



Crystal structure and Hirshfeld surface analysis of 2,4-diamino-6-methyl-1,3,5-triazin-1-ium trichloroacetate monohydrate

Ramalingam Sangeetha,^a Kasthuri Balasubramani,^{a*} Kaliyaperumal Thanigaimani^b and Savaridasson Jose Kavitha^c

Received 17 April 2018

Accepted 5 June 2018

Edited by G. Smith, Queensland University of Technology, Australia

Keywords: crystal structure; triazinium cation; trichloroacetate anion; three-dimensional hydrogen-bonded supramolecular framework; Hirshfeld surface analysis.

CCDC reference: 1587723

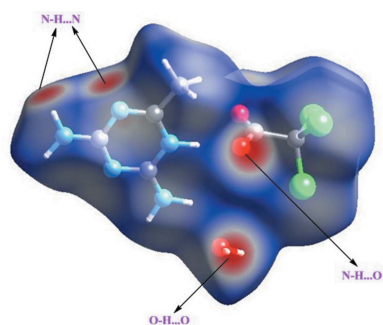
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Chemistry, Governemnt Arts College (Autonomous), Karur 639 005, Tamil Nadu, India, ^bDepartment of Chemistry, Government Arts College, Thiruchirappalli 620 022, Tamil Nadu, India, and ^cDepartment of Chemistry, Mother Teresa Womens University, Kodaikanal 624 102, Tamil Nadu, India. *Correspondence e-mail: manavaibala@gmail.com

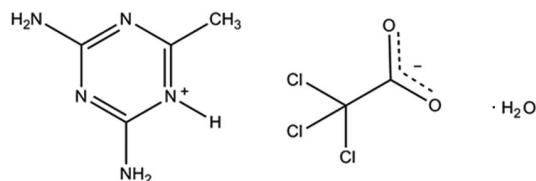
The asymmetric unit of the title molecular salt, $C_4H_8N_5^+ \cdot C_2Cl_3O_2^- \cdot H_2O$, comprises a 2,4-diamino-6-methyl-1,3,5-triazin-1-ium cation, a trichloroacetate anion and a water molecule of solvation. The protonated N atom of the cation forms a hydrogen bond with a carboxyl O atom of the anion, which also acts as a hydrogen-atom acceptor with the water molecule. The cations form centrosymmetric dimeric units through $R_2^2(8)$ N—H...N bond pairs and are extended into zigzag chains along the *c*-axis direction, also through similar cyclic $R_2^2(8)$ dual N—H...N hydrogen-bonding interactions. The water molecule acts as a dual acceptor forming N—H...O hydrogen bonds between the amine groups of the cations, forming cyclic $R_3^3(8)$ motifs. The second H atom of the water molecule also acts as a donor in an O—H...O hydrogen bond with the second carboxyl O atom, linking the chains along the *b*-axis direction. These interactions give rise to an overall three-dimensional supramolecular structure. A Hirshfeld surface analysis was employed in order to study the intermolecular interactions.

1. Chemical context

Triazine heterocyclic π -conjugated structures are attractive owing to the chemical flexibility of their systems and have many applications in medicinal chemistry, materials science and organic synthesis (Boesveld & Lappert, 1997; Boesveld *et al.*, 1999; Reid *et al.*, 2011). 1,3,5-Triazine derivatives represent an important class of compounds because of their potential to be biologically active. They are known to be anti-protozoal agents (Baliani *et al.*, 2005), anticancer agents (Menicagli *et al.*, 2004), estrogen receptor modulators (Henke *et al.*, 2002), anti-malarials (Agarwal *et al.*, 2005), cyclin-dependent kinase modulators (Kuo *et al.*, 2005) and anti-microbial agents (Koc *et al.*, 2010). These compounds still continue to be the object of considerable interest mainly because of their applications in various fields, including the production of herbicides and polymer photostabilizers. Triazine derivatives have been used as building blocks for subtle chemical architectures comprising organic–inorganic hybrid frameworks (Mathias *et al.*, 1994; Zerkowski & Whitesides, 1994; MacDonald & Whitesides, 1994; Guru Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). In these approaches, interplay between molecules is achieved by using diverse styles of non-covalent interactions, which include hydrogen bonds or ionic, hydro-



phobic, van der Waals or dispersive forces. Herein, the crystal structure of the title compound salt, 2,4-diamino-6-methyl-1,3,5-triazine-5-ium trichloroacetate monohydrate is reported. Hirshfeld surface analysis and 2D fingerprint plots were employed in order to quantify the contributions of the various intermolecular interactions present in the structure.



