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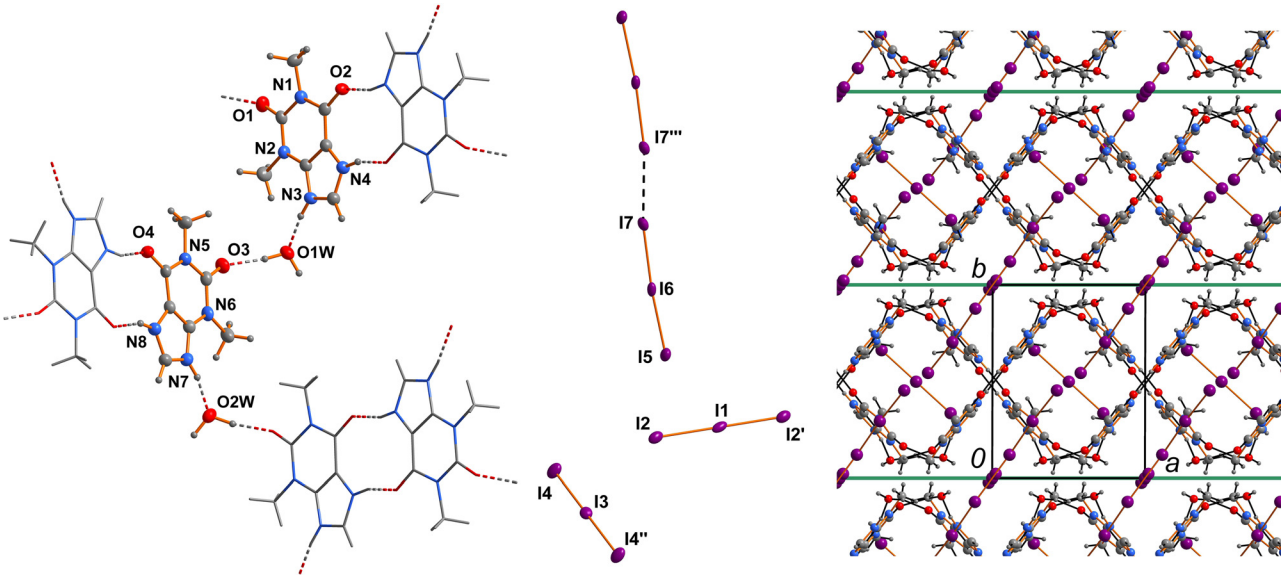
An I_6^{2-} anion in the crystal structure of theophyllinium triiodide monohydrate, $C_7H_{11}I_3N_4O_3$



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Abstract

$C_7H_{11}I_3N_4O_3$, triclinic, $P\bar{1}$ (no. 2), a = 9.28478(14) Å, b = 12.2214(2) Å, c = 13.4088(2) Å, α = 76.2062(14)°, β = 88.2421(13)°, γ = 89.4102(13)°, Z = 4, V = 1476.95(4) Å^3, $R_{gt}(F)$ = 0.0198, wR_{ref} = 0.0494, T = 100 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Dark red block
Size:	0.16 × 0.09 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.35 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	32.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	64027, 10661, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 9468
$N(param)_{refined}$:	342
Programs:	Diamond [1], CrysAlis^{PRO} [2], SHELX [3–5]

Source of material

All chemicals were obtained from commercial sources and used as purchased. The title compound was synthesised by dissolving 0.15 g theophylline (0.8 mmol) in 5 mL of 57%

