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2,4,6-Triamino-1,3,5-triazine-1,3-dium aquapentafluoroaluminate

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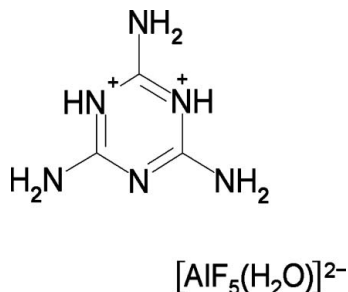
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{N}-\text{C}) = 0.004$ Å; R factor = 0.054; wR factor = 0.133; data-to-parameter ratio = 16.4.

The title compound, $(\text{C}_3\text{H}_8\text{N}_6)[\text{AlF}_5(\text{H}_2\text{O})]$, was obtained by solvothermal synthesis from the reaction of aluminium hydroxide, 1,3,5-triazine-2,4,6-triamine (melamine), aqueous HF and water at 323 K for 48 h. The structure consists of $[\text{AlF}_5(\text{H}_2\text{O})]^{2-}$ octahedra and diprotonated melaminium cations. Cohesion is ensured by a three-dimensional network of hydrogen bonds.

Related literature

For related literature, see: Adil, Ben Ali *et al.* (2006); Adil, Leblanc & Maisonneuve (2006); Farrugia (1999); Goreschnik *et al.* (2002, 2003); Rother *et al.* (1996, 1998); Schroder *et al.* (1993); Tang *et al.* (2001).



Experimental

Crystal data

$(\text{C}_3\text{H}_8\text{N}_6)[\text{AlF}_5(\text{H}_2\text{O})]$
 $M_r = 268.13$
 Monoclinic, $P2_1/c$
 $a = 7.571$ (2) Å
 $b = 8.823$ (2) Å
 $c = 13.484$ (5) Å
 $\beta = 105.53$ (3)°

$V = 867.8$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 298$ (2) K
 $0.20 \times 0.13 \times 0.08$ mm

Data collection

Siemens AED2 diffractometer
 Absorption correction: none
 2500 measured reflections
 2500 independent reflections

1441 reflections with $I > 2\sigma(I)$
 3 standard reflections
 frequency: 120 min
 intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.133$
 $S = 1.04$
 2500 reflections
 152 parameters
 2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1W}\cdots\text{N1}^{\text{i}}$	0.90 (4)	1.94 (5)	2.789 (3)	156 (5)
$\text{O1W}-\text{H2W}\cdots\text{F1}^{\text{ii}}$	0.90 (4)	1.63 (4)	2.515 (3)	169 (5)
$\text{N2}-\text{H2}\cdots\text{F4}^{\text{iii}}$	0.86	1.75	2.601 (3)	169
$\text{N3}-\text{H3}\cdots\text{F2}^{\text{iv}}$	0.86	2.11	2.871 (3)	148
$\text{N3}-\text{H3}\cdots\text{F3}^{\text{iv}}$	0.86	2.28	2.990 (3)	140
$\text{N3}-\text{H3}\cdots\text{F1}^{\text{iv}}$	0.86	2.52	2.953 (4)	112
$\text{N4}-\text{H4A}\cdots\text{F5}^{\text{v}}$	0.86	2.07	2.763 (3)	138
$\text{N4}-\text{H4B}\cdots\text{F2}^{\text{iii}}$	0.86	1.89	2.739 (3)	168
$\text{N5}-\text{H5A}\cdots\text{F3}$	0.86	2.06	2.837 (3)	151
$\text{N5}-\text{H5B}\cdots\text{F3}^{\text{iv}}$	0.86	2.02	2.804 (4)	151
$\text{N5}-\text{H5B}\cdots\text{F4}$	0.86	2.39	2.863 (3)	115
$\text{N6}-\text{H6A}\cdots\text{F1}^{\text{vi}}$	0.86	2.04	2.836 (4)	154
$\text{N6}-\text{H6B}\cdots\text{F2}^{\text{iv}}$	0.86	2.08	2.860 (4)	150

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

Data collection: *STADIA* (Stoe & Cie, 1998); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*, *enCIFer* (Version 1.2; Allen *et al.*, 2004) and *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2317).