2. Structural commentary

The molecular structure with atomic numbering scheme is shown in Fig. 1. The asymmetric unit comprises a 2,4-diamino-6-methyl-1,3,5-triazine-5-ium cation, a trichloroacetate anion and a water molecule of solvation (O1W). Proton transfer occurs from one of the carboxylic acid oxygen atoms (O1) to atom N5 of the cation, with a resulting N5—H1N5...O1 hydrogen bond [2.652 (3) Å, Table 1]. The water molecule is also hydrogen bonded to atom O1 [2.835 (3) Å]. The proton transfer to the cation results in a widening of the C3—N5—C2 bond angle of the triazinium ring to 119.06 (19)°, compared to the comparative angle found in neutral 2,4-diamino-6-methyl-1,3,5-triazine [114.4 (7)°; Aoki *et al.*, 1994]. The C—O bond distances within the carboxyl group of the trichloroacetate anion are 1.212 (3) and 1.251 (3) Å.

3. Supramolecular features

In the crystal, pairs of 2,4-diamino-6-methyl-1,3,5-triazine-5-ium cations associate through lateral centrosymmetric interactions *via* N2—H2N2...N1ⁱⁱⁱ and N4—H2N4...N3^{iv} hydrogen bonds (Table 1) with cyclic $R_2^2(8)$ graph-set motifs. These interactions result in the formation of zigzag chains extending along the *c*-axis direction (Fig. 2). The cations in the chains are further linked through amine N2—H1N2...O1Wⁱⁱ

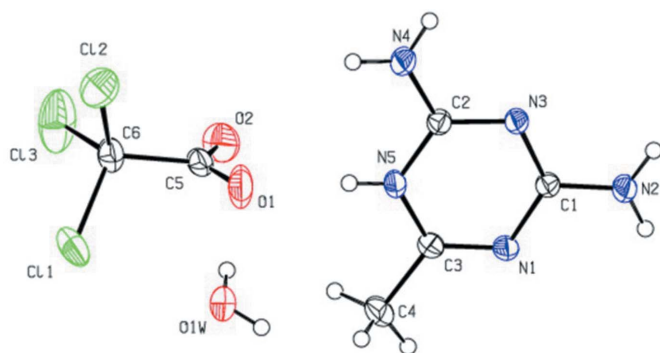


Figure 1
The molecular structure and atom-numbering scheme for the title salt, with displacement ellipsoids drawn at the 40% probability level.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N5—H1N5...O1 ⁱ	0.86	1.79	2.652 (3)	178
N2—H1N2...O1W ⁱⁱ	0.86	2.03	2.886 (3)	174
N2—H2N2...N1 ⁱⁱⁱ	0.86	2.21	3.071 (3)	174
N4—H2N4...N3 ^{iv}	0.86	2.18	3.034 (3)	173
N4—H1N4...O1W ^v	0.86	2.22	2.834 (3)	128
O1W—H1O1...O1	0.86 (4)	1.97 (4)	2.835 (3)	176 (3)
O1W—H2O2...O2 ^{vi}	0.78 (4)	1.97 (4)	2.741 (3)	173 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x, y, -z + \frac{1}{2}$; (iv) $-x, y, -z + \frac{3}{2}$; (v) $x, -y + 1, z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

and N4—H1N4...O1W^v hydrogen bonds in $R_2^2(8)$ motifs (Fig. 3), producing a complementary *DADA* (*D* = donor and *A* = acceptor) hydrogen-bonded array with an $R_2^2(8)$, $R_2^2(8)$, $R_2^2(8)$ graph-set motif sequence (Fig. 3). The water molecule acts as a donor to form a second O1W—H2O2...O2^{vi} hydrogen bond, which together with the O1W—H1O1...O1 hydrogen-bond sequence links the trichloroacetate anions into chains along the *b*-axis direction. Overall, a three-dimensional supramolecular structure is generated (Fig. 4).

