research papers

Three-dimensional organic–inorganic hybrid sodium halide perovskite: $C_4H_{12}N_2 \cdot NaI_3$ and a hydrogen-bonded supramolecular three-dimensional network in $3C_4H_{12}N_2 \cdot NaI_4 \cdot 3I \cdot H_2O$

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The rational selection of ligands is vitally important in the construction of new organic–inorganic hybrid three-dimensional perovskite complexes. As part of an exploration of perovskite-type materials, two new Na–I compounds based on the piperazine ligand, namely poly[piperazinediium [tri-μ-iodido-sodium]], $\{(C_4H_{12}N_2)[NaI_3]\}_n$, **1**, and *catena*-poly[tris(piperazinediium) [[triiodidosodium]-μ-iodido] triiodide monohydrate], $\{(C_4H_{12}N_2)_3[NaI_4]I_3 \cdot H_2O\}_n$, **2**, have been synthesized by adjusting the stoichiometric ratio of sodium iodide and piperazine, and were characterized by single-crystal X-ray diffraction. In the crystal structures of **1** and **2**, each Na^I cation is linked to six I atoms, but the compounds show completely different configurations. In **1**, the structure includes a perovskite-like array of vertex-sharing NaI_6 octahedra stretching along the direction of the three axes, and each piperazinediium dication is enclosed in the NaI_3 perovskite cage. However, in **2**, each Na^I atom bridges a single I atom to form a one-dimensional linear chain, and complex intermolecular hydrogen bonds connect these one-dimensional chains into a three-dimensional supramolecular network.

1. Introduction

In recent decades, three-dimensional organic–inorganic hybrid perovskites have been of interest to researchers, not only for their remarkable structural variability and highly tunable properties, but also for their rich physical properties, such as superconductivity, ionic conductivity and ferroelectric related properties (Jin *et al.*, 2009; Saparov & Mitzi, 2016; Veldhuis *et al.*, 2016). Such hybrid perovskites have a simple generic formula of AMX_3 (A = organic cation, M = metal cation and X = halogen anion) and the structural characteristic of corner-sharing MX_6 octahedra. Among them, there have been a large number of reports on the halometallates of Pb^{II} and Sn^{II} ions because of their superior semiconducting properties, but related systems containing alkali metal halides are rare (Lee *et al.*, 2003; Shi *et al.*, 2017; Liao *et al.*, 2016b; Galkowski *et al.*, 2016; Yang *et al.*, 2015; Liao *et al.*, 2016a). To be precise, the first alkali metal halide perovskites, $RMCl_3$ (R = piperazine and M = K, Rb and Cs), were found less than ten years ago (Paton & Harrison, 2010). In recent years, due to the development of molecular ferroelectric materials (You *et al.*, 2017; Xu *et al.*, 2017; Liao *et al.*, 2017), three-dimensional alkali metal halide perovskites have attracted the attention of researchers again. Just last year, Xiong and co-workers reported two high-T_c three-dimensional perovskite ferroelectric materials, *i.e.* [3-ammoniopyrrolidinium]·$RbBr_3$ and

Table 1
Experimental details.

	1	2
Crystal data		
Chemical formula	$(C_4H_{12}N_2)[NaI_3]$	$(C_4H_{12}N_2)_3[NaI_4]I_3 \cdot H_2O$
M_r	491.85	1193.77
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/n$
Temperature (K)	293	293
a, b, c (Å)	9.842 (6), 9.309 (6), 12.538 (8)	12.186 (2), 22.828 (5), 12.214 (2)
β (°)	93.450 (9)	111.89 (3)
V (Å^3)	1146.6 (13)	3152.7 (12)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	8.16	6.92
Crystal size (mm)	$0.38 \times 0.28 \times 0.20$	$0.38 \times 0.28 \times 0.20$
Data collection		
Diffractometer		Rigaku SCXmini
Absorption correction		Multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min}, T_{max}	0.080, 0.195	0.112, 0.251
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3288, 1311, 1153	20677, 7234, 4432
R_{int}	0.083	0.075
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.648	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.165, 1.03	0.085, 0.142, 1.09
No. of reflections	1311	7234
No. of parameters	48	252
No. of restraints	0	2
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.80, −1.66	1.23, −1.05

Computer programs: *CrystalClear* (Rigaku, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg & Putz, 2005).

[*N*-methyl-1,4-diazoniabicyclo[2.2.2]octane]·RbI$_3$ (Pan *et al.*, 2017; Zhang *et al.*, 2017).

Following on from this work, we report the new three-dimensional organic–inorganic hybrid perovskite C$_4$H$_{12}$N$_2$·NaI$_3$ (**1**). In addition, considering that the dimensionality of three-dimensional perovskites can often be switched by alteration of the experimental conditions (*e.g.* CH$_3$NH$_3$·PbI$_3$; Jodlowski *et al.*, 2016), we obtained a new compound, *i.e.* 3C$_4$H$_{12}$N$_2$·NaI$_4$·3I·H$_2$O (**2**) with a peculiar one-dimensional [NaI$_5$]$^{4-}$ linear chain and a three-dimensional hydrogen-bonded supramolecular network by adjusting the stoichiometry of piperazine and sodium iodide.

2. Experimental

2.1. Synthesis and crystallization

2.1.1. Synthesis of C$_4$H$_{12}$N$_2$·NaI$_3$, (1). An aqueous solution (20 ml) of sodium iodide (1.49 g, 10 mmol) was added dropwise to an equimolar ratio of piperazine (0.86 g, 10 mmol) in water (5 ml) with stirring. The solution was then filtered to remove insoluble impurities. Yellow block-shaped crystals of **1** suitable for X-ray diffraction were obtained by slow volatilization of the aqueous solution at 330 K after 2 d.

2.1.2. Synthesis of 3C$_4$H$_{12}$N$_2$·NaI$_4$·3I·H$_2$O, (2). An aqueous solution (20 ml) of sodium iodide (0.75 g, 5 mmol) was added dropwise to an aqueous solution (5 ml) of piperazine (1.29 g, 15 mmol). The solution was stirred for 20 min

and then filtered to remove insoluble impurities. Yellow needle-shaped crystals of **2** were obtained by slow volatilization of the aqueous solution at 330 K after 2 d.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms bonded to O atoms were located from difference Fourier maps and refined with an
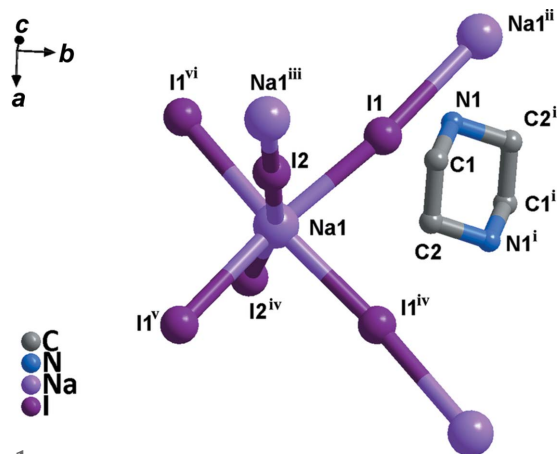

Figure 1
A view of the asymmetric unit in compound **1**. All H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1$, $-y + 2$, $-z + 1$; (ii) $x - \frac{1}{2}$, $y + \frac{1}{2}$, z; (iii) $-x + 1$, $-y + 1$, $-z + 1$; (iv) $-x + 1$, y, $-z + \frac{1}{2}$; (v) $x + \frac{1}{2}$, $y - \frac{1}{2}$, z; (vi) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$.]

