

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

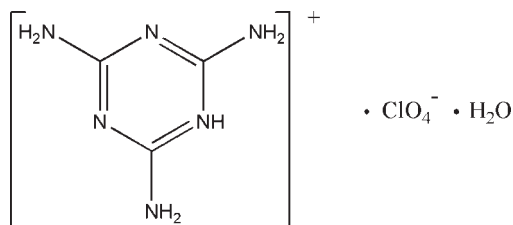
Received 24 April 2010; accepted 19 May 2010

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{N}-\text{C}) = 0.003$ 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, $\text{C}_3\text{H}_7\text{N}_6^+\cdot\text{ClO}_4^-\cdot\text{H}_2\text{O}$, the constituents are linked *via* hydrogen bonds of the $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{Cl}$ types. All the H atoms of the melaminium cation are involved in the hydrogen bonds. The melaminium residues are interconnected by four $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming chains parallel to (111). The ribbons are interconnected by other hydrogen bonds as well as by $\pi-\pi$ 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

$\text{C}_3\text{H}_7\text{N}_6^+\cdot\text{ClO}_4^-\cdot\text{H}_2\text{O}$
 $M_r = 244.61$
 Triclinic, $P\bar{1}$
 $a = 5.654(4)$ Å
 $b = 7.553(7)$ Å
 $c = 11.893(10)$ Å
 $\alpha = 102.72(4)^\circ$
 $\beta = 94.58(3)^\circ$

$\gamma = 110.78(2)^\circ$
 $V = 456.1(7)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.44$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.20 \times 0.20$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

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
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

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

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supplementary materials

Acta Cryst. (2010). E66, o1463 [doi:10.1107/S160053681001857X]

Melaminium perchlorate monohydrate

M. M. Zhao and P. P. Shi

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 monopерchlorate 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.

Experimental

Single crystals of melaminium monopерchlorate 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.

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The coordinates of the water hydrogens have been refined under restraints 0.84 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. (The constrained and the restrained values fit well to the trial refinement with the freely refined hydrogen parameters.)

Figures

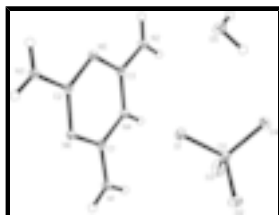


Fig. 1. The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 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

$\text{C}_3\text{H}_7\text{N}_6^+\cdot\text{ClO}_4^-\cdot\text{H}_2\text{O}$

$M_r = 244.61$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 5.654(4)$ Å

$b = 7.553(7)$ Å

$c = 11.893(10)$ Å

$\alpha = 102.72(4)^\circ$

$\beta = 94.58(3)^\circ$

$\gamma = 110.78(2)^\circ$

$V = 456.1(7)$ Å³

$Z = 2$

$F(000) = 252$

$D_x = 1.781$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1388 reflections

$\theta = 3.0\text{--}27.6^\circ$

$\mu = 0.44$ mm⁻¹

$T = 293$ K

Prism, colorless

$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku SCXmini
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: 28.5714 pixels mm⁻¹

2051 independent reflections

1719 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.0^\circ$

CCD_Profile_fitting scans $h = -7 \rightarrow 7$
 Absorption correction: multi-scan $k = -9 \rightarrow 9$
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.916$, $T_{\max} = 0.916$ $l = -15 \rightarrow 14$
 4902 measured reflections

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.091$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.90$	$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.0106P]$
2051 reflections	where $P = (F_o^2 + 2F_c^2)/3$
163 parameters	$(\Delta/\sigma)_{\max} = 0.001$
10 restraints	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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)

supplementary materials

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 (\AA^2)

	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)
C11	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 (\AA , $^\circ$)

