Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Melaminium perchlorate monohydrate

Min Min Zhao* and Ping Ping Shi

Ordered Matter Science Research Center, College of Chemistry and Chemical, Engineering, Southeast University, Nanjing 211189, People's Republic of China
Correspondence e-mail: zmmzyahfdzg@126.com

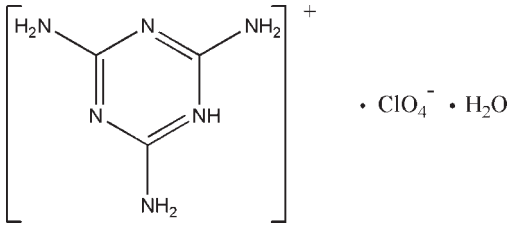
Received 24 April 2010; accepted 19 May 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(N–C) = 0.003 Å; R factor = 0.031; wR factor = 0.091; data-to-parameter ratio = 12.6.

In the title hydrated salt, 2,4,6-triamino-1,3,5-triazin-1-ium perchlorate monohydrate, $C_3H_7N_6^+\cdot ClO_4^-\cdot H_2O$, the constituents are linked *via* hydrogen bonds of the O—H···O, N—H···O, N—H···N and N—H···Cl types. All the H atoms of the melaminium cation are involved in the hydrogen bonds. The melaminium residues are interconnected by four N—H···N hydrogen bonds, forming chains parallel to (111). The ribbons are interconnected by other hydrogen bonds as well as by π–π interactions [centroid–centroid distance = 3.8097 (7) Å].

Related literature

For similar organic acid–base compounds, see: Martin & Pinkerton (1995); Perpétuo & Janczak (2006). For their ferroelectric properties, see: Hang *et al.* (2009), Li *et al.* (2008). For impedance studies, see; Uthrakumar *et al.* (2008).



Experimental

Crystal data

$C_3H_7N_6^+\cdot ClO_4^-\cdot H_2O$
M_r = 244.61
Triclinic, $P\overline{1}$
a = 5.654 (4) Å
b = 7.553 (7) Å
c = 11.893 (10) Å
α = 102.72 (4)°
β = 94.58 (3)°
γ = 110.78 (2)°
V = 456.1 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 293 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.916, T_{max} = 0.916
4902 measured reflections
2051 independent reflections
1719 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.091
S = 0.90
2051 reflections
163 parameters
10 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O4	0.85 (1)	2.16 (1)	2.960 (3)	158 (2)
O5—H5B···O5^{i}	0.85 (1)	2.64 (2)	3.081 (3)	114 (2)
O5—H5A···O3^{ii}	0.84 (1)	2.16 (1)	2.883 (3)	144 (2)
O5—H5A···O2^{iii}	0.84 (1)	2.38 (2)	2.867 (3)	117 (1)
N1—H1B···O1^{iv}	0.86 (1)	2.19 (1)	2.890 (2)	139 (2)
N1—H1B···O5^{iv}	0.86 (1)	2.48 (2)	3.146 (3)	135 (2)
N1—H1A···N6^{v}	0.86 (1)	2.14 (1)	2.998 (3)	178 (2)
N2—H2B···O4^{ii}	0.86 (1)	2.31 (1)	3.086 (3)	151 (2)
N2—H2B···O2^{vi}	0.86 (1)	2.56 (2)	3.108 (3)	123 (2)
N2—H2A···O2^{iii}	0.86 (1)	2.20 (1)	2.979 (3)	150 (2)
N2—H2A···Cl1^{iii}	0.86 (1)	2.99 (1)	3.792 (3)	157 (2)
N3—H3B···N5^{vii}	0.85 (1)	2.23 (1)	3.084 (3)	173 (2)
N3—H3A···O1^{viii}	0.86 (1)	2.19 (1)	3.029 (3)	168 (2)
N4—H4A···O5^{iv}	0.84 (1)	1.90 (1)	2.723 (2)	168 (2)

Symmetry codes: (i) $-x+3, -y+2, -z+2$; (ii) $-x+2, -y+2, -z+2$; (iii) $x, y-1, z$; (iv) $x-1, y, z$; (v) $-x+1, -y+2, -z+1$; (vi) $x-1, y-1, z$; (vii) $-x+2, -y+1, -z+1$; (viii) $-x+2, -y+2, -z+1$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

The authors are grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2764).