4. Hirshfeld surface analysis

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and 2D fingerprint plots are useful tools for describing the surface

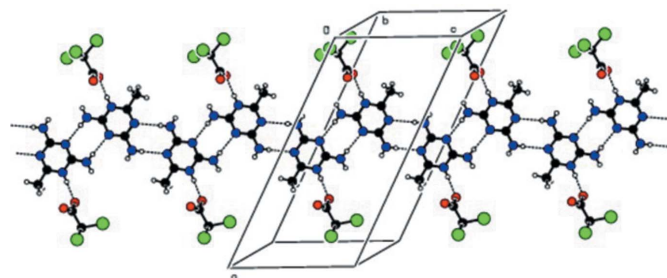


Figure 2
A packing view showing the centrosymmetric N—H...N hydrogen-bonded cation pairs with TCA anions, extending into chains along the *c*-axis direction. Water molecules are omitted.

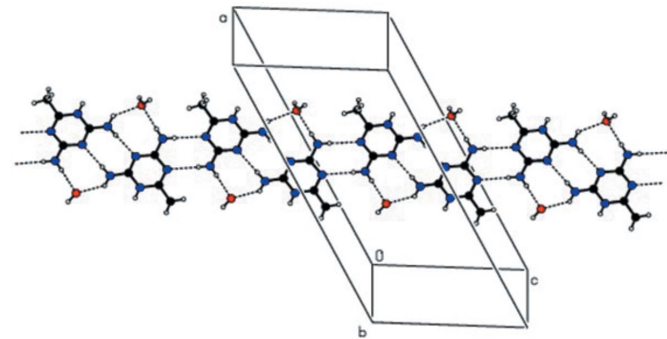


Figure 3
Another view of the extended chains with the TCA anions omitted, showing the *DADA* array and the participation of the water molecules in hydrogen bonding.

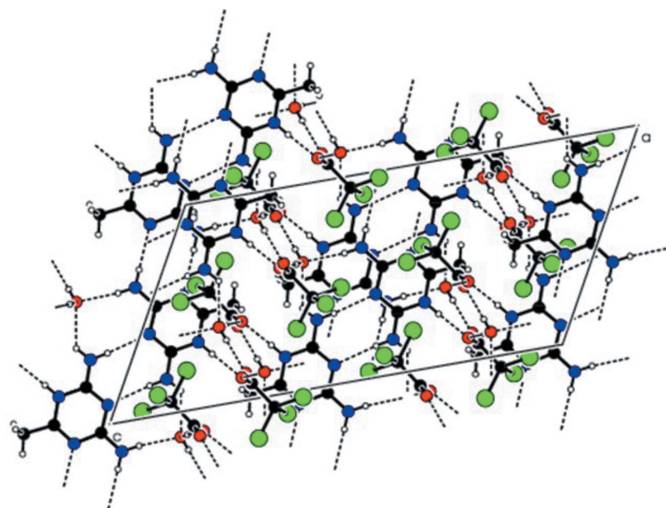


Figure 4
An overall view of the three-dimensional hydrogen-bonded supra-molecular structure.

characteristics of the crystal structure and were generated using CrystalExplorer 3.0 (Wolff *et al.*, 2012). The normalized contact distance (d_{norm}) is based on the distances from the nearest atom inside (d_i) and outside (d_e) the surface. The 3D d_{norm} surface of the title compound is shown in Fig. 5. The red points represent closer contacts and negative d_{norm} values on the surface corresponding to the N—H...O, N—H...N and O—H...O interactions. Two-dimensional fingerprint plots are shown in Fig. 6. H...H interactions (24.5%) are present as a major contributor while H...O/O...H (22.9%), N...H/H...N (10.2%), H...Cl (15.1%) N...H (10.2%), N...Cl (8.0%), C...Cl (5.6%), C...H (2.6%), Cl...O (2.4%), C...N (1.6%) and C...C (0.2%) contacts also make significant contributions to the Hirshfeld surface.