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supporting information

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2,4,6-Triamino-1,3,5-triazine-1,3-dium aquapentafluoroaluminate

A. Cadiou, A. Hemon-Ribaud, M. Leblanc and V. Maisonneuve

S1. Comment

Numerous hybrid fluoroaluminates with linear or branched amines are reported; during the last five years more than 20 compounds were evidenced (Goreshnik *et al.*, 2002; Adil, Ben Ali *et al.*, 2006; Adil, Leblanc & Maisonneuve, 2006). At the opposite, only few hybrid fluoroaluminates with cyclic amines are known (Schroder *et al.*, 1993; Rother *et al.*, 1996; Rother *et al.*, 1998; Tang *et al.*, 2001; Goreshnik *et al.*, 2003). 1,3,5-triazine-2,4,6-triamine (melamine) with three primary amines, three tertiary amines and a conjugated planar configuration was selected. $(\text{C}_3\text{H}_8\text{N}_6)[\text{AlF}_5(\text{H}_2\text{O})]$ is synthesized and constitutes the first melamine templated fluoroaluminate.

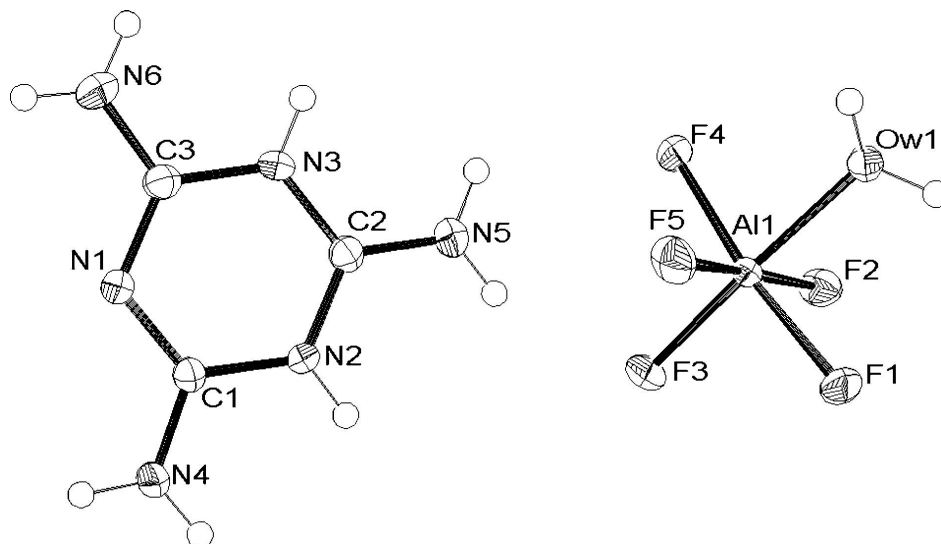
The structure is built up from isolated $[\text{AlF}_5(\text{H}_2\text{O})]^{2-}$ anions and diprotonated $(\text{C}_3\text{H}_8\text{N}_6)^{2+}$ cations (Fig. 1). A distortion of the aluminium coordination octahedron results from the presence of the water molecule: Al—F distances range from 1.758 (2) to 1.829 (2) Å and Al—O distance is 1.929 (3) Å. Melaminium cations are planar and two tertiary amines are protonated. C, N, H atomic positions are related by a pseudo two fold symmetry axis along the N1—C2—N5 direction. Hydrogen bonded octahedra form infinite inorganic chains along *b* axis (Fig. 2); the O1W—H2W \cdots F1 hydrogen bonds (2.51 Å) are short. Every melaminium cation is surrounded by five $[\text{AlF}_5(\text{H}_2\text{O})]$ octahedra (Fig. 3).