References

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Hang, T., Fu, D. W., Ye, Q. & Xiong, R. G. (2009). *Cryst. Growth Des.* **5**, 2026–2029.
Li, X. Z., Qu, Z. R. & Xiong, R. G. (2008). *Chin. J. Chem.* **11**, 1959–1962.
Martin, A. & Pinkerton, A. A. (1995). *Acta Cryst.* C**51**, 2174–2177.
Perpétuo, G. J. & Janczak, J. (2006). *Acta Cryst.* C**62**, o372–o375.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Uthrakumar, R., Vesta, C., Raj, C. J., Dinakaran, S., Dhas, R. C. & Das, S. J. (2008). *Cryst. Res. Technol.* **43**, 428–432.

supporting information

Acta Cryst. (2010). E**66**, o1463 [https://doi.org/10.1107/S160053681001857X]

Melaminium perchlorate monohydrate

Min Min Zhao and Ping Ping Shi

S1. Comment

The melamine molecule and its organic and inorganic complexes or salts were widely researched by ancient Chemists (Martin *et al.* 1995; Perpétuo & Janczak, 2006). This study is a part of systematic investigation of dielectric ferroelectric materials, including organic ligands (Li *et al.*, 2008), metal-organic coordination compounds (Hang *et al.*, 2009) and organic inorganic hybrid. Melaminium monoperchlorate monohydrate has no dielectric disuniform from 90 K to 430 K, (m.p. > 470 K).

The asymmetric unit of the title compound is composed of cationic ($C_3H_7N_6^+$), anionic (ClO_4^-) and one dissociative water molecular(Fig 1). The melaminium cation is protonated at only one melamine ring N atom. The six-membered aromatic ring of melaminium residues exhibit distortions from the regular hexagonal form. The internal C—N—C angle at the protonated N atom(119.41 (14) °) is greater than the other two C—N—C angles of the ring(115.45 (14) ° and 115.48 (14) °) and the internal N—C—N angles involving the nonprotonated ring N atoms (126.09 (15) °) are obviously greater than those containing protonated and non-protonated N atoms(121.65 (15) ° and 121.88 (15) °).

Fig. 2 shows a view down the *c* axis. The melaminium cations are interconnected by four N—H···N hydrogen bonds, forming ribbons parallel to (1 1 1). The ribbons are interconnected by other hydrogen bonds as well as by π-electron ring - π-electron ring interactions with the distance between the centroids of the neighbour melaminium rings (1-*x*,1-*y*,1-*z*) equal to 3.8097 Å. Melamine and its derivatives and organic and inorganic complexes or salts can develop well defined non-covalent supramolecular architectures *via* multiple hydrogen bonds. The hydrogen bonds are summarized in Tab. 1. The H atom of the protonated ring N atom (H4a) is donated to the water molecule, being involved in a strong N—H···O hydrogen bond. The other amine H atoms are involved in N—H···O, N—H···N and N—H···Cl hydrogen bonds. ClO_4^- anions take part in electrostatics equilibrium with the melaminium cations. They are also involved in N—H···O, O—H···O, and N—H···Cl hydrogen bonds.

S2. Experimental

Single crystals of melaminium monoperchlorate monohydrate are prepared by slow evaporation at room temperature of an water solution of melamine and perchloric acid.

Dielectric studies (capacitance and dielectric loss measurements) were performed on powder samples which have been pressed into tablets on the surfaces of which a conducting carbon glue was deposited. The automatic impedance TongHui2828 Analyzer has been used (Uthrakumar *et al.*, 2008). In the measured temperature ranges (90 K to 450 K, m.p. > 470 K), the title structure showed no dielectric disuniform.

S3. Refinement

All the hydrogens were discernible in the difference electron density maps. The positions of the H atoms of the melamine cations were refined using a riding model with N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(N). The coordinates if the water

hydrogens have been refined under restrains 0.84 Å; U_{iso}(H) = 1.2U_{eq}(O). (The constrained and the restrained values fit well to the trial refinement with the freely refined hydrogen parameters.)