Table 2
Selected geometric parameters (Å, °) for **1**.

C2—C1	1.504 (14)	Na1—I2	3.156 (2)
C2—N1^i	1.532 (14)	Na1—I1	3.325 (5)
N1—C1	1.456 (13)		
Na1—I1—Na1^{ii}	169.12 (12)	I2—Na1—I1^v	84.40 (9)
Na1^{iii}—I2—Na1	180.0	I2^{iv}—Na1—I1^{vi}	84.40 (9)
N1—C1—C2	111.6 (8)	I1^{vi}—Na1—I1^v	100.45 (19)
I2^{iv}—Na1—I1	101.40 (10)	I1—Na1—I1^v	169.12 (12)
I2—Na1—I1^{iv}	101.40 (10)	I1^{iv}—Na1—I1^{vi}	169.12 (12)
I2^{iv}—Na1—I2	166.6 (3)	I1^{iv}—Na1—I2	86.15 (18)
I2—Na1—I1	88.41 (8)	I1^{iv}—Na1—I1^v	87.29 (5)
I2^{iv}—Na1—I1^{iv}	88.41 (8)	I1—Na1—I1^{vi}	87.29 (5)
I2^{iv}—Na1—I1^v	87.06 (9)	C1—C2—N1^i	108.4 (9)
I2—Na1—I1^{vi}	87.06 (9)	C1—N1—C2^i	110.2 (8)

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

Table 3
Hydrogen-bond geometry (Å, °) for **1**.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1D···I1^i	0.97	3.12	3.937 (11)	143
C1—H1C···I2	0.97	3.23	3.914 (11)	129
C1—H1C···I1^{vii}	0.97	3.14	3.790 (10)	126
C2—H2B···I1^{viii}	0.97	3.17	3.930 (11)	136
C2—H2A···I1^{iv}	0.97	3.23	3.930 (13)	131
N1—H1B···I1^i	0.89	2.80	3.628 (10)	156
N1—H1A···I2^{ii}	0.89	3.11	3.677 (8)	123
N1—H1A···I1^{vii}	0.89	3.14	3.746 (8)	127

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

O—H distance restraint of 0.85 (1) Å. Other H atoms were placed in idealized positions and included as riding, with C—H = 0.97 Å (methylene) or N—H = 0.89 Å. $U_{iso}(H)$ values were set at $1.2U_{eq}(C,N)$ for methylene and piperazinediium, and at $1.5U_{eq}(O)$ of water H atoms.

3. Results and discussion

3.1. Structure of $C_4H_{12}N_2 \cdot NaI_3$, (1)

Compound **1** crystallizes in the monoclinic system (space group $C2/c$) and exhibits the three-dimensional perovskite framework. The asymmetry unit (Fig. 1) includes one Na^I cation located on a twofold axis, one half of a piperazinediium dication located about a centre of inversion and two iodide ions attached to the Na^I cation. As shown in Fig. 2, **1** is different from $C_4H_{12}N_2 \cdot KCl_3 \cdot H_2O$, due to the Na—I bond length being less than that of K—Cl (Table 2); the NaI$_6$ perovskite cage encloses one piperazinediium cation and prevents the entry of water molecules. In addition, the H atoms on the C and N atoms of piperazinediium form weak hydrogen bonds with the I atoms in the cage, resulting in
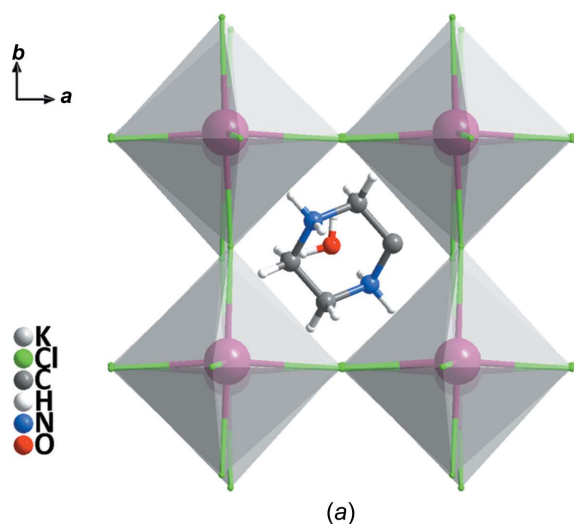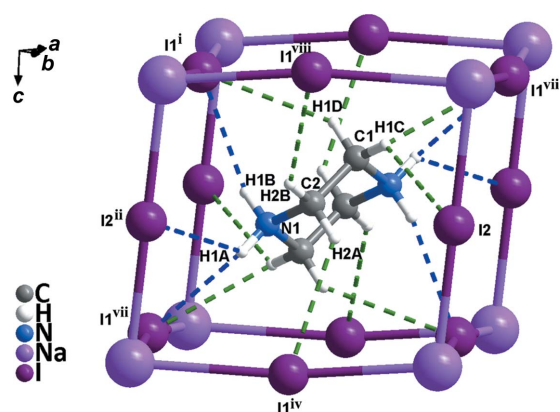

Figure 3
The hydrogen bonds (dashed lines) in **1** of the C and N atoms of the piperazinediium cation with the I atoms of the NaI$_6$ octahedra. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (iv) $-x + 1, y, -z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.]