S2. Experimental

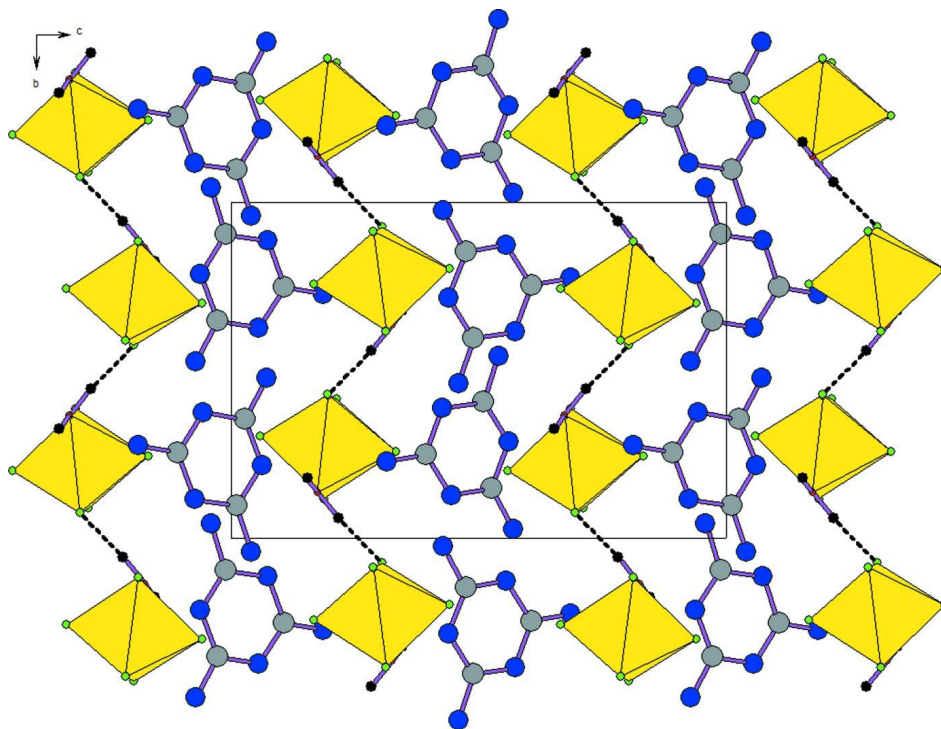
The title compound was prepared under hydrothermal conditions at 323 K for 48 h using Teflon-lined autoclaves from a started mixture of $\text{Al}(\text{OH})_3$ (Sochal), 1,3,5-triazine-2,4,6-triamine named melamine (Janssen chimica), HF aqueous solution (40%, Prolabo) and deionized water in the molar ratio 1:0.5:8.5:55.5. The resulting crystalline product was washed with water and dried in air. Needle crystals suitable for single-crystal X-ray diffraction were selected using an optical microscope.

S3. Refinement

The structure was solved by direct methods (*SHELXS86*) and refined with *SHELXL97*; these programs are included in *WinGX* package (Farrugia, 1999). Hydrogen atoms of amine cations were located applying geometrical constraints which imply equal distances and angles to the central atom (AFIX option). Hydrogen atoms of water molecules were found in difference Fourier maps and the O—H distances were constrained to be equal to 0.9 Å (*DFIX* option). H atoms were refined with an isotropic thermal parameters and non-hydrogen atoms were refined with anisotropic thermal factors. The maximum residual electron density peak is located at 0.46 Å from Al. Protonation takes place on the two over three tertiary amine groups.

**Figure 1**

View of the melaminium cation and $[\text{AlF}_5(\text{H}_2\text{O})]^{2-}$ anion with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

(100) projection of $(\text{C}_3\text{H}_8\text{N}_6) \cdot [\text{AlF}_5(\text{H}_2\text{O})]$ structure.