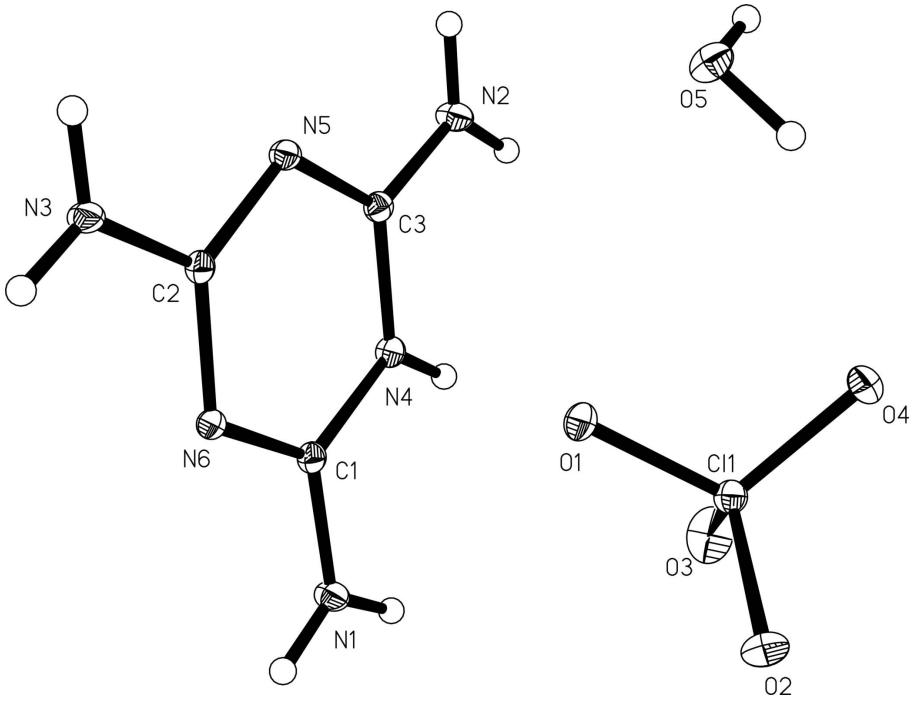


Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

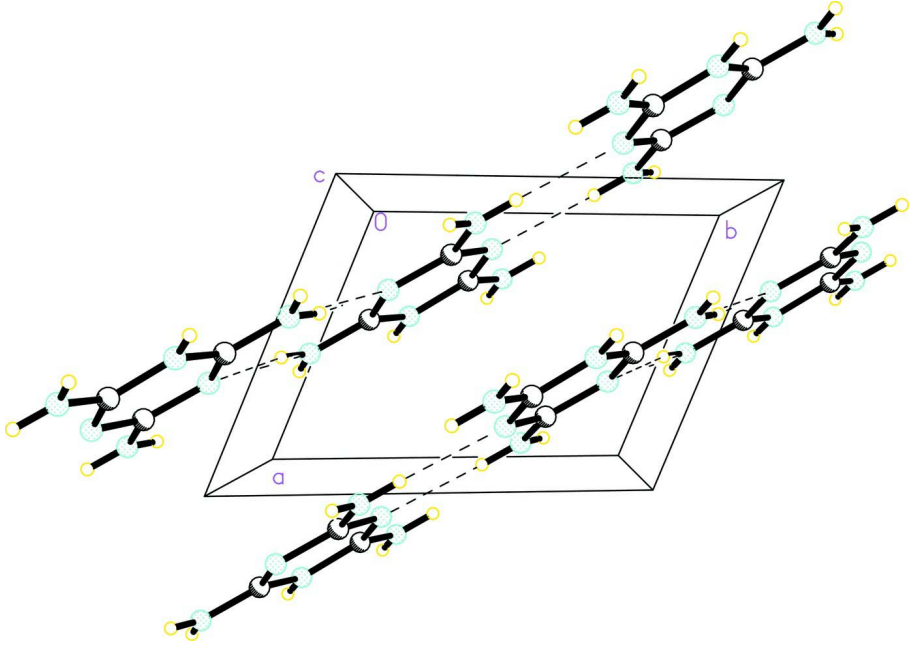


Figure 2

A view of the packing of the title compound, stacking along the *c* axis. Dashed lines indicate hydrogen bonds.

