the range usually found for this cation and the angles are similar to those expected for sp^3 hybridization. Thus for **1** the sheets are held together by hydrogen bonds formed between and the oxygen atoms of the framework. This H-bonding arrangement is illustrated in Fig. 3. It shows that the ammonium ion is firmly fixed in the structure by means of nine N—H···O hydrogen bonds, which prevent free ammonium-ion rotation at 298 K. The ammonium cations are located at the center of the six-ring windows of the upper layer.

S2. Experimental

The title compound was prepared under mild hydrothermal conditions and autogenous pressure. The starting reagents were $InCl_3$ (Sigma-Aldrich, 98%), H_3PO_3 (Aldrich, 99%), $(NH_4)_2CO_3$ (Fluka, 30–33% of NH_3) and deionized water in a 2:15:4:280 molar ratio. The mixture was placed in a 23 ml Teflon-lined steel autoclave, heated at 453 K for 72 h and followed by slow cooling to room temperature. Well formed colorless crystals were recovered by vacuum filtration, washed with deionized water and dried in a desiccator.

S3. Refinement

Part of the H atoms was localized from a difference Fourier map (HP2 and HN1) others were placed in calculated position according to geometrical constraints. Hydrogen atom positions of the ammonium cation were refined with their N—H and H—H distances restrained to one common refined value (0.87 Å and 1.33 Å respectively)

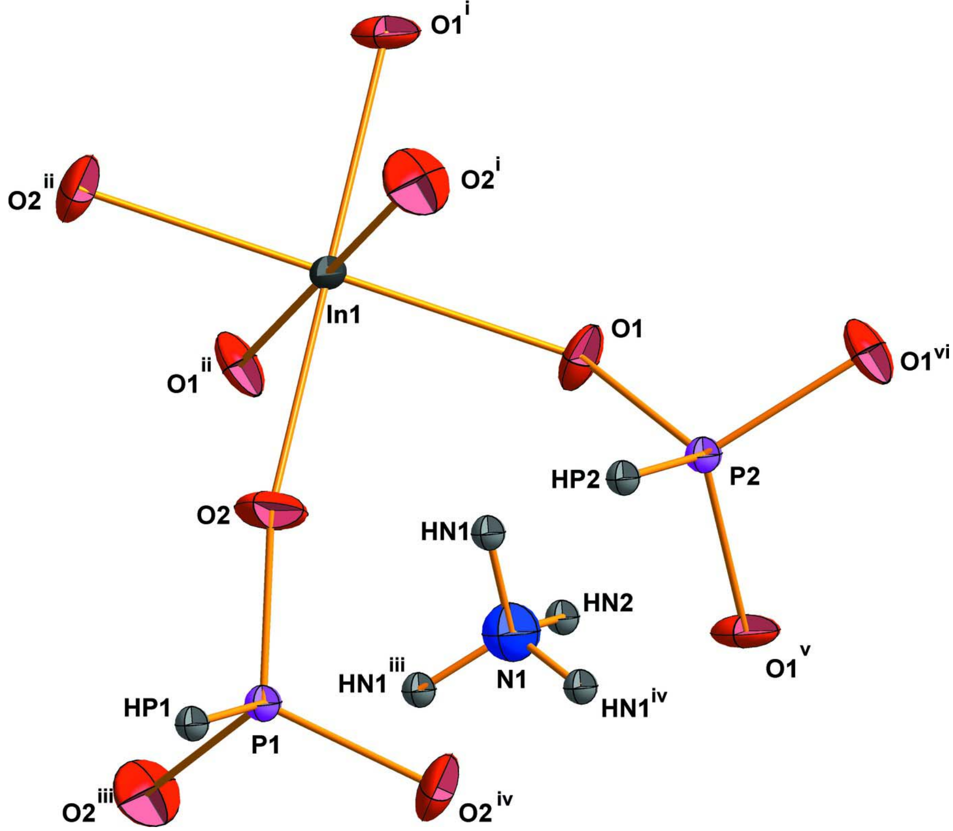

Figure 1

The asymmetric unit and symmetry-related atoms of $NH_4[In(HPO_3)_2]$, shown with 50% probability displacement ellipsoids. [symmetry codes: (i) -*y*, *x*-*y* + 1, *z*; (ii) -*x* + *y* - 1, -*x*, *z*; (iii) -*y* - 1, *x*-*y*, *z*; (iv) -*x* + *y* - 1, -*x* - 1, *z*; (v) -*y*, *x*-*y*, *z*; (vi) -*x* + *y*, -*x*, *z*].