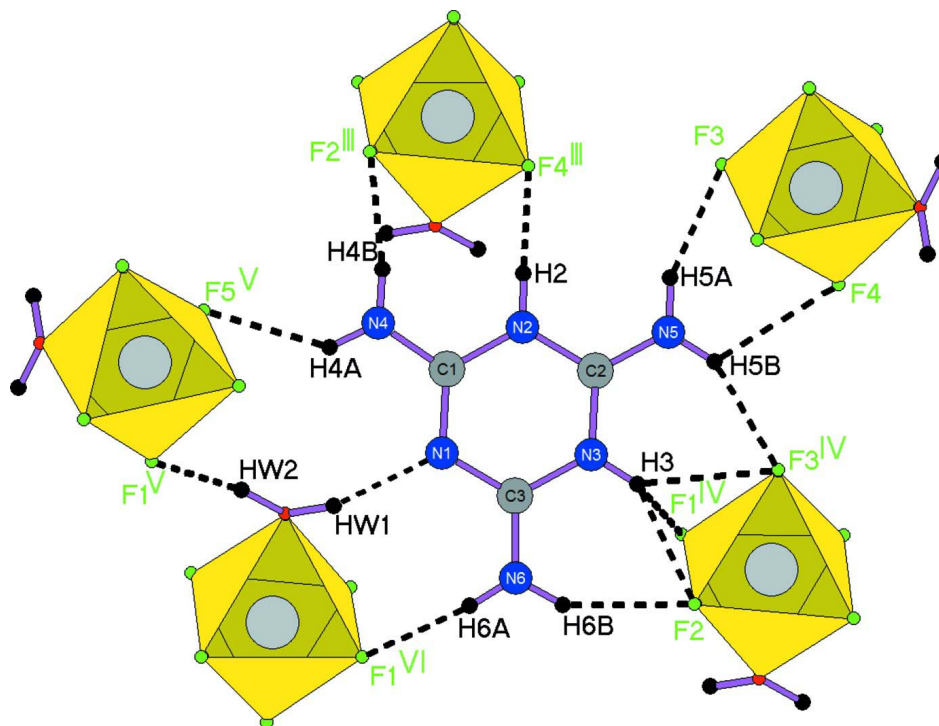


Figure 3

Network of hydrogen bonds between melaminium cations and $[\text{AlF}_5(\text{H}_2\text{O})]$ octahedra. [Symmetry codes: (iii) $1 - x, y - 1/2, 1/2 - z$; (iv) $1 - x, 1/2 + y, 1/2 - z$; (v) $1 - x, -y, -z$; (vi) $1 + x, 1/2 - y, z - 1/2$]

2,4,6-Triamino-1,3,5-triazine-1,3-dium aquapentafluoroaluminate

Crystal data

$(\text{C}_3\text{H}_8\text{N}_6)[\text{AlF}_5(\text{H}_2\text{O})]$

$M_r = 268.13$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 7.571 (2) \text{ \AA}$

$b = 8.823 (2) \text{ \AA}$

$c = 13.484 (5) \text{ \AA}$

$\beta = 105.53 (3)^\circ$

$V = 867.8 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 544$

$D_x = 2.052 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 28\text{--}32^\circ$

$\mu = 0.31 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Parallelepiped, colourless

$0.20 \times 0.13 \times 0.08 \text{ mm}$

Data collection

Siemens AED2
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$2\theta/\omega$ scans