2,4,6-triamino-1,3,5-triazin-1-ium perchlorate monohydrate

Crystal data

$C_3H_7N_6^+·ClO_4^-·H_2O$
$M_r = 244.61$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.654$ (4) Å
$b = 7.553$ (7) Å
$c = 11.893$ (10) Å
$\alpha = 102.72$ (4)°
$\beta = 94.58$ (3)°
$\gamma = 110.78$ (2)°
$V = 456.1$ (7) Å^3
$Z = 2$
$F(000) = 252$
$D_x = 1.781$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1388 reflections
$\theta = 3.0$–$27.6°$
$\mu = 0.44$ mm^{-1}
$T = 293$ K
Prism, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
CCD_Profile_fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.916$, $T_{max} = 0.916$
4902 measured reflections
2051 independent reflections
1719 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.091$
$S = 0.90$
2051 reflections
163 parameters
10 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
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.0106P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

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. 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}
C1	0.5601 (3)	0.8552 (2)	0.63004 (14)	0.0133 (3)
C2	0.7940 (3)	0.7067 (2)	0.53001 (14)	0.0129 (3)

C3	0.7094 (3)	0.6425 (2)	0.70349 (14)	0.0130 (3)
O1	1.0855 (2)	1.12497 (17)	0.75979 (9)	0.0166 (3)
O2	1.1733 (2)	1.45744 (17)	0.84904 (11)	0.0201 (3)
O3	0.8606 (3)	1.2106 (2)	0.90661 (11)	0.0274 (3)
O4	1.2993 (3)	1.26696 (19)	0.95543 (11)	0.0244 (3)
O5	1.3200 (3)	0.87257 (18)	0.88354 (10)	0.0196 (3)
H5B	1.346 (4)	0.9895 (10)	0.9193 (14)	0.023*
H5A	1.259 (4)	0.7975 (19)	0.9260 (13)	0.023*
Cl1	1.10439 (7)	1.26476 (5)	0.86874 (3)	0.01324 (13)
N1	0.4347 (3)	0.9749 (2)	0.64603 (13)	0.0172 (3)
H1B	0.357 (3)	0.990 (3)	0.7040 (12)	0.021*
H1A	0.409 (4)	1.034 (3)	0.5952 (13)	0.021*
N2	0.7213 (3)	0.5547 (2)	0.78757 (13)	0.0169 (3)
H2B	0.657 (4)	0.576 (3)	0.8500 (11)	0.020*
H2A	0.818 (3)	0.489 (3)	0.7840 (16)	0.020*
N3	0.8987 (3)	0.6748 (2)	0.43553 (13)	0.0162 (3)
H3B	0.975 (3)	0.594 (2)	0.4283 (17)	0.019*
H3A	0.890 (4)	0.741 (3)	0.3865 (13)	0.019*
N4	0.5745 (3)	0.7610 (2)	0.71408 (11)	0.0131 (3)
H4A	0.500 (3)	0.784 (3)	0.7707 (11)	0.016*
N5	0.8221 (3)	0.61161 (19)	0.61130 (11)	0.0131 (3)
N6	0.6663 (3)	0.8296 (2)	0.53570 (11)	0.0129 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0126 (7)	0.0127 (7)	0.0130 (8)	0.0043 (6)	0.0003 (6)	0.0015 (6)
C2	0.0130 (7)	0.0121 (7)	0.0118 (8)	0.0041 (6)	0.0006 (6)	0.0012 (6)
C3	0.0115 (7)	0.0123 (7)	0.0136 (8)	0.0036 (6)	0.0014 (6)	0.0024 (6)
O1	0.0217 (6)	0.0173 (6)	0.0111 (6)	0.0095 (5)	0.0030 (5)	0.0008 (5)
O2	0.0241 (7)	0.0143 (6)	0.0249 (7)	0.0091 (5)	0.0061 (5)	0.0073 (5)
O3	0.0210 (7)	0.0342 (8)	0.0240 (7)	0.0048 (6)	0.0153 (6)	0.0072 (6)
O4	0.0325 (8)	0.0254 (7)	0.0162 (6)	0.0170 (6)	−0.0064 (5)	0.0012 (5)
O5	0.0282 (7)	0.0153 (6)	0.0185 (6)	0.0093 (5)	0.0111 (5)	0.0067 (5)
Cl1	0.0151 (2)	0.0145 (2)	0.0113 (2)	0.00664 (15)	0.00399 (14)	0.00364 (15)
N1	0.0233 (8)	0.0230 (8)	0.0138 (7)	0.0167 (6)	0.0076 (6)	0.0069 (6)
N2	0.0202 (8)	0.0240 (8)	0.0151 (7)	0.0145 (6)	0.0089 (6)	0.0099 (6)
N3	0.0240 (8)	0.0194 (7)	0.0136 (7)	0.0151 (6)	0.0082 (6)	0.0077 (6)
N4	0.0151 (7)	0.0163 (7)	0.0102 (7)	0.0079 (6)	0.0060 (5)	0.0039 (6)
N5	0.0154 (7)	0.0146 (7)	0.0119 (7)	0.0079 (6)	0.0040 (5)	0.0044 (5)
N6	0.0159 (7)	0.0145 (6)	0.0103 (7)	0.0084 (6)	0.0028 (5)	0.0029 (5)