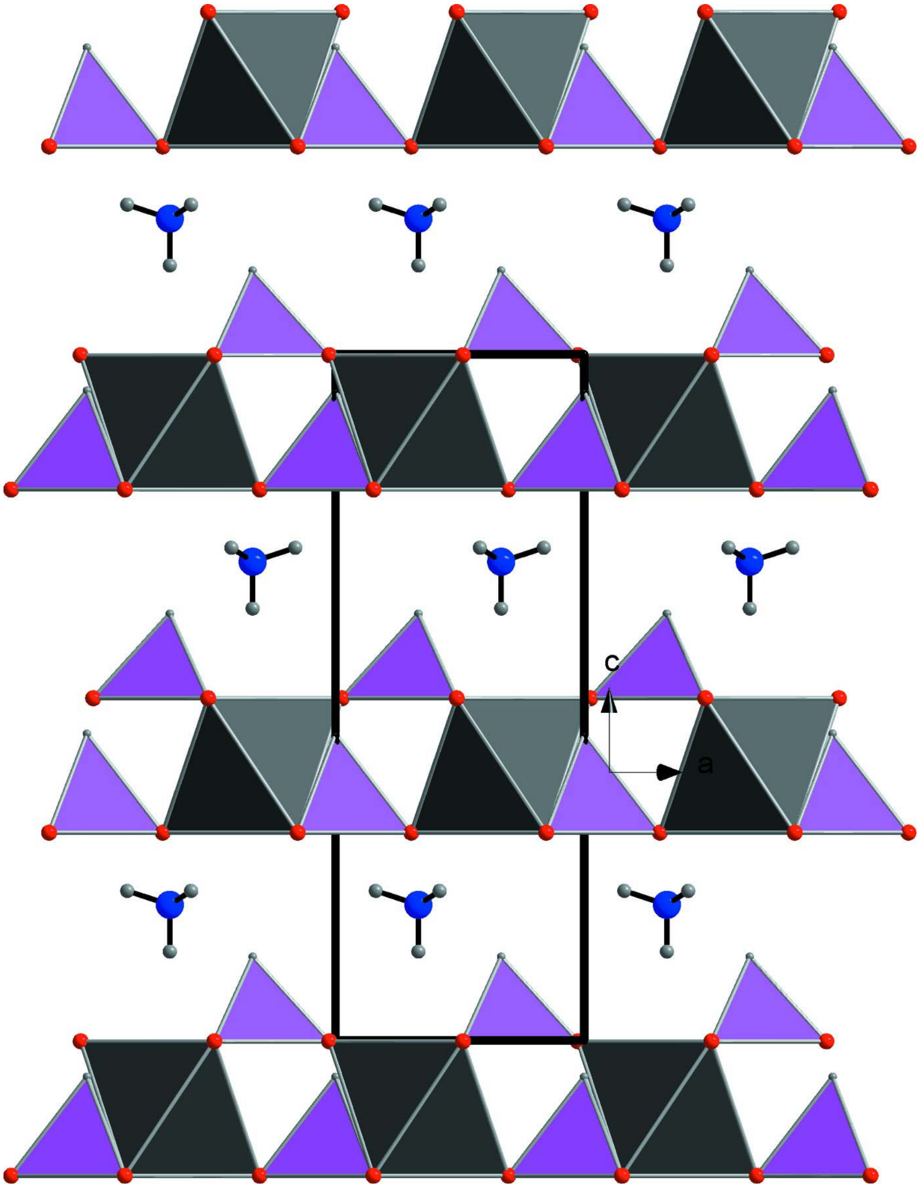

Figure 2

Projection along the [010] direction, showing the two-dimensional framework in $NH_4[In(HPO_3)_2]$.