significant octahedral tilting (Fig. 3). According to Glazer's 23 tilt system (Glazer, 1972, 1975), the octahedral tilting of compound **1** should belong to the 'a⁻b⁻b⁻' type. Detailed information of the C—H···I and N—H···I hydrogen bonds is given in Table 3. It can be seen from the packing diagram (Fig. 4) that the piperazinediium cations in the *ab* plane are
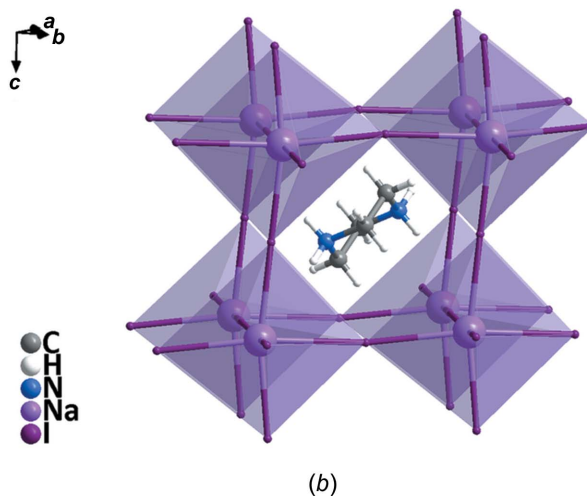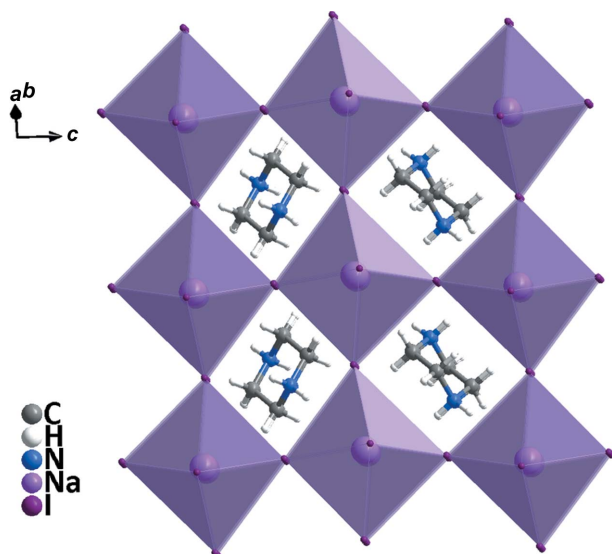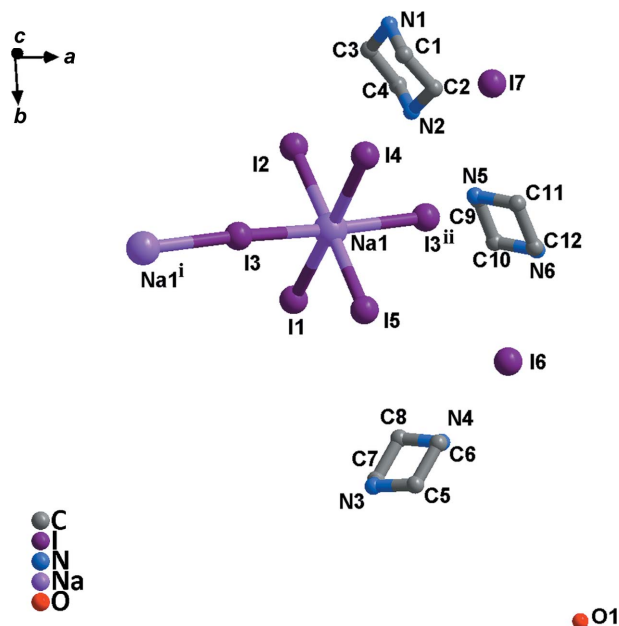

Figure 2
(*a*) A view of the three-dimensional perovskite cage of $C_4H_{12}N_2 \cdot KCl_3 \cdot H_2O$. (*b*) A view of the three-dimensional perovskite cage of compound **1**.

Table 4
Selected geometric parameters (Å, °) for **2**.

C1—N1	1.515 (14)	C9—C10	1.480 (18)
C1—C2	1.511 (18)	C10—N6	1.477 (13)
C2—N2	1.451 (16)	C11—C12	1.514 (17)
C3—N1	1.481 (14)	C11—N5	1.487 (13)
C3—C4	1.519 (16)	C12—N6	1.509 (13)
C4—N2	1.447 (17)	I1—Na1	3.419 (6)
C5—C6	1.527 (16)	I2—Na1	3.205 (5)
C5—N3	1.472 (13)	I3—Na1	3.381 (5)
C6—N4	1.452 (14)	I3—Na1^{i}	3.456 (5)
C7—C8	1.532 (16)	I4—Na1	3.515 (6)
C7—N3	1.475 (13)	I5—Na1	3.180 (5)
C8—N4	1.486 (14)	Na1—I3^{ii}	3.456 (5)
C9—N5	1.493 (14)		
C10—N6—C12	111.1 (9)	I3—Na1—I1	91.38 (13)
C10—C9—N5	110.8 (10)	I5—Na1—I4	94.12 (14)
C11—N5—C9	110.5 (8)	I5—Na1—I3^{ii}	92.63 (13)
C2—C1—N1	111.0 (10)	I5—Na1—I1	86.95 (13)
C3—N1—C1	109.5 (10)	I5—Na1—I3	88.73 (12)
C4—N2—C2	114.6 (12)	I5—Na1—I2	177.4 (2)
C5—N3—C7	112.7 (10)	N1—C3—C4	113.1 (10)
C6—N4—C8	111.8 (10)	N2—C4—C3	109.0 (11)
I1—Na1—I4	178.20 (17)	N2—C2—C1	108.3 (11)
I1—Na1—I3^{ii}	91.40 (13)	N3—C7—C8	110.8 (10)
I2—Na1—I4	84.32 (12)	N3—C5—C6	110.7 (10)
I2—Na1—I3^{ii}	89.46 (12)	N4—C8—C7	105.3 (11)
I2—Na1—I1	94.56 (14)	N4—C6—C5	106.4 (10)
I2—Na1—I3	89.12 (13)	N5—C11—C12	111.3 (10)
I3^{ii}—Na1—I4	90.00 (12)	N6—C12—C11	109.0 (10)
I3—Na1—I4	87.19 (13)	N6—C10—C9	110.8 (10)
I3—Na1—I3^{ii}	176.97 (18)	Na1—I3—Na1^{i}	176.87 (7)

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

Figure 5
A view of the asymmetric unit in compound **2**. All H atoms have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]
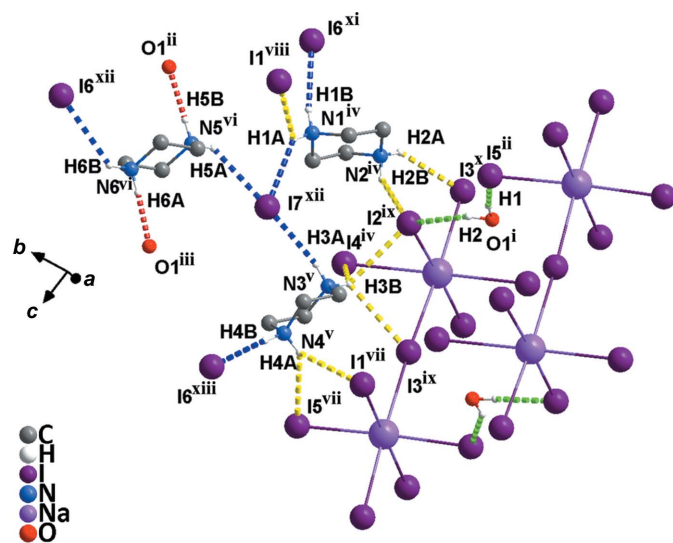
3.2. Structure of $3C_4H_{12}N_2 \cdot NaI_4 \cdot 3I \cdot H_2O$, (2)

Compound **2** crystallizes in the monoclinic system (space group $P2_1/n$) but displays a one-dimensional linear chain-like geometry. The asymmetry unit contains three whole piperazinediium cations, one lattice water molecule, two dissociated iodide ions and one Na atom in a glide plane coordinated with five iodide ions. As can be seen from Fig. 5, each Na atom is coordinated by six I atoms, and two Na atoms are bridged by one I atom and extended in an infinite manner along a hori-

arranged along the same direction; however, the piperazinediium cations along the c axis are arranged in a zigzag manner, *viz.* '\/\/'. In summary, compound **1** has the familiar three-dimensional perovskite framework structure, where the piperazinediium cations are confined in the cavities enclosed by corner-sharing NaI_6 octahedra and stabilized by C—H···I and N—H···I hydrogen bonds.