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
I1	0.500000	0.500000	0.000000	0.02532 (4)
I2	0.72732 (2)	0.33676 (2)	0.07837 (2)	0.02769 (3)
I3	1.000000	0.000000	0.000000	0.02295 (4)
I4	1.02609 (2)	0.02172 (2)	0.21160 (2)	0.03136 (4)
I5	0.57743 (2)	0.54620 (2)	0.33657 (2)	0.02765 (3)
I6	0.73787 (2)	0.70545 (2)	0.42497 (2)	0.02148 (3)
I7	0.88759 (2)	0.87813 (2)	0.49904 (2)	0.02638 (3)
O1	0.41956 (15)	0.16286 (12)	1.23298 (11)	0.0185 (3)
O2	0.08812 (15)	0.44441 (12)	1.14120 (10)	0.0167 (2)
O3	0.60392 (16)	0.14289 (12)	0.75245 (12)	0.0196 (3)
O4	0.92322 (14)	0.43309 (11)	0.64932 (10)	0.0156 (2)
O1W	0.32904 (16)	0.09026 (13)	0.81330 (12)	0.0185 (3)
H1W	0.276 (5)	0.079 (4)	0.779 (4)	0.070*
H2W	0.404 (5)	0.100 (4)	0.787 (4)	0.070*
O2W	0.68244 (17)	0.10492 (12)	0.31027 (12)	0.0188 (3)
H3W	0.749 (5)	0.102 (4)	0.273 (4)	0.070*
H4W	0.613 (5)	0.126 (4)	0.271 (4)	0.070*
N1	0.25906 (16)	0.30691 (12)	1.18344 (11)	0.0127 (2)
N2	0.33499 (16)	0.19142 (13)	1.07175 (12)	0.0140 (3)
N3	0.22853 (17)	0.24766 (13)	0.90240 (12)	0.0134 (3)
H3	0.269 (4)	0.204 (3)	0.874 (3)	0.040 (9)*
N4	0.09020 (17)	0.38360 (13)	0.93048 (12)	0.0136 (3)
H4	0.036 (3)	0.433 (3)	0.922 (2)	0.024 (7)*
N5	0.76286 (16)	0.28713 (13)	0.69941 (12)	0.0137 (3)
N6	0.67551 (17)	0.18425 (13)	0.58392 (12)	0.0149 (3)
N7	0.76881 (17)	0.25466 (13)	0.40763 (12)	0.0146 (3)
H7	0.737 (4)	0.208 (3)	0.378 (3)	0.037 (9)*
N8	0.90281 (17)	0.39127 (13)	0.43327 (12)	0.0139 (3)
H8	0.959 (3)	0.444 (3)	0.422 (2)	0.029 (8)*
C1	0.34262 (18)	0.21677 (15)	1.16653 (14)	0.0138 (3)
C2	0.16130 (18)	0.37001 (14)	1.11619 (13)	0.0126 (3)
C3	0.16029 (18)	0.33834 (14)	1.02042 (13)	0.0122 (3)
C4	0.13298 (19)	0.32846 (15)	0.86107 (14)	0.0142 (3)
H4A	0.101217	0.343470	0.792438	0.017*
C5	0.24671 (18)	0.25369 (14)	1.00170 (13)	0.0117 (3)
C6	0.4201 (2)	0.09643 (17)	1.05228 (17)	0.0214 (4)
H6A	0.401621	0.029425	1.107913	0.032*
H6B	0.522839	0.115106	1.049107	0.032*
H6C	0.392834	0.081339	0.986830	0.032*
C7	0.2848 (2)	0.34158 (18)	1.27933 (15)	0.0201 (4)
H7A	0.211494	0.396645	1.289020	0.030*
H7B	0.380586	0.375655	1.275285	0.030*
H7C	0.279616	0.275510	1.337465	0.030*
C8	0.67575 (19)	0.20124 (15)	0.68211 (14)	0.0149 (3)
C9	0.84730 (18)	0.36076 (14)	0.62594 (13)	0.0126 (3)
C10	0.83601 (19)	0.34098 (15)	0.52618 (13)	0.0129 (3)
C11	0.8603 (2)	0.33829 (16)	0.36381 (14)	0.0157 (3)
H11	0.890156	0.356637	0.293400	0.019*
C12	0.75388 (18)	0.25518 (14)	0.50885 (13)	0.0132 (3)
C13	0.5931 (2)	0.08943 (16)	0.56482 (17)	0.0203 (4)
H13A	0.493918	0.113672	0.548487	0.030*
H13B	0.592654	0.027091	0.626305	0.030*
H13C	0.638013	0.064361	0.506951	0.030*
C14	0.7572 (2)	0.30077 (17)	0.80578 (14)	0.0179 (3)
H14A	0.805933	0.370717	0.808440	0.027*
H14B	0.805391	0.236699	0.850665	0.027*
H14C	0.656419	0.303973	0.828954	0.027*

aqueous hydroiodid acid. Red crystals were harvested from the mother liquor after two days in the fridge at 5 °C.

Experimental details

A small isometric crystal of the title compound was directly selected from the mother liquor and mounted on a Rigaku XtaLAB Synergy equipped with the HyPix-6000 detector [2] using a nylon loop at 100 K. An absorption correction (numerical absorption correction) was applied [2]. The structure solution and the refinement succeeded using the SHELX program system [3–5]. Atomic coordinates of hydrogen atoms belonging to the water molecules and those hydrogen atoms attached to nitrogen were refined freely. All other hydrogen atoms were added using a corresponding riding model with fixed U_{iso} parameters. The maximum residual peak of 2.26 eÅ^{-3} is found 0.64 Å apart from I7 and the deepest hole of –1.75 eÅ^{-3} is found 0.56 Å apart from I7.