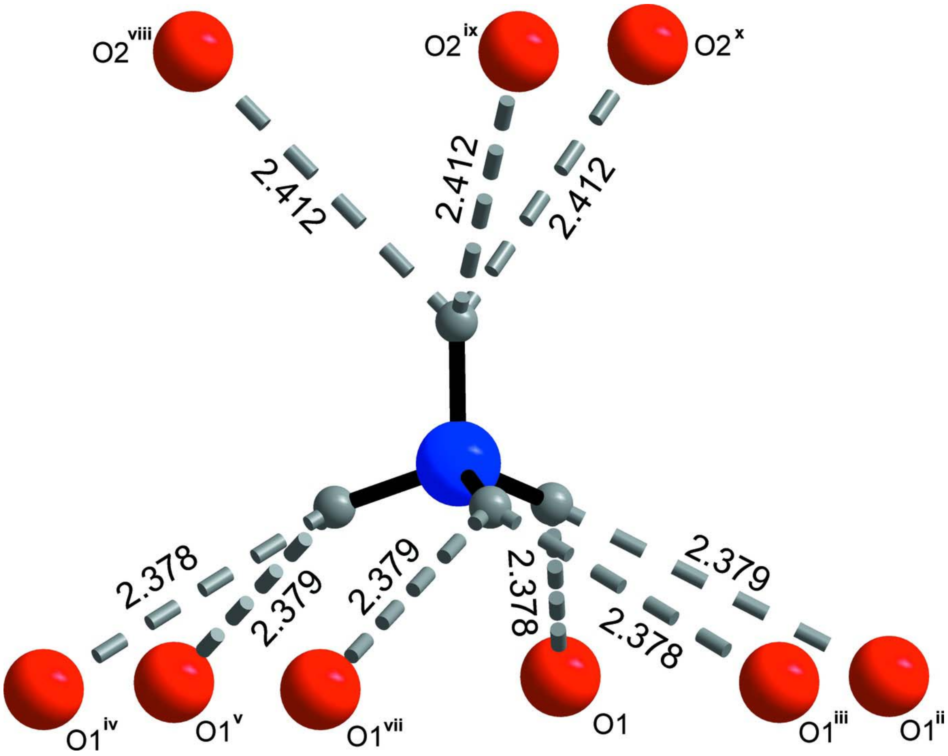

Figure 3

H-bonding arrangement between the ammonium cations and the host framework [symmetry codes: (ii) *-x* + *y* - 1, *-x*, *z*; (iii) *-y* - 1, *x-y*, *z*; (iv) *-x* + *y* - 1, *-x* - 1, *z*; (v) *-y*, *x-y*, *z*; (vii) *x* - 1, *y* - 1, *z*; (viii) *x-y*, *x*, -0.5 + *z*, (ix) *y* - 1, *-x* + *y* - 1, -0.5 + *z*; (*x*) *-x* - 1, *-y*, -0.5 + *z*].

Ammonium diphosphitoindate(III)

Crystal data

$NH_4[In(HPO_3)_2]$
$M_r = 292.82$
Hexagonal, $P6_3mc$
$a = 5.4705$ (1) Å
$c = 13.0895$ (4) Å
$V = 339.24$ (1) Å^3
$Z = 2$
$F(000) = 280$

$D_x = 2.867$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1590 reflections
$\theta = 2.9$–$42.1°$
$\mu = 3.93$ mm^{-1}
$T = 293$ K
Block, colourless
0.1 × 0.05 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD rotation images, thick slices scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min} = 0.66$, $T_{max} = 0.92$

7774 measured reflections
962 independent reflections
912 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 42.0°$, $\theta_{min} = 4.3°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.041$
$S = 1.26$
962 reflections
30 parameters
5 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
$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.0737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -1.39$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.092 (4)
Absolute structure: Flack (1983), 459 Friedel pairs
Absolute structure parameter: −0.01 (2)