2500 measured reflections

2500 independent reflections

1441 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.000$

$\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.8^\circ$

$h = -10 \rightarrow 10$

$k = 0 \rightarrow 12$

$l = 0 \rightarrow 18$

3 standard reflections every 120 min

intensity decay: 4%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.133$
 $S = 1.04$
 2500 reflections
 152 parameters
 2 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
 $w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.9389P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
All	0.2088 (1)	0.2232 (1)	0.30136 (7)	0.0163 (2)
F1	0.0457 (3)	0.0750 (2)	0.30467 (16)	0.0288 (5)
F2	0.2911 (3)	0.1978 (2)	0.44074 (14)	0.0251 (4)
F3	0.3778 (3)	0.0880 (2)	0.28702 (17)	0.0299 (5)
F4	0.3610 (3)	0.3839 (2)	0.31272 (16)	0.0267 (5)
F5	0.1237 (3)	0.2429 (2)	0.16732 (14)	0.0304 (5)
O1W	0.0310 (3)	0.3648 (3)	0.32584 (18)	0.0214 (5)
H1W	-0.062 (5)	0.324 (5)	0.346 (4)	0.062 (12)*
H2W	-0.007 (7)	0.444 (4)	0.284 (3)	0.062 (12)*
N1	0.7845 (4)	0.2143 (3)	-0.0619 (2)	0.0202 (6)
N2	0.6746 (4)	0.1144 (3)	0.0739 (2)	0.0195 (6)
H2	0.6499	0.0359	0.1056	0.023*
N3	0.6895 (4)	0.3729 (3)	0.0557 (2)	0.0203 (6)
H3	0.6714	0.4633	0.0748	0.024*
N4	0.7594 (4)	-0.0423 (3)	-0.0409 (2)	0.0232 (6)
H4A	0.7996	-0.0586	-0.0938	0.028*
H4B	0.7310	-0.1173	-0.0074	0.028*
N5	0.5822 (4)	0.2735 (3)	0.1861 (2)	0.0271 (6)
H5A	0.5543	0.1966	0.2181	0.033*
H5B	0.5664	0.3638	0.2063	0.033*
N6	0.8013 (4)	0.4736 (3)	-0.0717 (2)	0.0293 (7)
H6A	0.8446	0.4652	-0.1242	0.035*
H6B	0.7850	0.5619	-0.0486	0.035*
C1	0.7414 (4)	0.0960 (3)	-0.0113 (2)	0.0179 (6)

C2	0.6481 (4)	0.2534 (4)	0.1076 (2)	0.0191 (6)
C3	0.7602 (4)	0.3525 (4)	-0.0271 (2)	0.0199 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0209 (5)	0.0127 (4)	0.0176 (4)	-0.0002 (4)	0.0090 (3)	-0.0014 (4)
F1	0.0359 (13)	0.0199 (10)	0.0351 (11)	-0.0115 (9)	0.0175 (10)	-0.0075 (9)
F2	0.0330 (11)	0.0214 (10)	0.0204 (9)	0.0027 (8)	0.0063 (8)	0.0020 (8)
F3	0.0355 (13)	0.0191 (10)	0.0413 (12)	0.0089 (9)	0.0207 (10)	0.0013 (9)
F4	0.0292 (12)	0.0191 (9)	0.0379 (11)	-0.0069 (8)	0.0197 (10)	-0.0054 (9)
F5	0.0435 (13)	0.0312 (11)	0.0188 (9)	0.0044 (10)	0.0122 (9)	-0.0009 (8)
O1W	0.0240 (13)	0.0179 (11)	0.0251 (12)	0.0055 (10)	0.0113 (10)	0.0066 (9)
N1	0.0263 (14)	0.0171 (13)	0.0202 (13)	-0.0005 (11)	0.0114 (11)	0.0003 (11)
N2	0.0256 (15)	0.0133 (12)	0.0236 (13)	-0.0001 (11)	0.0134 (12)	0.0016 (10)
N3	0.0260 (15)	0.0125 (12)	0.0240 (13)	-0.0006 (10)	0.0097 (12)	-0.0026 (10)
N4	0.0354 (18)	0.0180 (13)	0.0204 (13)	0.0015 (12)	0.0152 (12)	-0.0003 (11)
N5	0.0340 (17)	0.0241 (14)	0.0288 (15)	-0.0016 (13)	0.0181 (13)	-0.0034 (13)
N6	0.0402 (19)	0.0190 (14)	0.0328 (16)	-0.0052 (13)	0.0166 (15)	0.0020 (12)
C1	0.0200 (16)	0.0181 (15)	0.0166 (14)	0.0008 (12)	0.0065 (12)	-0.0002 (12)
C2	0.0168 (15)	0.0205 (15)	0.0204 (14)	-0.0022 (12)	0.0056 (12)	-0.0025 (12)
C3	0.0192 (16)	0.0177 (15)	0.0228 (15)	-0.0005 (12)	0.0056 (13)	0.0006 (13)