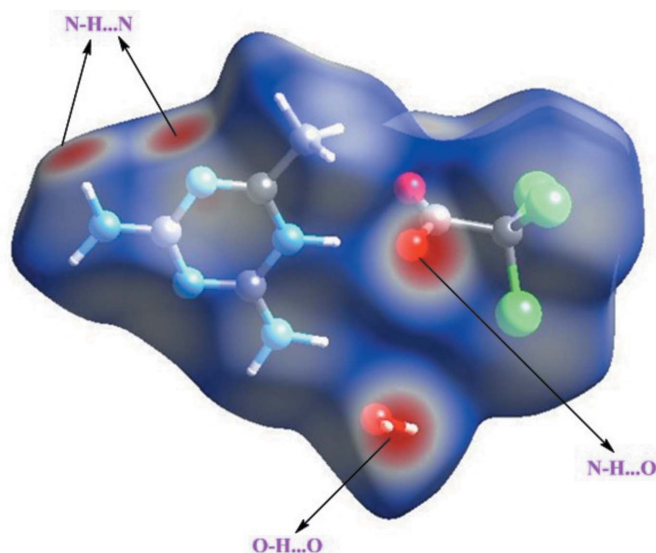


Figure 5
The three-dimensional Hirshfeld surface of the title compound

5. Database survey

A search of the Cambridge Structural Database (Version 5.37, update February 2016; Groom *et al.*, 2016) for 2,4-diamino-6-methyl-1,3,5-triazine yielded 22 structures of proton-transfer salts with carboxylic acids: AZUYUQ (with tetrafluoroboric acid; Gomathi & Muthiah, 2011); CICZUK (with trifluoroacetic acid; Perpétuo & Janczak, 2007); GIMRIE (with hydrogen chloride; Portalone & Colapietro, 2007); KUSQEV (with hydrogen chloride; Qian & Huang, 2010); LUGGEB (with 3,5-dihydroxybenzoic acid; Xiao *et al.*, 2014); NAGLIR (with dimesylamide; Wijaya *et al.*, 2004); QUWXAI (with 2-carboxybenzoic acid), QUWXEM [with (*Z*)-2-carboxyethene-1-carboxylic acid] and QUWXIQ (with 3-hydroxypyridine-2-carboxylic acid) (Thanigaimani *et al.*, 2010); ROGPIN [with oxalic acid (methanol clathrate)], ROGPOT [with malonic acid (tetrahydrate clathrate)], ROGPUZ [with succinic acid (clathrate)], ROGQAG [with acetylenedicarboxylic acid (monohydrate clathrate)], ROGQEK [glutaric acid (clathrate)], ROGQIO [thiodiglycolic acid (clathrate)], ROGQOU [diglycolic acid (monohydrate clathrate)], ROMZOJ [fumaric acid (clathrate)] (Delori *et al.*, 2008); SOLTIX (with nitric acid; Fan *et al.*, 2009); YODCAX (with 2,3,5,6-tetrafluoroterephthalic acid; Wang *et al.*, 2014); ZAQJEI (with oxalic acid; Narimani & Yamin, 2012); ZUDSOI [with 6-chlorouracil-1-ide (*N,N*-dimethylacetamide

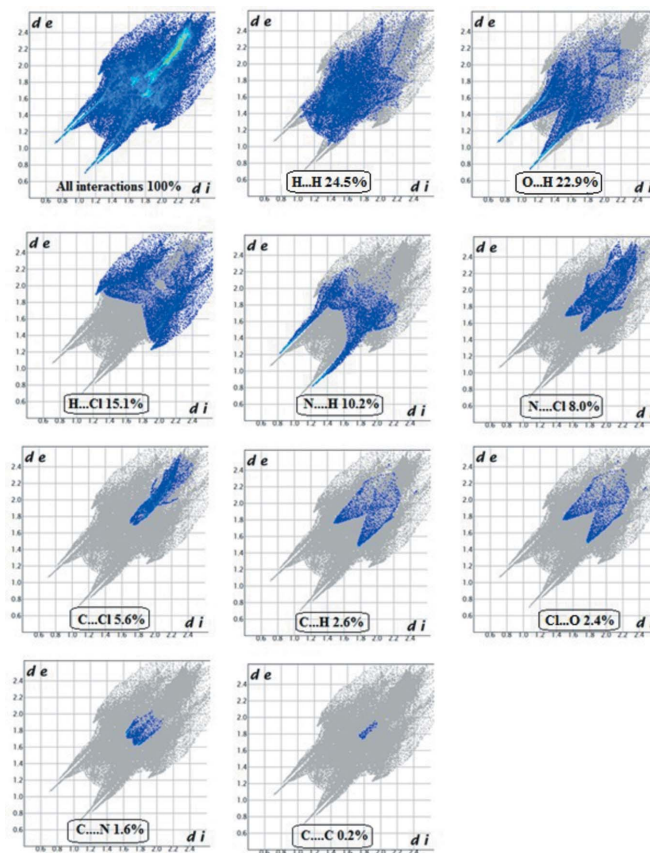


Figure 6
Two-dimensional fingerprint plots for the title compound

solvate)], ZUDSUO [with 6-chlorouracil-1-ide (*N,N*-dimethylformamide solvate monohydrate)] (Gerhardt & Egert, 2015).