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}
In1	−0.3333	0.3333	−0.5985	0.01029 (5)
P1	−0.6667	−0.3333	−0.47231 (7)	0.00954 (13)
P2	0.0000	0.0000	−0.65957 (6)	0.00968 (14)
O1	−0.15240 (16)	0.15240 (16)	−0.69716 (14)	0.0201 (3)
O2	−0.5126 (2)	−0.0252 (4)	−0.5013 (2)	0.0276 (4)
N1	−0.6667	−0.3333	−0.8024 (3)	0.0222 (7)
HP1	−0.6667	−0.3333	−0.378 (9)	0.027*
HP2	0.0000	0.0000	−0.553 (6)	0.027*
HN1	−0.5809 (18)	−0.162 (4)	−0.782 (3)	0.027*
HN2	−0.6667	−0.3333	−0.8705 (8)	0.027*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
In1	0.00741 (6)	0.00741 (6)	0.01606 (8)	0.00371 (3)	0.000	0.000
P1	0.00840 (19)	0.00840 (19)	0.0118 (3)	0.00420 (9)	0.000	0.000
P2	0.00826 (19)	0.00826 (19)	0.0125 (4)	0.00413 (9)	0.000	0.000
O1	0.0275 (7)	0.0275 (7)	0.0188 (6)	0.0240 (8)	−0.0001 (2)	0.0001 (2)
O2	0.0282 (7)	0.0120 (7)	0.0374 (9)	0.0060 (4)	0.0053 (4)	0.0106 (7)
N1	0.0232 (10)	0.0232 (10)	0.0203 (16)	0.0116 (5)	0.000	0.000

Geometric parameters (Å, º)

In1—O2^{i}	2.1226 (19)	P1—O2^{iii}	1.5082 (18)
In1—O2	2.1226 (19)	P1—O2	1.5082 (18)
In1—O2^{ii}	2.1226 (19)	P1—O2^{iv}	1.5082 (18)
In1—O1	2.1461 (17)	P2—O1^{v}	1.5255 (16)
In1—O1^{ii}	2.1461 (17)	P2—O1^{vi}	1.5255 (16)
In1—O1^{i}	2.1461 (17)	P2—O1	1.5255 (15)

O2^{i}—In1—O2	87.75 (10)	O2^{ii}—In1—O1^{i}	92.35 (6)
O2^{i}—In1—O2^{ii}	87.75 (10)	O1—In1—O1^{i}	87.55 (7)
O2—In1—O2^{ii}	87.75 (10)	O1^{ii}—In1—O1^{i}	87.55 (7)
O2^{i}—In1—O1	92.35 (6)	O2^{iii}—P1—O2	113.89 (9)
O2—In1—O1	92.35 (6)	O2^{iii}—P1—O2^{iv}	113.89 (9)
O2^{ii}—In1—O1	179.86 (9)	O2—P1—O2^{iv}	113.89 (9)
O2^{i}—In1—O1^{ii}	179.86 (9)	O1^{v}—P2—O1^{vi}	110.12 (7)
O2—In1—O1^{ii}	92.35 (6)	O1^{v}—P2—O1	110.12 (7)
O2^{ii}—In1—O1^{ii}	92.35 (6)	O1^{vi}—P2—O1	110.12 (7)
O1—In1—O1^{ii}	87.55 (7)	P2—O1—In1	124.21 (11)
O2^{i}—In1—O1^{i}	92.35 (6)	P1—O2—In1	157.74 (17)
O2—In1—O1^{i}	179.86 (10)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H*N*1···O1	0.86 (2)	2.38 (2)	3.066 (2)	138 (2)
N1—H*N*1···O1^{ii}	0.86 (2)	2.38 (2)	3.066 (2)	138 (2)
N1—H*N*2···O2^{vii}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)
N1—H*N*2···O2^{viii}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)
N1—H*N*2···O2^{ix}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)
N1—H*N*2···O2^{x}	0.89 (1)	2.41 (1)	3.109 (4)	135 (1)

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