Figure 4
A packing view of compound **1**, showing the three-dimensional perovskite structure.

Table 5
Hydrogen-bond geometry (Å, °) for **2**.

D—H···A	D—H	H···A	D···A	D—H···A
N6^{vi}—H6B···I6^{vi}	0.89	2.99	3.626 (11)	130
N6^{vi}—H6A···O1^{iii}	0.89	1.97	2.856 (16)	175
N5^{vi}—H5B···O1^{ii}	0.89	1.99	2.878 (15)	178
N5^{vi}—H5A···I7^{xii}	0.89	2.83	3.557 (10)	140
N4^{v}—H4B···I6^{xiii}	0.89	2.55	3.440 (12)	175
N4^{v}—H4A···I5^{vii}	0.89	2.99	3.663 (13)	134
N4^{v}—H4A···I1^{vii}	0.89	3.25	3.881 (14)	130
N3^{v}—H3B···I4^{iv}	0.89	3.22	3.748 (11)	121
N3^{v}—H3B···I3^{ix}	0.89	3.22	3.767 (12)	122
N3^{v}—H3B···I2^{ix}	0.89	3.04	3.610 (11)	124
N3^{v}—H3A···I7^{xii}	0.89	2.68	3.543 (12)	165
N2^{iv}—H2B···I2^{ix}	0.89	3.14	3.867 (16)	140
N2^{iv}—H2A···I3^{ix}	0.89	2.70	3.405 (13)	138
N1^{iv}—H1B···I6^{xi}	0.89	2.62	3.496 (11)	169
N1^{iv}—H1A···I7^{xii}	0.89	2.92	3.613 (11)	136
N1^{iv}—H1A···I1^{viii}	0.89	3.32	3.804 (11)	117
O1^{i}—H2···I2^{ix}	0.85 (1)	2.68 (9)	3.471 (12)	155 (18)
O1^{i}—H1···I5^{ii}	0.85 (1)	2.69 (4)	3.501 (11)	161 (11)

Symmetry codes: (i) $x - 2, y, z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, -y + 2, -z + 1$; (iv) $-x - 1, -y + 1, -z + 1$; (v) $x - \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $x - 2, y + 1, z$; (vii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (viii) $x - \frac{3}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ix) $-x - 1, -y + 1, -z + 1$; (x) $-x - \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (xi) $x - \frac{5}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (xii) $x - 2, y + 1, z$; (xiii) $x - \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

Figure 6
A partial view of the crystal packing of compound **2**, showing the intermolecular N—H⋯I (blee and yellow dashed lines), N—H⋯O (red dashed lines) and O—H⋯I (green dashed lines) hydrogen bonds. All H atoms on C atoms have been omitted for clarity. [Symmetry codes: (i) $x - 2, y, z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, -y + 2, -z + 1$; (iv) $-x - 1, -y + 1, -z + 1$; (v) $x - \frac{3}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$; (vi) $x - 2, y + 1, z$; (vii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (viii) $x - \frac{3}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ix) $-x - 1, -y + 1, -z + 1$; (x) $-x - \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (xi) $x - \frac{5}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (xii) $x - 2, y + 1, z$; (xiii) $x - \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.]
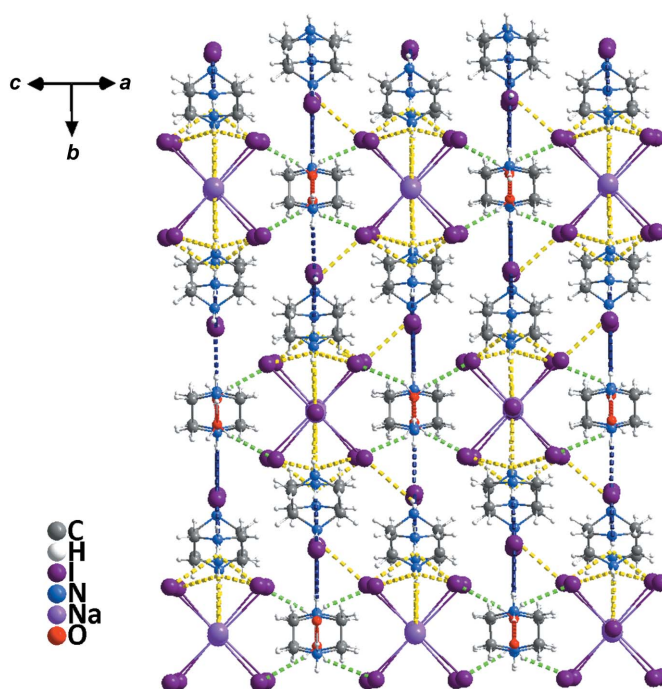
zontal direction, thus presenting a one-dimensional linear chain. As shown in Table 4, the length of the Na—I bonds are within the reasonable range 3.180 (5)–3.515 (6) Å and the I—Na—I angles are in the ranges 84.32 (14)–94.56 (16) and

Figure 7
The hydrogen bonds of the O—H⋯I (green dashed lines) and N—H⋯O (red dashed lines) types in **2**, showing the two-dimensional network on the *ac* plane.

Figure 8
A packing view of compound **2**, showing the three-dimensional hydrogen-bonded network.

176.97 (18)–178.20 (17)°. It is worth noting that there are very complex hydrogen bonds in compound **2**. These hydrogen bonds can be divided roughly into four types (Fig. 6): (i) piperazinediium N atoms act as donors and water O atoms act as acceptors in N—H⋯O hydrogen bonds (red dashed lines); (ii) water O atoms act as donors and I atoms in the metal halide chain act as acceptors in O—H⋯I hydrogen bonds (green dashed lines); (iii) piperazinediium N atoms act as donors and bridging I atoms act as acceptors in N—H⋯I hydrogen bonds (yellow dashed lines); (iv) piperazinediium N atoms act as donors and the free I atoms act as acceptors in N—H⋯I hydrogen bonds (blue dashed lines). Detailed information of the hydrogen bonds is given in Table 5. As shown in Fig. 7, the water H atoms form hydrogen bonds with the I atoms on the two sides of the NaI$_5$ chain (*i.e.* O1^i—H1⋯I5^{ii} and O1^i—H2⋯I2^{ix}; Table 5), thus forming a two-dimensional network on the *ac* plane. On the other hand, the free I atoms (*i.e.* I6 and I7) and the bridging I atoms (*i.e.* I3) form N—H⋯I hydrogen bonds with the H atoms of the piperazinediium N atoms, which extends the two-dimensional network into a three-dimensional hydrogen-bonded supramolecular network (Fig. 8).