6. Synthesis and crystallization

The title compound was prepared by mixing a hot methanolic solution (20 ml) of 2,4-diamino-6-methyl-1,3,5-triazine (1.25 mg) and an aqueous solution (10 ml) of trichloroacetic acid (1.63 mg) in a 1:1 molar ratio. The reaction mixture was warmed over a water bath for a few minutes. The resultant solution was then allowed to cool slowly at room temperature. After a few days, colourless block-shaped crystals of the title compound were separated out.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C- and N-bound H atoms were placed in calculated positions and were included in the refinement in the riding-model approximation with C—H = 0.96 Å and N—H = 0.86 Å (NH, NH₂), with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C,N})$. The water-bound H atoms were located in a difference-Fourier map and were freely refined [O—H = 0.78 (4) and 0.86 (4) Å].

Acknowledgements

The authors wish to thank the SAIF–STIC, Cochin, Kerala for the data collection.

Funding information

KB thanks the Department of Science and Technology (DST–SERB), New Delhi, India, for financial support (grant No. SB/FT/CS-058/2013). RS thanks the Department of Science and Technology (DST), New Delhi, India, for financial support in the form of an INSPIRE fellowship (INSPIRE code No. IF131050).

References

Agarwal, A., Srivastava, K., Puri, S. K. & Chauhan, P. M. S. (2005). *Bioorg. Med. Chem. Lett.* **15**, 531–533.
 Aoki, K., Inaba, M., Teratani, S., Yamazaki, H. & Miyashita, Y. (1994). *Inorg. Chem.* **33**, 3018–3020.
 Baliani, A., Bueno, G. J., Stewart, M. L., Yardley, V., Brun, R., Barrett, P. M. & Gilbert, I. H. (2005). *J. Med. Chem.* **48**, 5570–5579.
 Boesveld, W. M., Hitchcock, P. B. & Lappert, M. F. (1999). *J. Chem. Soc. Dalton Trans.* pp. 4041–4046.
 Boesveld, W. M. & Lappert, M. F. (1997). *Chem. Commun.* pp. 2091–2092.
 Bruker (2004). *APEX2, SAINT, XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Delori, A., Suresh, E. & Pedireddi, V. R. (2008). *Chem. Eur. J.* **14**, 6967–6977.
 Fan, Y., You, W., Qian, H.-F., Liu, J.-L. & Huang, W. (2009). *Acta Cryst.* **E65**, o494.
 Gerhardt, V. & Egert, E. (2015). *Acta Cryst.* **B71**, 209–220.
 Gomathi, S. & Muthiah, P. T. (2011). *Acta Cryst.* **E67**, o2762.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₄ H ₈ N ₅ ⁺ ·C ₂ Cl ₃ O ₂ ⁻ ·H ₂ O
M_r	306.54
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	293
a, b, c (Å)	21.7056 (18), 11.9074 (9), 10.9562 (6)
β (°)	119.084 (5)
V (Å ³)	2474.7 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.75
Crystal size (mm)	0.35 × 0.30 × 0.30
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
$T_{\text{min}}, T_{\text{max}}$	0.781, 0.807
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9801, 3027, 2280
R_{int}	0.027
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.159, 1.01
No. of reflections	3027
No. of parameters	163
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.68, -0.59

