Crystal structure of 3-aminium-pyridin-1-ium bis(triiodide) dihydrate, $C_5H_{12}I_6N_2O_2$

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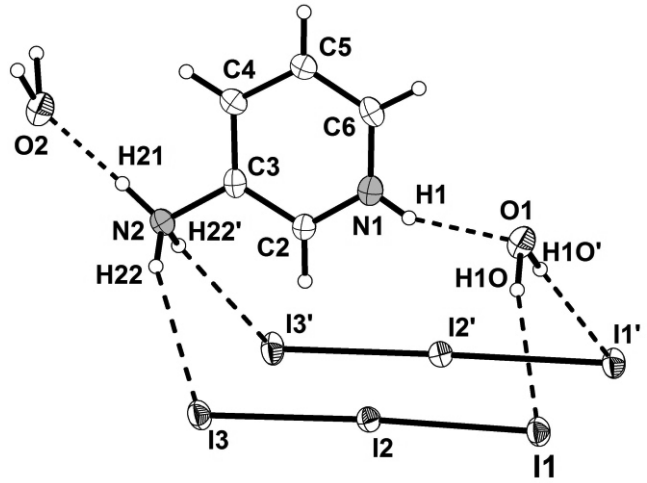

Abstract

$C_5H_{12}I_6N_2O_2$, orthorhombic, $Cmc2_1$ (no. 36), a = 11.58920(14) Å, b = 8.53178(11) Å, c = 17.4355(2) Å, V = 1724.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0155, $wR_{ref}(F^2)$ = 0.0342, T = 293 K.

Table 1. Data collection and handling.

Crystal:	orange needles, size 0.0160×0.0662×0.4609 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	108.01 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	69.25°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16385, 3655
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3526
$N(param)_{refined}$:	99
Programs:	SHELX [1], DIAMOND [2]

Source of material

3-Aminopyridine (0.16 g; 1.7 mmol) was dissolved in 10 ml concentrated hydroiodic acid yielding a brown mixture. This mixture was heated to 90 °C and then slowly cooled to room temperature. Within 3-4 days orange needles grew from this solution. **Elemental analysis** ($C_5H_{12}N_2I_6O_2$): Calcd., %: C, 6.72; H, 1.35; N, 3.13; I, 85.21. Found, %: C, 6.83; H, 1.28; N, 3.19; I, 85.02. For details on the elemental analytical methods used, see general procedures given in the literature [3, 4]. For the quantitative analysis of iodine alternatively aluminium was used as the reducing agent. The **Raman spectrum** (Bruker MULTIRAM spectrometer (Nd:YAG-Laser at 1064 nm; RT-InGaAs-detector; backscattering geometry)) shows two strong bands at 140 and 115 cm^{-1} indicating a slightly asymmetric triiodide anion [5].

Experimental details

One of the water molecules (O2/O2a) is disordered over two sites close to the mirror plane (ratio: 1/1; for clarity only one of the two half occupied positions is shown in the figure). Positional coordinates of hydrogen atoms involved in hydrogen bonds were refined using distance restraints. U_{iso} values for all hydrogen atoms were set to plausible values. The Flack parameter of 0.01(2) was determined using 1624 quotients [(I+)–(I–)]/[(I+)+(I–)] [6].