4. Summary

Two new organic–inorganic hybrid sodium halides have been synthesized by adjusting the stoichiometric ratio of sodium iodide and piperazine. C$_4$H$_{12}$N$_2$·NaI$_3$, **1**, presents an interesting three-dimensional perovskite structure. However, compound 3C$_4$H$_{12}$N$_2$·NaI$_4$·3I·H$_2$O, **2**, features a singular three-dimensional hydrogen-bonded network. The different

structures of compounds **1** and **2** show that the stoichiometric ratio plays a key role in the synthesis of various frameworks.

References

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supporting information

Three-dimensional organic–inorganic hybrid sodium halide perovskite: $C_4H_{12}N_2$·NaI_3 and a hydrogen-bonded supramolecular three-dimensional network in $3C_4H_{12}N_2$·NaI_4·$3I$·H_2O

Xiao-Gang Chen, Ji-Xing Gao, Xiu-Ni Hua and Wei-Qiang Liao

Computing details

For both structures, data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear* (Rigaku, 2008); data reduction: *CrystalClear* (Rigaku, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) for C2C; *SHELXL2014*/7 (Sheldrick, 2015) for C. For both structures, molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

Poly[piperazinediium [tri-*µ*-iodido-sodium]] (C2C)

Crystal data

$(C_4H_{12}N_2)[NaI_3]$	$F(000) = 880$
$M_r = 491.85$	$D_x = 2.849$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.842$ (6) Å	Cell parameters from 1311 reflections
$b = 9.309$ (6) Å	$\theta = 3.0$–27.4°
$c = 12.538$ (8) Å	$\mu = 8.16$ mm^{-1}
$\beta = 93.450$ (9)°	$T = 293$ K
$V = 1146.6$ (13) Å^3	Thick sheet, pale yellow
$Z = 4$	$0.38 \times 0.28 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer	1311 independent reflections
	1153 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.083$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2008)	$\theta_{max} = 27.4°$, $\theta_{min} = 3.0°$
	$h = -12\rightarrow12$
$T_{min} = 0.080$, $T_{max} = 0.195$	$k = -12\rightarrow11$
3288 measured reflections	$l = -13\rightarrow16$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.165$	$w = 1/[\sigma^2(F_o^2) + (0.0991P)^2 + 35.0953P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1311 reflections	$(\Delta/\sigma)_{max} < 0.001$
48 parameters	$\Delta\rho_{max} = 1.80$ e Å^{-3}

$\Delta\rho_{min} = -1.66$ e Å^{-3}

Extinction correction: SHELXL2014
(Sheldrick, 2015)
Extinction coefficient: 0.0060 (7)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.6137 (11)	0.9015 (13)	0.5161 (10)	0.038 (2)
H2A	0.5962	0.8325	0.4589	0.045*
H2B	0.6967	0.8737	0.5564	0.045*
N1	0.3706 (8)	0.9477 (9)	0.5305 (7)	0.0297 (17)
H1A	0.3033	0.9475	0.5748	0.036*
H1B	0.3496	0.8858	0.4780	0.036*
C1	0.4967 (10)	0.9034 (11)	0.5879 (7)	0.030 (2)
H1C	0.4850	0.8082	0.6175	0.036*
H1D	0.5173	0.9690	0.6468	0.036*
Na1	0.5000	0.5394 (8)	0.2500	0.0416 (14)
I1	0.27208 (6)	0.80033 (7)	0.26933 (5)	0.0303 (3)
I2	0.5000	0.5000	0.5000	0.0300 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.031 (5)	0.040 (5)	0.043 (6)	0.011 (4)	0.007 (4)	0.016 (5)
N1	0.022 (4)	0.032 (4)	0.035 (4)	−0.005 (3)	0.007 (3)	0.008 (3)
C1	0.039 (5)	0.034 (5)	0.018 (4)	−0.003 (4)	0.004 (3)	0.012 (4)
Na1	0.053 (4)	0.046 (4)	0.027 (3)	0.000	0.008 (3)	0.000
I1	0.0337 (4)	0.0296 (4)	0.0278 (4)	−0.0045 (2)	0.0037 (3)	−0.0039 (2)
I2	0.0287 (5)	0.0368 (5)	0.0248 (5)	−0.0031 (3)	0.0036 (3)	−0.0013 (3)

Geometric parameters (Å, º)

C2—C1	1.504 (14)	C1—H1D	0.9700
C2—N1^i	1.532 (14)	Na1—I2^{ii}	3.156 (2)
C2—H2A	0.9700	Na1—I2	3.156 (2)
C2—H2B	0.9700	Na1—I1^{ii}	3.325 (5)
N1—C1	1.456 (13)	Na1—I1	3.325 (5)
N1—C2^i	1.532 (14)	Na1—I1^{iii}	3.479 (5)
N1—H1A	0.8900	Na1—I1^{iv}	3.479 (5)
N1—H1B	0.8900	I1—Na1^v	3.479 (5)
C1—H1C	0.9700	I2—Na1^{vi}	3.156 (2)
Na1—I1—Na1^v	169.12 (12)	C1—C2—N1^i	108.4 (9)

Na1^{vi}—I2—Na1	180.0	C1—C2—H2A	110.0
N1—C1—C2	111.6 (8)	N1^{i}—C2—H2A	110.0
I2^{ii}—Na1—I1	101.40 (10)	C1—C2—H2B	110.0
I2—Na1—I1^{ii}	101.40 (10)	N1^{i}—C2—H2B	110.0
I2^{ii}—Na1—I2	166.6 (3)	H2A—C2—H2B	108.4
I2—Na1—I1	88.41 (8)	C1—N1—C2^{i}	110.2 (8)
I2^{ii}—Na1—I1^{ii}	88.41 (8)	C1—N1—H1A	109.6
I2^{ii}—Na1—I1^{iv}	87.06 (9)	C2^{i}—N1—H1A	109.6
I2—Na1—I1^{iii}	87.06 (9)	C1—N1—H1B	109.6
I2—Na1—I1^{iv}	84.40 (9)	C2^{i}—N1—H1B	109.6
I2^{ii}—Na1—I1^{iii}	84.40 (9)	H1A—N1—H1B	108.1
I1^{iii}—Na1—I1^{iv}	100.45 (19)	N1—C1—H1C	109.3
I1—Na1—I1^{iv}	169.12 (12)	C2—C1—H1C	109.3
I1^{ii}—Na1—I1^{iii}	169.12 (12)	N1—C1—H1D	109.3
I1^{ii}—Na1—I1	86.15 (18)	C2—C1—H1D	109.3
I1^{ii}—Na1—I1^{iv}	87.29 (5)	H1C—C1—H1D	108.0
I1—Na1—I1^{iii}	87.29 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*D*···I1^{i}	0.97	3.12	3.937 (11)	143
C1—H1*C*···I2	0.97	3.23	3.914 (11)	129
C1—H1*C*···I1^{vii}	0.97	3.14	3.790 (10)	126
C2—H2*B*···I1^{viii}	0.97	3.17	3.930 (11)	136
C2—H2*A*···I1^{ii}	0.97	3.23	3.930 (13)	131
N1—H1*B*···I1^{i}	0.89	2.80	3.628 (10)	156
N1—H1*A*···I2^{v}	0.89	3.11	3.677 (8)	123
N1—H1*A*···I1^{vii}	0.89	3.14	3.746 (8)	127