Comment

Introduction

The term polyiodides – formerly named periodides [6] – describes a class of compounds that is defined as the anionic part of a salt-type structure, which fullfills the general formula I_{2m-n}^{n-} (n = 2–5, m = integer). Almost all of the currently known polyiodides consist of I^-, I_3^- and I_2 subunits. These two simple ions and the I_2 molecule show a strong tendency to form extended, halogen bonded structures [7–11]. Polyiodides are of interest not only because of their structures, but also because of reported applications. Some important applications are listed in our preceeding article [12]. We have already shown that planar, nitrogen-based heterocyclic cations support the formation of iodine rich compounds [13, 14]. Especially using different methylxanthinium cations, some polyiodide salts have already been characterised by us [15, 16] and others [17–19]. The bonding properties of short-chain polyiodides like I_4^{2-} [12, 20, 21] and especially I_6^{2-} [22–24] are still of general interest.

Structural comments

The asymmetric unit of the title structure contains two crystallographically independent theophyllinium cations, one I_3^- anion in a general position, two halves of I_3^- anions on inversion centers (Wyckoff sites 1*a* and 1*e*) and two water molecules in general positions (see the figure). Thus, the overall composition can be summerized as theophyllinium triiodide monohydrate [systematic name: 1,3-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-9-ium triiodide—water (1/1)].

Each of the two crystallographically independent theophyllinium cations forms a dimer with a symmetry related theophyllinium cation by NH···O hydrogen bonds (see the left part of the figure). These dimers are furthermore connected *via* O–H···O hydrogen bonds between the water molecules and the cations to furnish a wavy layer. The bond lengths and angles within the cations as well as the geometric parameters in the various hydrogen bonds are in the expected ranges [16]. The two I_3^- anions located on inversion centers (see the middle section of the Figure; I2–I1–I2′; I4–I3–I3″; ′ = 1–*x* 1–*y*, –*z*, ″ = 2–*x*, –*y*, –*z*) are not connected to any other triiodide anions and feature only weak hydrogen bonds to water molecules and the cations. The triiodide anion located in a general position is attached to its symmetry-related triiodide anion (inversion symmetry; Wyckoff site 1*b*) (see middle part of the figure; I7···I7‴ distance = 3.6605(3) Å; symmetry operation: 2–*x*, 2–*y*, 1–*z*). This secondary I···I bonding interaction is weak, but significantly shorter than any van der Waals distances in various scales [25]. To classify this secondary halogen bond in more detail a comparison with some literature known I_6^{2-} anions is needed. Structures of catenated triodides have not been considered for this comparison. To the best of our knowledge, the shortest halogen bonded triiodide—triiodide distance of 3.5017(2) Å is found in a structure, which is characterised by strong charge supported hydrogen bonds between the coutercation and both terminal I atoms of the I_6^{2-} anion [22]. A distance of 3.6317(4) Å is found for the I_6^{2-} anion trapped in the van der Waals void of a hydrogen bonded framework [23]. Recently even in the case of a distance of 3.848 Å [24] a halogen bonding interaction was discussed by the authors. Thus the I7···I7‴ distance of 3.6733(12) Å in the title structure is in the upper part of the scope of such halogen bonds, but we think that the motif must be discussed as another I_6^{2-} anion. In detail, each triiodide part within the I_6^{2-} anion shows a bonding angle of 175.08(2)° and the angle between the two I_3^- ions (I8–I7···I7‴) is 160.74(1)°. In general all I–I bonding parameters of the triiodide anions are in the expected ranges (I1–I2 = 2.9307(2) Å; I3–I4 = 2.9296(2) Å; I5–I6 = 2.9463(2) Å; I6–I7 = 2.9183(2) Å) [13].

A packing diagram with a view against the *c* axis is shown in the right part of the figure. Classical hydrogen bonding interactions only occur in the aforementioned layers consisting of the cations and the water molecules. These layers are stacked along the *b* axis. The hydrogen bonded layers are connected *via* van der Waals interactions only (green line in the right part of the figure). The triiodide anions as well as the I_6^{2-} anions fill the voids within and between these layers. One of the triiodide anions (right part of the figure, I4–I3–I4″) and the I_6^{2-} anions are oriented along [110], whereas the triiodide anion I2–I1–I2′ is almost oriented along [1–10].

Conclusion

Recently we have shown that hydrogen bonded motifs constructed by theophyllinium cations form layered and more complex frameworks, that are able to stabilize interesting couter anions [[26] and references cited there]. The title structure is one more example to show the performance of the theophyllinium cation to act as a tecton in crystal engineering.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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