Geometric parameters (Å, °)

Al1—F5	1.757 (2)	N3—C2	1.347 (4)
Al1—F3	1.797 (2)	N3—C3	1.374 (4)
Al1—F4	1.807 (2)	N3—H3	0.8600
Al1—F1	1.807 (2)	N4—C1	1.302 (4)
Al1—F2	1.829 (2)	N4—H4A	0.8600
Al1—O1W	1.929 (2)	N4—H4B	0.8600
O1W—H1W	0.90 (4)	N5—C2	1.299 (4)
O1W—H2W	0.90 (4)	N5—H5A	0.8600
N1—C1	1.334 (4)	N5—H5B	0.8600
N1—C3	1.337 (4)	N6—C3	1.304 (4)
N2—C2	1.342 (4)	N6—H6A	0.8600
N2—C1	1.383 (4)	N6—H6B	0.8600
N2—H2	0.8600		
F5—Al1—F3	91.76 (11)	C2—N3—H3	119.5
F5—Al1—F4	93.42 (11)	C3—N3—H3	119.5
F3—Al1—F4	94.23 (10)	C1—N4—H4A	120.0
F5—Al1—F1	91.84 (11)	C1—N4—H4B	120.0
F3—Al1—F1	91.90 (10)	H4A—N4—H4B	120.0
F4—Al1—F1	171.80 (10)	C2—N5—H5A	120.0
F5—Al1—F2	177.98 (12)	C2—N5—H5B	120.0
F3—Al1—F2	88.45 (11)	H5A—N5—H5B	120.0
F4—Al1—F2	88.57 (10)	C3—N6—H6A	120.0

F1—A11—F2	86.15 (10)	C3—N6—H6B	120.0
F5—A11—O1W	91.80 (11)	H6A—N6—H6B	120.0
F3—A11—O1W	176.37 (11)	N4—C1—N1	121.1 (3)
F4—A11—O1W	86.32 (10)	N4—C1—N2	117.1 (3)
F1—A11—O1W	87.23 (10)	N1—C1—N2	121.8 (3)
F2—A11—O1W	87.97 (10)	N5—C2—N2	121.7 (3)
H1W—O1W—H2W	111 (4)	N5—C2—N3	120.7 (3)
C1—N1—C3	117.3 (3)	N2—C2—N3	117.6 (3)
C2—N2—C1	120.6 (3)	N6—C3—N1	120.9 (3)
C2—N2—H2	119.7	N6—C3—N3	117.4 (3)
C1—N2—H2	119.7	N1—C3—N3	121.7 (3)
C2—N3—C3	121.0 (3)		

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1W \cdots N1 ⁱ	0.90 (4)	1.94 (5)	2.789 (3)	156 (5)
O1W—H2W \cdots F1 ⁱⁱ	0.90 (4)	1.63 (4)	2.515 (3)	169 (5)
N2—H2 \cdots F4 ⁱⁱⁱ	0.86	1.75	2.601 (3)	169
N3—H3 \cdots F2 ^{iv}	0.86	2.11	2.871 (3)	148
N3—H3 \cdots F3 ^{iv}	0.86	2.28	2.990 (3)	140
N3—H3 \cdots F1 ^{iv}	0.86	2.52	2.953 (4)	112
N4—H4A \cdots F5 ^v	0.86	2.07	2.763 (3)	138
N4—H4B \cdots F2 ⁱⁱⁱ	0.86	1.89	2.739 (3)	168
N5—H5A \cdots F3	0.86	2.06	2.837 (3)	151
N5—H5B \cdots F3 ^{iv}	0.86	2.02	2.804 (4)	151
N5—H5B \cdots F4	0.86	2.39	2.863 (3)	115
N6—H6A \cdots F1 ^{vi}	0.86	2.04	2.836 (4)	154
N6—H6B \cdots F2 ^{iv}	0.86	2.08	2.860 (4)	150

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