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1; (ii) −*x*+1, *y*, −*z*+1/2; (v) *x*−1/2, *y*+1/2, *z*; (vii) −*x*+1/2, −*y*+3/2, −*z*+1; (viii) *x*+1/2, −*y*+3/2, *z*+1/2.

catena-**Poly[tris(piperazinediium) [*μ*-iodido-triiodidosodium] triiodide monohydrate] (C)**

Crystal data

(C$_4$H$_{12}$N$_2$)$_3$[NaI$_4$]I$_3$·H$_2$O	*F*(000) = 2168
M$_r$ = 1193.77	*D*$_x$ = 2.515 Mg m$^{−3}$
Monoclinic, *P*2$_1$/*n*	Mo *Kα* radiation, *λ* = 0.71073 Å
a = 12.186 (2) Å	Cell parameters from 7234 reflections
b = 22.828 (5) Å	*θ* = 3.0–27.5°
c = 12.214 (2) Å	*μ* = 6.92 mm$^{−1}$
β = 111.89 (3)°	*T* = 293 K
V = 3152.7 (12) Å^3	Bar, pale yellow
Z = 4	0.38 × 0.28 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer	Absorption correction: multi-scan (CrystalClear; Rigaku, 2008)
ω scans	*T*$_{min}$ = 0.112, *T*$_{max}$ = 0.251

20677 measured reflections
7234 independent reflections
4432 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$

$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -12 \rightarrow 15$
$k = -29 \rightarrow 29$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.085$
$wR(F^2) = 0.142$
$S = 1.09$
7234 reflections
252 parameters
2 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 33.3838P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.024$
$\Delta\rho_{max} = 1.23$ e Å^{-3}
$\Delta\rho_{min} = -1.05$ e Å^{-3}
Extinction correction: SHELXL2014
(Sheldrick, 2015)
Extinction coefficient: 0.0060 (7)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5220 (12)	0.0196 (6)	0.6547 (11)	0.056 (4)
H1C	0.5688	−0.0046	0.6232	0.068*
H1D	0.4545	0.0342	0.5889	0.068*
C2	0.5959 (12)	0.0706 (6)	0.7215 (13)	0.059 (4)
H2C	0.6662	0.0564	0.7846	0.071*
H2D	0.6203	0.0944	0.6689	0.071*
C3	0.4140 (10)	0.0205 (6)	0.7881 (11)	0.051 (4)
H3C	0.3933	−0.0026	0.8442	0.061*
H3D	0.3411	0.0335	0.7270	0.061*
C4	0.4843 (12)	0.0737 (6)	0.8507 (12)	0.060 (4)
H4C	0.4349	0.0990	0.8768	0.072*
H4D	0.5514	0.0614	0.9195	0.072*
C5	0.5148 (9)	0.5834 (5)	0.1450 (10)	0.042 (3)
H5C	0.5565	0.6192	0.1791	0.050*
H5D	0.5100	0.5809	0.0640	0.050*
C6	0.5831 (10)	0.5308 (6)	0.2146 (10)	0.048 (3)
H6C	0.5446	0.4946	0.1790	0.058*
H6D	0.6632	0.5306	0.2159	0.058*
C7	0.3947 (11)	0.5840 (6)	0.2674 (9)	0.046 (3)
H7A	0.3138	0.5823	0.2638	0.056*
H7B	0.4304	0.6197	0.3085	0.056*
C8	0.4636 (10)	0.5310 (6)	0.3357 (10)	0.051 (4)
H8A	0.4668	0.5313	0.4162	0.061*
H8B	0.4267	0.4948	0.2981	0.061*

C9	0.7130 (11)	0.2167 (6)	0.5849 (11)	0.054 (4)
H9A	0.6342	0.2104	0.5848	0.065*
H9B	0.7667	0.1902	0.6418	0.065*
C10	0.7496 (11)	0.2779 (6)	0.6197 (11)	0.052 (4)
H10A	0.6930	0.3046	0.5657	0.062*
H10B	0.7504	0.2851	0.6983	0.062*
C11	0.8322 (10)	0.2155 (6)	0.4619 (11)	0.050 (4)
H11A	0.8300	0.2085	0.3828	0.060*
H11B	0.8890	0.1887	0.5149	0.060*
C12	0.8713 (11)	0.2779 (6)	0.4977 (10)	0.048 (3)
H12A	0.9508	0.2837	0.4996	0.058*
H12B	0.8189	0.3050	0.4409	0.058*
H1	0.984 (8)	0.803 (4)	0.168 (8)	0.03 (3)*
H2	0.940 (14)	0.810 (4)	0.233 (13)	0.12 (7)*
I1	0.16282 (7)	0.35776 (4)	0.65969 (7)	0.0437 (2)
I2	0.19192 (8)	0.14533 (4)	0.64746 (8)	0.0530 (3)
I3	0.04389 (7)	0.24624 (3)	0.29429 (7)	0.0400 (2)
I4	0.41057 (7)	0.14436 (4)	0.41939 (7)	0.0459 (2)
I5	0.38048 (8)	0.35852 (4)	0.42790 (8)	0.0544 (3)
I6	0.77355 (7)	0.43764 (4)	0.52414 (7)	0.0412 (2)
I7	0.77778 (7)	0.05265 (4)	0.52459 (7)	0.0420 (2)
N1	0.4792 (9)	−0.0172 (5)	0.7341 (9)	0.055 (3)
H1A	0.4320	−0.0455	0.6923	0.066*
H1B	0.5407	−0.0337	0.7904	0.066*
N2	0.5249 (12)	0.1051 (5)	0.7700 (13)	0.096 (5)
H2A	0.5673	0.1359	0.8076	0.116*
H2B	0.4622	0.1188	0.7107	0.116*
N3	0.3948 (9)	0.5853 (5)	0.1468 (9)	0.057 (3)
H3A	0.3537	0.5548	0.1066	0.068*
H3B	0.3587	0.6178	0.1107	0.068*
N4	0.5841 (10)	0.5368 (5)	0.3333 (10)	0.072 (4)
H4A	0.6138	0.5716	0.3621	0.086*
H4B	0.6309	0.5094	0.3793	0.086*
N5	0.7133 (7)	0.2041 (4)	0.4651 (7)	0.033 (2)
H5A	0.6936	0.1668	0.4466	0.040*
H5B	0.6599	0.2265	0.4119	0.040*
N6	0.8684 (8)	0.2893 (4)	0.6183 (8)	0.042 (3)
H6A	0.9210	0.2664	0.6711	0.050*
H6B	0.8884	0.3264	0.6386	0.050*
Na1	0.2893 (5)	0.2536 (2)	0.5431 (5)	0.0628 (15)
O1	0.9568 (9)	0.7784 (5)	0.2044 (9)	0.055 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.083 (10)	0.052 (9)	0.041 (8)	−0.015 (8)	0.031 (8)	−0.003 (7)
C2	0.054 (8)	0.062 (10)	0.081 (11)	0.004 (8)	0.049 (8)	0.019 (8)
C3	0.047 (7)	0.055 (9)	0.068 (9)	−0.021 (7)	0.043 (7)	−0.032 (7)