Computer programs: *APEX2*, *SAINTE* and *XPREP* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Guru Row, T. N. (1999). *Coord. Chem. Rev.* **183**, 81–100.
 Henke, B. R., Consler, T. G., Go, N., Hale, R. L., Hohman, D. R., Jones, S. A., Lu, A. T., Moore, L. B., Moore, J. T., Orband-Miller, L. A., Robinett, R. G., Shearin, J., Spearing, P. K., Stewart, E. L., Turnbull, P. S., Weaver, S. L., Williams, S. P., Wisely, G. B. & Lambert, M. H. (2002). *J. Med. Chem.* **45**, 5492–5505.
 Koc, Z. E., Bingol, H., Saf, A. O., Torlak, E. & Coskun, A. (2010). *J. Hazard. Mater.* **183**, 251–255.
 Krische, M. J. & Lehn, J. M. (2000). *Struct. Bond.* **96**, 3–29.
 Kuo, G. H., DeAngelis, A., Emanuel, S., Wang, A., Zhang, Y., Connolly, P. J., Chen, X., Gruninger, R. H., Rugg, C., Fuentes-Pesquera, A., Middleton, S. A., Jolliffe, L. & Murray, W. V. (2005). *J. Med. Chem.* **48**, 4535–4546.
 MacDonald, J. C. & Whitesides, G. M. (1994). *Chem. Rev.* **94**, 2383–2420.
 Mathias, J. P., Simanek, E. E., Zerkowski, J. A., Seto, C. T. & Whitesides, G. M. (1994). *J. Am. Chem. Soc.* **116**, 4316–4325.
 Menicagli, R., Samaritani, S., Signore, G., Vaglini, F. & Dalla Via, L. (2004). *J. Med. Chem.* **47**, 4649–4652.
 Narimani, L. & Yamin, B. M. (2012). *Acta Cryst.* **E68**, o1475.
 Perpétuo, G. J. & Janczak, J. (2007). *Acta Cryst.* **C63**, o271–o273.
 Portalone, G. & Colapietro, M. (2007). *Acta Cryst.* **C63**, o655–o658.
 Qian, H.-F. & Huang, W. (2010). *Acta Cryst.* **E66**, o759.
 Reid, D. J., Cull, J. E. W., Chisholm, K. D. S., Langlois, A., Lin, P.-H., Long, J., Lebel, O., Korobkov, I., Wang, R., Wuest, J. D., Murugesu, M. & Scott, J. (2011). *Dalton Trans.* **40**, 5009–5017.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sherrington, D. C. & Taskinen, K. A. (2001). *Chem. Soc. Rev.* **30**, 83–93.
 Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Thanigaimani, K., Devi, P., Muthiah, P. T., Lynch, D. E. & Butcher, R. J. (2010). *Acta Cryst.* **C66**, o324–o328.
- Wang, L., Hu, Y., Wang, W., Liu, F. & Huang, K. (2014). *CrystEngComm*, **16**, 4142–4161.
- Wijaya, K., Moers, O., Henschel, D., Blaschette, A. & Jones, P. G. (2004). *Z. Naturforsch. B Chem. Sci.* **59**, 747–756.
- Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *CrystalExplorer* 3.0. University of Western Australia.
- Xiao, Z. Y., Wang, W. Q., Xue, R. Y., Zhao, L., Wang, L. & Zhang, Y. H. (2014). *Sci. China Chem.* **57**, 1731–1737.
- Zerkowski, J. A. & Whitesides, G. M. (1994). *J. Am. Chem. Soc.* **116**, 4298–4304.

supporting information

Acta Cryst. (2018). E74, 944-948 [https://doi.org/10.1107/S2056989018008307]

Crystal structure and Hirshfeld surface analysis of 2,4-diamino-6-methyl-1,3,5-triazin-1-ium trichloroacetate monohydrate

Ramalingam Sangeetha, Kasthuri Balasubramani, Kaliyaperumal Thanigaimani and Savaridasson Jose Kavitha

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

2,4-Diamino-6-methyl-1,3,5-triazin-1-ium trichloroacetate monohydrate

Crystal data

$C_4H_8N_5^+ \cdot C_2Cl_3O_2^- \cdot H_2O$

$M_r = 306.54$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 21.7056$ (18) Å

$b = 11.9074$ (9) Å

$c = 10.9562$ (6) Å

$\beta = 119.084$ (5)°

$V = 2474.7$ (3) Å³

$Z = 8$

$F(000) = 1248$

$D_x = 1.645$ Mg m⁻³

$D_m = 1.646$ Mg m⁻³

D_m measured by Not Measured

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

Cell parameters from 3519 reflections

$\theta = 6.6$ – 56.0 °

$\mu = 0.75$ mm⁻¹

$T = 293$ K

Block, colorless

$0.35 \times 0.30 \times 0.30$ mm

Data collection

Bruker Kappa APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 18.4 pixels mm⁻¹

ω and ϕ scan

Absorption correction: multi-scan

(SADABS; Bruker, 2004)