C1—N6	1.324 (2)	O3—C11	1.4318 (16)
C1—N1	1.325 (2)	O4—C11	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—C11	1.4493 (16)	N3—H3A	0.855 (5)
O2—C11	1.4446 (18)	N4—H4A	0.840 (5)
N6—C1—N1	120.73 (15)	O2—C11—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—C11—O4	110.66 (10)	C3—N4—C1	119.41 (14)
O3—C11—O2	109.04 (8)	C3—N4—H4A	124.6 (13)
O4—C11—O2	109.67 (9)	C1—N4—H4A	116.0 (13)
O3—C11—O1	109.34 (9)	C3—N5—C2	115.48 (14)
O4—C11—O1	109.31 (9)	C1—N6—C2	115.45 (14)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5B \cdots O4	0.85 (1)	2.16 (1)	2.960 (3)	158.(2)
O5—H5B \cdots O5 ⁱ	0.85 (1)	2.64 (2)	3.081 (3)	114.(2)
O5—H5A \cdots O3 ⁱⁱ	0.84 (1)	2.16 (1)	2.883 (3)	144.(2)
O5—H5A \cdots O2 ⁱⁱⁱ	0.84 (1)	2.38 (2)	2.867 (3)	117.(1)
N1—H1B \cdots O1 ^{iv}	0.86 (1)	2.19 (1)	2.890 (2)	139.(2)
N1—H1B \cdots O5 ^{iv}	0.86 (1)	2.48 (2)	3.146 (3)	135.(2)
N1—H1A \cdots N6 ^v	0.86 (1)	2.14 (1)	2.998 (3)	178.(2)
N2—H2B \cdots O4 ⁱⁱ	0.86 (1)	2.31 (1)	3.086 (3)	151.(2)
N2—H2B \cdots O2 ^{vi}	0.86 (1)	2.56 (2)	3.108 (3)	123.(2)
N2—H2A \cdots O2 ⁱⁱⁱ	0.86 (1)	2.20 (1)	2.979 (3)	150.(2)
N2—H2A \cdots C11 ⁱⁱⁱ	0.86 (1)	2.99 (1)	3.792 (3)	157.(2)
N3—H3B \cdots N5 ^{vii}	0.85 (1)	2.23 (1)	3.084 (3)	173.(2)
N3—H3A \cdots O1 ^{viii}	0.86 (1)	2.19 (1)	3.029 (3)	168.(2)
N4—H4A \cdots 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) $-x+2, -y+2, -z+1$.

Fig. 1

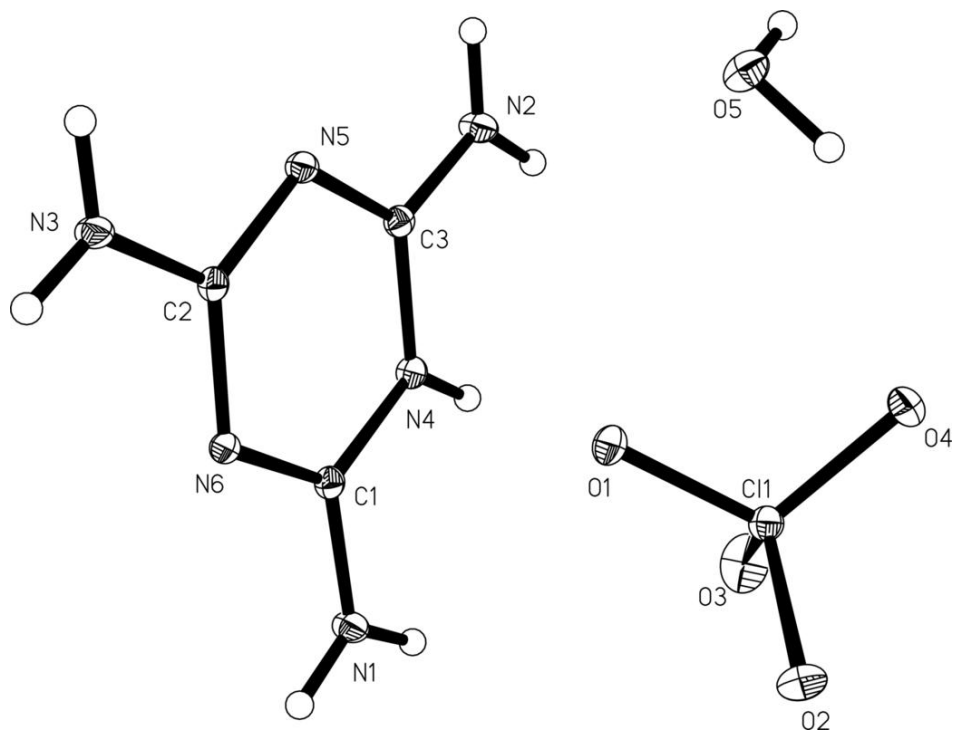


Fig. 2