Discussion

Because of their biological activity there is a general interest in aminopyridines [7]. Especially the monoprotonated cations are known to inactivate K^+ channels reversibly [8]. Polyiodides are defined as extended ionic structures that fulfill the general formula $I_{(2m+n)}^{n-}$ (n = 1–4, m = integer). They are formally built from I^-, I_3^- and I_2 units and show a strong tendency to concatenate to extended motifs by halogen halogen interactions [9, 10]. Moreover there is a focus on diaminium and pyridinium iodides and corresponding polyiodides, as they have a significant influence on the redox chemistry in dye-sensitized solar cells [11, 12]. In the recent past, several groups have synthesized new polyiodides using stick-shaped cations whose lengths and shapes fit with the structures of the polyiodide anions [13-16]. In particular, the semi-flexible α,ω-diazaniumalkane dications have successfully been used for the synthesis of a series of new polyiodide salts [4, 17-20]. Nitrogen based heterocyclic cations are also known to template the synthesis of new polyiodides [21-23]. This contribution is part of our ongoing interest in the structural chemistry of iodide and polyiodide containing compounds. The asymmetric unit of the title structure is composed of one half of a dication, and one half water molecule (O1) both lying on a mirror plane; a second water molecule (O2) appears disordered over two positions near to a mirror plane and one triodide anion is located in a general position (see figure; ellipsoids are drawn at the 70 % probability level). All moieties are connected by N–H···I, O–H···I and N–H···O hydrogen bonds whose parameters are in accord with those reported in the literature [24]. Hydrogen bonded subunits are composed of one dication, two anions and two water molecules (Hydrogen bonds shown as dashed lines in the figure). The C–C and C–N bond lengths in the heterocyclic ring are in the range expected for a protonated aminopyridine (C–N: 1.342(7) and 1.350(7) Å; C–C: 1.369(7)-1.391(6) Å). The exocyclic C3–N2 distance has a value of 1.459(7) Å perfectly fitting with the appearance of a single bond. The I–I distances of the triiodide anion with values of 2.9520(4) and 2.9049(3) Å are also in the expected range of a slightly asymmetric triiodide anion confirming the findings of the Raman spectroscopy.

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	4*a*		½	0.803(8)	0.473(4)	0.017
H(2)	4*a*		½	0.8600	0.5967	0.014
H(4)	4*a*		½	0.3949	0.6328	0.015
H(5)	4*a*		½	0.3563	0.5007	0.015
H(6)	4*a*		½	0.5693	0.4198	0.016
H(21)	4*a*		½	0.572(4)	0.739(3)	0.016
H(22)	8*b*		0.440(2)	0.733(3)	0.717(3)	0.016
H(1O)	8*b*		0.564(4)	0.992(5)	0.383(3)	0.026
H(2O)	8*b*	0.5	0.419(2)	0.308(3)	0.784(3)	0.027
H(2OA)	8*b*	0.5	0.538(2)	0.308(3)	0.784(3)	0.027

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	8*b*		0.29627(2)	1.24309(3)	0.38284(2)	0.0161(1)	0.0163(1)	0.00975(9)	0.00111(7)	0.0001(1)	0.00163(8)
I(2)	8*b*		0.30559(2)	1.11864(3)	0.54070(2)	0.00997(8)	0.01223(8)	0.01061(8)	0.00022(7)	0.0002(1)	0.00010(7)
I(3)	8*b*		0.30193(2)	1.00621(3)	0.69795(2)	0.0164(1)	0.0182(1)	0.0096(1)	0.00421(7)	0.0007(1)	0.00152(8)
N(1)	4*a*		½	0.7300(5)	0.5022(3)	0.012(2)	0.016(2)	0.013(2)	0	0	0.002(2)
C(2)	4*a*		½	0.7579(5)	0.5781(3)	0.014(2)	0.012(2)	0.011(2)	0	0	0.001(2)
C(3)	4*a*		½	0.6331(6)	0.6272(3)	0.008(2)	0.016(2)	0.010(2)	0	0	0.001(2)
C(4)	4*a*		½	0.4798(6)	0.5994(3)	0.012(2)	0.013(2)	0.012(2)	0	0	–0.002(2)
C(5)	4*a*		½	0.4573(6)	0.5208(3)	0.011(2)	0.013(2)	0.013(2)	0	0	–0.001(2)
C(6)	4*a*		½	0.5839(6)	0.4726(3)	0.010(2)	0.019(2)	0.010(2)	0	0	–0.000(2)
N(2)	4*a*		½	0.6622(5)	0.7098(2)	0.017(2)	0.013(2)	0.010(2)	0	0	–0.001(1)
O(1)	4*a*		½	0.9197(4)	0.3788(2)	0.017(2)	0.017(2)	0.018(2)	0	0	0.004(2)
O(2)	8*b*	0.25	0.48	0.3740(5)	0.7801(3)	0.016(3)	0.018(2)	0.020(2)	0.000(4)	0.000(4)	0.007(2)
O(2A)	8*b*	0.25	0.52	0.3740(5)	0.7801(3)	0.016(3)	0.018(2)	0.020(2)	0.000(4)	0.000(4)	0.007(2)

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