$T_{\min} = 0.781$, $T_{\max} = 0.807$

9801 measured reflections

3027 independent reflections

2280 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 3.3$ °

$h = -27 \rightarrow 28$

$k = -15 \rightarrow 14$

$l = -14 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.159$

$S = 1.01$

3027 reflections

163 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

$$w = 1/[\sigma^2(F_o^2) + (0.0984P)^2 + 1.9287P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating -R-factor-obs 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.06709 (3)	0.61615 (7)	0.46638 (9)	0.0614 (3)
Cl2	0.13757 (4)	0.58198 (9)	0.30457 (7)	0.0653 (3)
Cl3	0.08995 (5)	0.39459 (7)	0.40021 (13)	0.0922 (4)
N1	0.06762 (9)	0.13611 (16)	0.43697 (17)	0.0272 (5)
N2	-0.05081 (9)	0.14541 (17)	0.35783 (18)	0.0318 (5)
N3	0.01987 (9)	0.13451 (15)	0.59533 (17)	0.0260 (5)
N4	0.09746 (10)	0.12278 (18)	0.82990 (18)	0.0361 (6)
N5	0.14168 (9)	0.13060 (16)	0.67706 (18)	0.0293 (5)
O1	0.22699 (10)	0.62450 (18)	0.6137 (2)	0.0559 (7)
C1	0.01284 (10)	0.13863 (17)	0.46625 (19)	0.0242 (5)
O2	0.22226 (11)	0.4396 (2)	0.6332 (2)	0.0575 (7)
C2	0.08544 (10)	0.13021 (17)	0.7000 (2)	0.0251 (5)
C3	0.13012 (11)	0.13324 (18)	0.5439 (2)	0.0274 (6)
C4	0.19386 (13)	0.1349 (3)	0.5269 (3)	0.0442 (8)
O1W	0.17844 (9)	0.8439 (2)	0.6222 (2)	0.0433 (6)
C5	0.19921 (11)	0.5296 (2)	0.5782 (2)	0.0362 (7)
C6	0.12614 (11)	0.5291 (2)	0.4432 (2)	0.0374 (6)
H1N5	0.18400	0.12920	0.74610	0.0350*
H1N2	-0.08710	0.14710	0.37000	0.0380*
H2N2	-0.05620	0.14810	0.27480	0.0380*
H2N4	0.06270	0.12070	0.84680	0.0430*
H4A	0.18040	0.12240	0.43060	0.0660*
H4B	0.22570	0.07680	0.58310	0.0660*
H4C	0.21670	0.20650	0.55590	0.0660*
H1N4	0.14000	0.12000	0.89770	0.0430*
H1O1	0.1914 (16)	0.776 (3)	0.619 (3)	0.045 (8)*
H2O2	0.205 (2)	0.868 (3)	0.695 (4)	0.068 (12)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0282 (3)	0.0761 (6)	0.0743 (5)	0.0099 (3)	0.0205 (3)	-0.0050 (4)
Cl2	0.0627 (5)	0.0932 (7)	0.0349 (4)	0.0076 (4)	0.0198 (3)	0.0068 (3)
Cl3	0.0671 (6)	0.0422 (5)	0.1127 (8)	-0.0123 (4)	0.0008 (5)	-0.0058 (5)
N1	0.0247 (8)	0.0366 (10)	0.0229 (8)	0.0001 (7)	0.0136 (7)	-0.0006 (7)
N2	0.0231 (8)	0.0491 (11)	0.0224 (8)	0.0025 (8)	0.0104 (7)	0.0010 (8)
N3	0.0217 (8)	0.0349 (10)	0.0214 (8)	0.0014 (6)	0.0105 (7)	0.0000 (6)
N4	0.0270 (9)	0.0596 (13)	0.0197 (8)	0.0012 (8)	0.0097 (7)	0.0017 (8)
N5	0.0192 (8)	0.0425 (11)	0.0236 (8)	0.0013 (7)	0.0084 (7)	0.0013 (7)
O1	0.0277 (9)	0.0623 (14)	0.0515 (11)	-0.0021 (8)	-0.0014 (8)	-0.0080 (9)
C1	0.0228 (9)	0.0270 (10)	0.0224 (9)	0.0003 (7)	0.0108 (8)	-0.0002 (7)
O2	0.0515 (11)	0.0702 (14)	0.0404 (10)	0.0242 (10)	0.0142 (9)	0.0166 (9)
C2	0.0241 (9)	0.0274 (10)	0.0231 (9)	0.0010 (7)	0.0109 (8)	0.0000 (7)
C3	0.0249 (9)	0.0317 (11)	0.0285 (10)	0.0016 (8)	0.0152 (8)	0.0017 (8)
C4	0.0266 (11)	0.0717 (18)	0.0401 (12)	0.0034 (11)	0.0208 (10)	0.0042 (12)
O1W	0.0283 (8)	0.0559 (13)	0.0346 (9)	0.0001 (8)	0.0066 (7)	-0.0048 (9)
C5	0.0236 (9)	0.0559 (15)	0.0263 (10)	0.0094 (10)	0.0100 (8)	0.0022 (10)
C6	0.0267 (10)	0.0378 (12)	0.0378 (11)	0.0020 (9)	0.0079 (9)	0.0014 (10)