Geometric parameters (Å, º)

C1—N6	1.324 (2)	O3—Cl1	1.4318 (16)
C1—N1	1.325 (2)	O4—Cl1	1.4406 (16)
C1—N4	1.362 (2)	O5—H5B	0.845 (5)
C2—N3	1.327 (2)	O5—H5A	0.843 (5)

C2—N5	1.356 (2)	N1—H1B	0.855 (5)
C2—N6	1.357 (2)	N1—H1A	0.860 (5)
C3—N2	1.325 (2)	N2—H2B	0.861 (5)
C3—N5	1.329 (2)	N2—H2A	0.859 (5)
C3—N4	1.360 (2)	N3—H3B	0.854 (5)
O1—Cl1	1.4493 (16)	N3—H3A	0.855 (5)
O2—Cl1	1.4446 (18)	N4—H4A	0.840 (5)
N6—C1—N1	120.73 (15)	O2—Cl1—O1	108.79 (9)
N6—C1—N4	121.88 (15)	C1—N1—H1B	123.3 (14)
N1—C1—N4	117.39 (15)	C1—N1—H1A	123.2 (14)
N3—C2—N5	116.85 (15)	H1B—N1—H1A	113.2 (19)
N3—C2—N6	117.06 (15)	C3—N2—H2B	122.9 (13)
N5—C2—N6	126.09 (15)	C3—N2—H2A	117.4 (13)
N2—C3—N5	120.63 (15)	H2B—N2—H2A	118.9 (18)
N2—C3—N4	117.70 (15)	C2—N3—H3B	119.0 (13)
N5—C3—N4	121.65 (15)	C2—N3—H3A	116.9 (13)
H5B—O5—H5A	109.5 (11)	H3B—N3—H3A	124.0 (19)
O3—Cl1—O4	110.66 (10)	C3—N4—C1	119.41 (14)
O3—Cl1—O2	109.04 (8)	C3—N4—H4A	124.6 (13)
O4—Cl1—O2	109.67 (9)	C1—N4—H4A	116.0 (13)
O3—Cl1—O1	109.34 (9)	C3—N5—C2	115.48 (14)
O4—Cl1—O1	109.31 (9)	C1—N6—C2	115.45 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*B*···O4	0.85 (1)	2.16 (1)	2.960 (3)	158 (2)
O5—H5*B*···O5^{i}	0.85 (1)	2.64 (2)	3.081 (3)	114 (2)
O5—H5*A*···O3^{ii}	0.84 (1)	2.16 (1)	2.883 (3)	144 (2)
O5—H5*A*···O2^{iii}	0.84 (1)	2.38 (2)	2.867 (3)	117 (1)
N1—H1*B*···O1^{iv}	0.86 (1)	2.19 (1)	2.890 (2)	139 (2)
N1—H1*B*···O5^{iv}	0.86 (1)	2.48 (2)	3.146 (3)	135 (2)
N1—H1*A*···N6^{v}	0.86 (1)	2.14 (1)	2.998 (3)	178 (2)
N2—H2*B*···O4^{ii}	0.86 (1)	2.31 (1)	3.086 (3)	151 (2)
N2—H2*B*···O2^{vi}	0.86 (1)	2.56 (2)	3.108 (3)	123 (2)
N2—H2*A*···O2^{iii}	0.86 (1)	2.20 (1)	2.979 (3)	150 (2)
N2—H2*A*···Cl1^{iii}	0.86 (1)	2.99 (1)	3.792 (3)	157 (2)
N3—H3*B*···N5^{vii}	0.85 (1)	2.23 (1)	3.084 (3)	173 (2)
N3—H3*A*···O1^{viii}	0.86 (1)	2.19 (1)	3.029 (3)	168 (2)
N4—H4*A*···O5^{iv}	0.84 (1)	1.90 (1)	2.723 (2)	168 (2)

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