C4	0.069 (10)	0.060 (10)	0.069 (10)	−0.010 (8)	0.047 (9)	−0.013 (8)
C5	0.037 (7)	0.048 (8)	0.045 (8)	0.001 (6)	0.021 (6)	0.002 (6)
C6	0.037 (7)	0.069 (10)	0.039 (8)	0.005 (7)	0.015 (6)	−0.015 (7)
C7	0.054 (8)	0.063 (10)	0.025 (7)	0.023 (7)	0.018 (6)	0.008 (6)
C8	0.041 (7)	0.082 (11)	0.030 (7)	0.004 (7)	0.015 (6)	−0.005 (7)
C9	0.045 (8)	0.069 (10)	0.056 (9)	−0.016 (7)	0.029 (7)	−0.012 (8)
C10	0.054 (8)	0.063 (10)	0.048 (8)	−0.019 (7)	0.030 (7)	−0.023 (7)
C11	0.048 (8)	0.057 (9)	0.058 (9)	−0.018 (7)	0.033 (7)	−0.022 (7)
C12	0.056 (8)	0.055 (9)	0.040 (8)	−0.006 (7)	0.024 (7)	−0.004 (6)
I1	0.0415 (5)	0.0397 (5)	0.0435 (5)	−0.0021 (4)	0.0084 (4)	−0.0001 (4)
I2	0.0637 (6)	0.0488 (6)	0.0507 (6)	0.0036 (5)	0.0260 (5)	−0.0005 (4)
I3	0.0472 (5)	0.0315 (4)	0.0473 (5)	0.0007 (4)	0.0247 (4)	0.0015 (4)
I4	0.0398 (5)	0.0429 (5)	0.0491 (5)	−0.0039 (4)	0.0096 (4)	0.0039 (4)
I5	0.0668 (6)	0.0471 (6)	0.0530 (6)	−0.0021 (5)	0.0268 (5)	−0.0028 (5)
I6	0.0399 (4)	0.0455 (5)	0.0373 (5)	0.0053 (4)	0.0134 (4)	0.0055 (4)
I7	0.0405 (5)	0.0433 (5)	0.0419 (5)	0.0023 (4)	0.0150 (4)	0.0036 (4)
N1	0.059 (7)	0.044 (7)	0.056 (7)	−0.007 (6)	0.015 (6)	−0.004 (6)
N2	0.104 (11)	0.034 (8)	0.149 (14)	−0.027 (8)	0.046 (11)	−0.022 (9)
N3	0.066 (7)	0.044 (7)	0.065 (8)	0.015 (6)	0.030 (6)	0.013 (6)
N4	0.065 (8)	0.077 (9)	0.060 (8)	0.032 (7)	0.008 (7)	0.015 (7)
N5	0.028 (5)	0.035 (6)	0.031 (6)	−0.007 (4)	0.004 (4)	−0.011 (4)
N6	0.043 (6)	0.037 (6)	0.051 (7)	−0.023 (5)	0.025 (5)	−0.020 (5)
Na1	0.068 (3)	0.052 (3)	0.069 (4)	−0.006 (3)	0.026 (3)	0.014 (3)
O1	0.068 (6)	0.047 (6)	0.065 (7)	−0.001 (5)	0.040 (6)	0.001 (5)

Geometric parameters (Å, º)

C1—N1	1.515 (14)	C4—H4D	0.9700
C1—C2	1.511 (18)	C5—H5C	0.9700
C2—N2	1.451 (16)	C5—H5D	0.9700
C3—N1	1.481 (14)	C6—H6C	0.9700
C3—C4	1.519 (16)	C6—H6D	0.9700
C4—N2	1.447 (17)	C7—H7A	0.9700
C5—C6	1.527 (16)	C7—H7B	0.9700
C5—N3	1.472 (13)	C8—H8A	0.9700
C6—N4	1.452 (14)	C8—H8B	0.9700
C7—C8	1.532 (16)	C9—H9A	0.9700
C7—N3	1.475 (13)	C9—H9B	0.9700
C8—N4	1.486 (14)	C10—H10A	0.9700
C9—N5	1.493 (14)	C10—H10B	0.9700
C9—C10	1.480 (18)	C11—H11A	0.9700
C10—N6	1.477 (13)	C11—H11B	0.9700
C11—C12	1.514 (17)	C12—H12A	0.9700
C11—N5	1.487 (13)	C12—H12B	0.9700
C12—N6	1.509 (13)	N1—H1A	0.8900
I1—Na1	3.419 (6)	N1—H1B	0.8900
I2—Na1	3.205 (5)	N2—H2A	0.8900
I3—Na1	3.381 (5)	N2—H2B	0.8900

I3—Na1ⁱ	3.456 (5)	N3—H3A	0.8900
I4—Na1	3.515 (6)	N3—H3B	0.8900
I5—Na1	3.180 (5)	N4—H4A	0.8900
Na1—I3ⁱⁱ	3.456 (5)	N4—H4B	0.8900
C1—H1C	0.9700	N5—H5A	0.8900
C1—H1D	0.9700	N5—H5B	0.8900
C2—H2C	0.9700	N6—H6A	0.8900
C2—H2D	0.9700	N6—H6B	0.8900
C3—H3C	0.9700	O1—H1	0.849 (10)
C3—H3D	0.9700	O1—H2	0.850 (10)
C4—H4C	0.9700		
C10—N6—C12	111.1 (9)	H6C—C6—H6D	108.6
C10—C9—N5	110.8 (10)	N3—C7—H7A	109.5
C11—N5—C9	110.5 (8)	C8—C7—H7A	109.5
C2—C1—N1	111.0 (10)	N3—C7—H7B	109.5
C3—N1—C1	109.5 (10)	C8—C7—H7B	109.5
C4—N2—C2	114.6 (12)	H7A—C7—H7B	108.1
C5—N3—C7	112.7 (10)	N4—C8—H8A	110.7
C6—N4—C8	111.8 (10)	C7—C8—H8A	110.7
I1—Na1—I4	178.20 (17)	N4—C8—H8B	110.7
I1—Na1—I3ⁱⁱ	91.40 (13)	C7—C8—H8B	110.7
I2—Na1—I4	84.32 (12)	H8A—C8—H8B	108.8
I2—Na1—I3ⁱⁱ	89.46 (12)	C10—C9—H9A	109.5
I2—Na1—I1	94.56 (14)	N5—C9—H9A	109.5
I2—Na1—I3	89.12 (13)	C10—C9—H9B	109.5
I3ⁱⁱ—Na1—I4	90.00 (12)	N5—C9—H9B	109.5
I3—Na1—I4	87.19 (13)	H9A—C9—H9B	108.1
I3—Na1—I3ⁱⁱ	176.97 (18)	N6—C10—H10A	109.5
I3—Na1—I1	91.38 (13)	C9—C10—H10A	109.5
I5—Na1—I4	94.12 (14)	N6—C10—H10B	109.5
I5—Na1—I3ⁱⁱ	92.63 (13)	C9—C10—H10B	109.5
I5—Na1—I1	86.95 (13)	H10A—C10—H10B	108.1
I5—Na1—I3	88.73 (12)	N5—C11—H11A	109.4
I5—Na1—I2	177.4 (2)	C12—C11—H11A	109.4
N1—C3—C4	113.1 (10)	N5—C11—H11B	109.4
N2—C4—C3	109.0 (11)	C12—C11—H11B	109.4
N2—C2—C1	108.3 (11)	H11A—C11—H11B	108.0
N3—C7—C8	110.8 (10)	N6—C12—H12A	109.9
N3—C5—C6	110.7 (10)	C11—C12—H12A	109.9
N4—C8—C7	105.3 (11)	N6—C12—H12B	109.9
N4—C6—C5	106.4 (10)	C11—C12—H12B	109.9
N5—C11—C12	111.3 (10)	H12A—C12—H12B	108.3
N6—C12—C11	109.0 (10)	C3—N1—H1A	109.8
N6—C10—C9	110.8 (10)	C1—N1—H1A	109.8
Na1—I3—Na1ⁱ	176.87 (7)	C3—N1—H1B	109.8
C2—C1—H1C	109.4	C1—N1—H1B	109.8
N1—C1—H1C	109.4	H1A—N1—H1B	108.2