Geometric parameters (\AA , $^\circ$)

Cl1—C6	1.760 (3)	N2—H1N2	0.8600
Cl2—C6	1.770 (2)	N2—H2N2	0.8600
Cl3—C6	1.745 (3)	C3—C4	1.483 (4)
N1—C1	1.374 (3)	N4—H2N4	0.8600
N1—C3	1.292 (3)	N4—H1N4	0.8600
N2—C1	1.316 (3)	N5—H1N5	0.8600
N3—C2	1.325 (3)	C4—H4B	0.9600
N3—C1	1.348 (3)	C4—H4C	0.9600
N4—C2	1.319 (3)	C4—H4A	0.9600
N5—C2	1.361 (3)	C5—C6	1.557 (3)
N5—C3	1.355 (3)	O1W—H1O1	0.86 (4)
O1—C5	1.251 (3)	O1W—H2O2	0.78 (4)
O2—C5	1.212 (3)		
C1—N1—C3	115.80 (18)	C2—N5—H1N5	121.00
C1—N3—C2	115.8 (2)	C3—N5—H1N5	120.00
C2—N5—C3	119.06 (19)	C3—C4—H4A	109.00
N1—C1—N2	116.02 (18)	C3—C4—H4B	110.00
N1—C1—N3	125.08 (19)	C3—C4—H4C	109.00
N2—C1—N3	118.9 (2)	H4A—C4—H4B	109.00
N3—C2—N4	120.1 (2)	H4A—C4—H4C	110.00
N3—C2—N5	121.50 (19)	H4B—C4—H4C	109.00
N4—C2—N5	118.3 (2)	O1—C5—O2	128.6 (2)
C1—N2—H1N2	120.00	O1—C5—C6	114.4 (2)
C1—N2—H2N2	120.00	O2—C5—C6	116.9 (2)

H1N2—N2—H2N2	120.00	C11—C6—C12	109.27 (13)
N1—C3—N5	122.7 (2)	C11—C6—C13	108.40 (15)
N1—C3—C4	121.2 (2)	C11—C6—C5	109.74 (15)
N5—C3—C4	116.1 (2)	C12—C6—C13	109.12 (12)
C2—N4—H2N4	120.00	C12—C6—C5	108.12 (17)
C2—N4—H1N4	120.00	C13—C6—C5	112.16 (16)
H2N4—N4—H1N4	120.00	H1O1—O1W—H2O2	107 (3)
C3—N1—C1—N2	177.8 (2)	C3—N5—C2—N4	177.2 (2)
C3—N1—C1—N3	-2.4 (3)	C2—N5—C3—N1	0.4 (3)
C1—N1—C3—N5	1.3 (3)	C2—N5—C3—C4	179.3 (2)
C1—N1—C3—C4	-177.5 (2)	O1—C5—C6—C11	-59.0 (3)
C2—N3—C1—N1	1.6 (3)	O1—C5—C6—C12	60.1 (3)
C2—N3—C1—N2	-178.58 (19)	O1—C5—C6—C13	-179.51 (19)
C1—N3—C2—N4	-178.1 (2)	O2—C5—C6—C11	122.4 (2)
C1—N3—C2—N5	0.3 (3)	O2—C5—C6—C12	-118.5 (2)
C3—N5—C2—N3	-1.3 (3)	O2—C5—C6—C13	1.9 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N5—H1N5...O1 ⁱ	0.86	1.79	2.652 (3)	178
N2—H1N2...O1W ⁱⁱ	0.86	2.03	2.886 (3)	174
N2—H2N2...N1 ⁱⁱⁱ	0.86	2.21	3.071 (3)	174
N4—H2N4...N3 ^{iv}	0.86	2.18	3.034 (3)	173
N4—H1N4...O1W ^v	0.86	2.22	2.834 (3)	128
O1W—H1O1...O1	0.86 (4)	1.97 (4)	2.835 (3)	176 (3)
O1W—H2O2...O2 ^{vi}	0.78 (4)	1.97 (4)	2.741 (3)	173 (3)

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