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A cyclic I_{10}^{2-} anion in the layered crystal structure of theophyllinium pentaiodide, $C_7H_9I_5N_4O_2$

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Abstract

$C_7H_9I_5N_4O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 9.46793(10)$ Å, $b = 11.58276(12)$ Å, $c = 16.41497(18)$ Å, $\beta = 100.844(1)^\circ$, $Z = 4$, $V = 1768.00(3)$ Å³, $R_{gt}(F) = 0.0306$, $wR_{ref}(F^2) = 0.0728$, $T = 130(2)$ 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 the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Black shiny block
Size:	$0.34 \times 0.27 \times 0.21$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	8.80 mm^{-1}
Diffractometer, scan mode:	Xcalibur-EOS, ω
$\theta_{\max}$, completeness:	28.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	52671, 4465, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4173
$N(\text{param})_{\text{refined}}$:	174
Programs:	Diamond [1], CrysAlis ^{PRO} [2], SHELX [3–5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	−0.05603(4)	0.41770(3)	0.25049(2)	0.03655(10)
I2	0.15381(3)	0.25151(2)	0.32685(2)	0.02540(8)
I3	0.36362(3)	0.07971(3)	0.41151(2)	0.03031(9)
I4	0.60290(4)	0.26148(3)	0.51239(2)	0.03868(10)
I5	0.80523(5)	0.40502(3)	0.60464(3)	0.04772(11)
O1	0.4504(3)	0.1977(3)	0.20058(18)	0.0233(6)
O2	0.0587(3)	0.3354(3)	0.02188(18)	0.0211(6)
N1	0.2572(3)	0.2679(3)	0.1107(2)	0.0178(6)
N2	0.4066(3)	0.3900(3)	0.2066(2)	0.0176(6)
N3	0.1428(4)	0.5726(3)	0.0963(2)	0.0183(6)
H3	0.072(7)	0.592(5)	0.066(4)	0.037(16)*
N4	0.3278(4)	0.5924(3)	0.1963(2)	0.0191(7)
H4	0.393(7)	0.624(6)	0.226(4)	0.045(18)*
C1	0.3766(4)	0.2808(4)	0.1746(2)	0.0179(7)
C2	0.3208(4)	0.4786(3)	0.1740(2)	0.0158(7)
C3	0.2051(4)	0.4651(3)	0.1108(2)	0.0151(7)
C4	0.1638(4)	0.3550(3)	0.0757(2)	0.0165(7)
C5	0.2179(4)	0.6469(4)	0.1477(3)	0.0203(8)
H5	0.197936	0.725295	0.149980	0.024*
C6	0.2273(5)	0.1494(4)	0.0797(3)	0.0272(9)
H6A	0.149744	0.150503	0.032647	0.041*
H6B	0.200953	0.102392	0.122624	0.041*
H6C	0.311695	0.117929	0.063472	0.041*
C7	0.5251(5)	0.4044(4)	0.2774(3)	0.0304(10)
H7A	0.527870	0.483025	0.296131	0.046*
H7B	0.614326	0.385626	0.260806	0.046*
H7C	0.510762	0.354048	0.321557	0.046*

Source of material

All chemicals were obtained from commercial sources and used as purchased. The Raman spectra were measured using a Bruker MULTIRAM spectrometer (Nd: YAG-laser at 1064 nm; InGaAs detector) with an apodized resolution of 8 cm⁻¹ in the region of 4000–70 cm⁻¹. The title compound was synthesized by dissolving 0.18 g (1 mmol) theophylline and 0.25 g (1 mmol) diiodine in 1 mL of 57% aqueous hydroiodic acid. Heating to ~350 K yielded a dark colored solution, which produced black, block crystals upon slow cooling to room temperature.

Experimental details

A single crystal of the title compound was directly selected from the mother liquor and rapidly transferred into the cold gas-stream ($T = 146$ K) of the Xcalibur four-circle diffractometer equipped with an EOS detector [2]. An absorption correction (Gaussian method) was applied [2]. The structure solution and the refinement were successfully carried out using the SHELX program system [3–5]. Hydrogen atoms which are involved in hydrogen bonds were refined freely. All other hydrogen bonds were added using a riding model with fixed U_{iso} parameters. The maximum residual peak of 3.63 eÅ⁻³ and the deepest hole of -2.15 eÅ⁻³ are found 0.79 and 0.68 Å, respectively, from atom I5.