C2—C1—H1D	109.4	C4—N2—H2A	108.6
N1—C1—H1D	109.4	C2—N2—H2A	108.6
H1C—C1—H1D	108.0	C4—N2—H2B	108.6
N2—C2—H2C	110.0	C2—N2—H2B	108.6
C1—C2—H2C	110.0	H2A—N2—H2B	107.6
N2—C2—H2D	110.0	C5—N3—H3A	109.1
C1—C2—H2D	110.0	C7—N3—H3A	109.1
H2C—C2—H2D	108.4	C5—N3—H3B	109.1
N1—C3—H3C	108.9	C7—N3—H3B	109.1
C4—C3—H3C	108.9	H3A—N3—H3B	107.8
N1—C3—H3D	108.9	C6—N4—H4A	109.3
C4—C3—H3D	108.9	C8—N4—H4A	109.3
H3C—C3—H3D	107.8	C6—N4—H4B	109.3
N2—C4—H4C	109.9	C8—N4—H4B	109.3
C3—C4—H4C	109.9	H4A—N4—H4B	107.9
N2—C4—H4D	109.9	C11—N5—H5A	109.6
C3—C4—H4D	109.9	C9—N5—H5A	109.6
H4C—C4—H4D	108.3	C11—N5—H5B	109.6
N3—C5—H5C	109.5	C9—N5—H5B	109.6
C6—C5—H5C	109.5	H5A—N5—H5B	108.1
N3—C5—H5D	109.5	C10—N6—H6A	109.4
C6—C5—H5D	109.5	C12—N6—H6A	109.4
H5C—C5—H5D	108.1	C10—N6—H6B	109.4
N4—C6—H6C	110.5	C12—N6—H6B	109.4
C5—C6—H6C	110.5	H6A—N6—H6B	108.0
N4—C6—H6D	110.5	H1—O1—H2	82 (10)
C5—C6—H6D	110.5		
N1—C1—C2—N2	−57.7 (15)	C1—C2—N2—C4	60.1 (16)
N1—C3—C4—N2	53.3 (17)	C6—C5—N3—C7	54.3 (14)
N3—C5—C6—N4	−57.8 (13)	C8—C7—N3—C5	−54.8 (14)
N3—C7—C8—N4	57.5 (13)	C5—C6—N4—C8	66.0 (14)
N5—C9—C10—N6	−58.0 (14)	C7—C8—N4—C6	−65.9 (13)
N5—C11—C12—N6	56.2 (13)	C12—C11—N5—C9	−56.9 (13)
C4—C3—N1—C1	−53.5 (15)	C10—C9—N5—C11	57.2 (14)
C2—C1—N1—C3	55.7 (14)	C9—C10—N6—C12	58.3 (14)
C3—C4—N2—C2	−57.2 (16)	C11—C12—N6—C10	−56.7 (13)

Symmetry codes: (i) *x*−1/2, −*y*+1/2, *z*−1/2; (ii) *x*+1/2, −*y*+1/2, *z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6vi[iii]—H6*B*···I6vi[iii]	0.89	2.99	3.626 (11)	130
N6vi[iii]—H6*A*···O1iii[iv]	0.89	1.97	2.856 (16)	175
N5vi[iii]—H5*B*···O1ii[v]	0.89	1.99	2.878 (15)	178
N5vi[iii]—H5*A*···I7xii[iii]	0.89	2.83	3.557 (10)	140
N4v[vi]—H4*B*···I6xiii[vii]	0.89	2.55	3.440 (12)	175

N4v[vi]—H4*A*···I5vii[viii]	0.89	2.99	3.663 (13)	134
N4v[vi]—H4*A*···I1vii[viii]	0.89	3.25	3.881 (14)	130
N3v[vi]—H3*B*···I4iv[ix]	0.89	3.22	3.748 (11)	121
N3v[vi]—H3*B*···I3ix[ix]	0.89	3.22	3.767 (12)	122
N3v[vi]—H3*B*···I2ix[ix]	0.89	3.04	3.610 (11)	124
N3v[vi]—H3*A*···I7xii[iii]	0.89	2.68	3.543 (12)	165
N2iv[ix]—H2*B*···I2ix[ix]	0.89	3.14	3.867 (16)	140
N2iv[ix]—H2*A*···I3ix[ix]	0.89	2.70	3.405 (13)	138
N1iv[ix]—H1*B*···I6xi[x]	0.89	2.62	3.496 (11)	169
N1iv[ix]—H1*A*···I7xii[iii]	0.89	2.92	3.613 (11)	136
N1iv[ix]—H1*A*···I1viii[xi]	0.89	3.32	3.804 (11)	117
O1i[xii]—H2···I2ix[ix]	0.85 (1)	2.68 (9)	3.471 (12)	155 (18)
O1i[xii]—H1···I5ii[v]	0.85 (1)	2.69 (4)	3.501 (11)	161 (11)

Symmetry codes: (iii) *x*−2, *y*+1, *z*; (iv) −*x*, −*y*+2, −*z*+1; (v) −*x*−1/2, *y*+1/2, −*z*+1/2; (vi) *x*−3/2, −*y*+1/2, *z*+1/2; (vii) *x*−3/2, −*y*+3/2, *z*+1/2; (viii) −*x*−1/2, *y*+1/2, −*z*+3/2; (ix) −*x*−1, −*y*+1, −*z*+1; (x) *x*−5/2, −*y*+3/2, *z*−1/2; (xi) *x*−3/2, −*y*+1/2, *z*−1/2; (xii) *x*+2, *y*, *z*.