Comment

Nowadays polyiodides (in the 19th century periodides [6]) are defined as the anionic parts of salt structures that fulfil the general formula I_{2m-n}^- ($n = 2-5$, $m = \text{integer}$). Nearly all polyiodides are constructed of I^- , I_3^- and I_2 units. These ions and the I_2 molecule tend to form extended motifs by means of halogen bonds [7–10]. The triiodide monoanion has been considered as the simplest polyiodide species. Extended theoretical studies on the phenomenon of halogen bonding led to a deeper understanding of its occurrence [11–13]. Polyiodides are of interest not only because of their structures, but also because of recently reported applications. Short-chain polyiodides play a key role in the charge-transfer processes of the classical dye-sensitized solar cells [14, 15]. Moreover, polyiodide species may be used as ambipolar zinc electrolytes [16] and promoted the development of optimized lithium-iodine redox batteries [17]. Apart from possible applications there is still an academic interest in the synthesis of new, tailored polyiodides using cationic templates whose lengths and shapes may influence the topology of the polyiodide anions [18–20]. We have shown that semi-flexible cations [21–23] and heterocyclic cations like pyridinium derivatives [24, 25] or naturally occurring base like nicotine [26] or caffeine [27] are excellent tectons for the synthesis of polyiodide containing salts. Many structures with the formal I_5^- anion are known

[9, 19, 26], but to the best of our knowledge, only one dimeric cyclic $(I_5^-)_2$ anion has been reported [28] until now.

From the reaction of theophylline (systematic name: 1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) with hydroiodic acid in the presence of excess iodine, black, shiny, block crystals of the title compound were obtained. The crystalline material loses its excess of iodine slowly at ambient conditions.

The asymmetric unit of the title compound consists of one *N*-protonated theophyllinium cation, one triiodide anion and one iodine molecule residing on general positions in the space group $P2_1/c$. The geometric parameters of the title cation are very similar to those known from the literature (Tab. 2) [29].

In the title structure each theophyllinium cation donates and accepts two hydrogen bonds to three (crystallographically dependent) adjacent cations *via* its N–H and C=O functional groups, respectively (see the figure). These hydrogen bonds lead to wavy layers. Six symmetry-related cations form annulated ring motifs (see the figure). The NH...O hydrogen-bond parameters are (N...O distances of 2.671(4) Å and 2.725(4) Å) in the expected ranges [27].

Between adjacent cationic, hydrogen-bonded theophyllinium layers the polyiodide anions are intercalated (see the figure). Each polyiodide I_{10}^{2-} moiety consists of two pentaiodide fragments, which show I–I distances which are in the typical range of single bonds to strong secondary interactions (I1–I2: 2.8787(4) Å; I2–I3: 2.9661(4) Å; I4–I5: 2.7636(6) Å; I3...I4: 3.3009(5) Å) [9]. The I5...I1' [$' = 1 - x, 1 - y, 1 - z$] distance of 3.6582(6) Å is in the typical range of weaker I...I interactions, but significantly shorter than any van der Waals distances in the various scales [30]. In the structure of the known cyclic I_{10}^{2-} , the four secondary I...I distances are crystallographically constrained and are at 3.441(1) Å [28] fairly accurate within the arithmetic mean of the distances derived for the title structure. Further significant I...I interactions can be ruled out as the corresponding iodine to iodine distances (>3.9 Å) are very close the sum of the van der Waals radii. The angles within the I_{10}^{2-} dianion are in accord with the expectations (I2–I1–I5': 77.41(1)°; I2–I3–I4: 98.22(1)°; I4–I3–I1–I5' [$' = 1 - x, 1 - y, 1 - z$]). Finally, it is worth mentioning that the hydrogen-bonded layers show a wavy shape fitting excellently with the needs of the neighboring polyiodide anions.

Within the Raman spectrum of the title compound the lines which are characteristic for the triiodide anion [31] are found at 108(vs) and 145(vs) cm⁻¹. For the solid phase of elemental iodine a I–I valence vibration is generally observed at 180 cm⁻¹ [32]. The Raman spectrum of the title compound shows a very strong line at 172 cm⁻¹. As the iodine molecule is weakly connected to two neighboring halogen bond donors,

a small shift of this line to lower wave numbers compared to elemental iodine is expected.

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