metal-organic papers

catena-Poly[N-[4-(1H-benzimidazol-3-yl)butyl]-benzimidazolium [[diiodobismuthate(III)]-di-μ_2-iodo]]

Yun-Yin Niu,[a] Ning Zhang,[a] Hong-Wei Hou[a] and Seik Weng Ng[b]*

[a]Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study

T = 291 K

Mean σ(C–C) = 0.009 Å

Disorder in main residue

R factor = 0.029

wR factor = 0.070

Data-to-parameter ratio = 22.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $\{(C_{18}H_{19}N_4)[BiI_4]\}_n$, the organic cation is protonated on one of the two tertiary imino N atoms; the cation has inversion symmetry, involving disorder of this H atom. Adjacent cations are linked by a disorder N—H···N hydrogen bond, forming a chain that runs along the a axis of the monoclinic unit cell. The anion exists as a polymeric chain that propogates along the c axis; the Bi atom lies on a special position of site symmetry 2.

Comment

The 1,4-bis(1H-benzimidazoyl-1)butane N-heterocycle affords adducts that display third-order non-linear optical activity with some transition metal salts (Chang *et al.*, 2005; Xiao *et al.*, 2004). In its reaction with bismuth(III) iodide, the same reagent is protonated, resulting in the title compound, (I). In this salt-like material (Fig. 1), the cation does not interact with Bi; instead, it interacts with adjacent cations to form a chain *via* a disordered N—H···N/N···H—N hydrogen bond (Table 2). The $[BiI_4]^-$ anion auto-associates through iodine bridges, resulting in the formation of a linear chain that runs approximately at right angles to the organic chain.

(I)
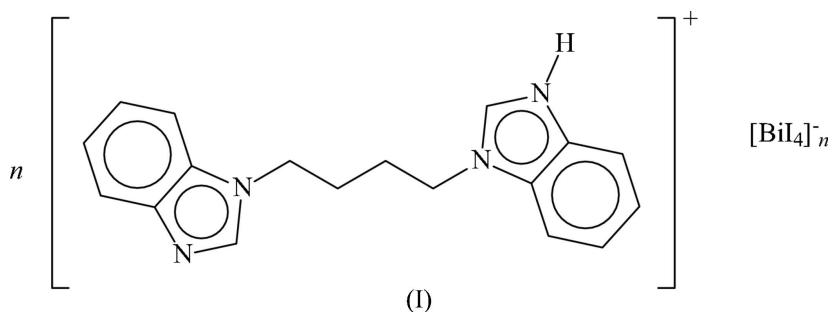
In the polyanionic chain, the octahedral Bi geometry arises from bridging by two of the I atoms; the I atom that is not involved in bridging is much closer to the Bi atom (Table 1). The BiI_6 octahedra are connected through only one edge. Such edge-sharing octahedra are uncommon; one example is bis(ethylenedithio)tetrathiafulvalenium tetraiodo-bismuthate (Geiser *et al.*, 1990).

Experimental

The heterocyclic reagent was synthesized as described previously by Xie *et al.* (2000). Bismuth(III) iodide (0.059 g, 0.1 mmol) dissolved in tetrahydrofuran (10 ml) was reacted with the organic reagent (0.058 g, 0.2 mmol) dissolved in methanol (10 ml). The clear solution was set aside for several hours for pink crystals of (I) to separate in about 20% yield.

Crystal data

(C$_{18}$H$_{19}$N$_4$)[BiI$_4$]
$M_r = 1007.95$
Monoclinic, $C2/c$
$a = 19.900$ (3) Å
$b = 16.809$ (2) Å
$c = 7.660$ (2) Å
$\beta = 106.23$ (2)°
$V = 2460.2$ (8) Å^3
$Z = 4$

$D_x = 2.721$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10565 reflections
$\theta = 3.2$–27.5°
$\mu = 12.20$ mm^{-1}
$T = 291$ (2) K
Prism, pink
$0.20 \times 0.18 \times 0.12$ mm

Data collection

Rigaki R-AXIS RAPID IP diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1995)
$T_{min} = 0.072$, $T_{max} = 0.322$
11767 measured reflections

2806 independent reflections
2608 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 25$
$k = -21 \rightarrow 21$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.070$
$S = 1.05$
2806 reflections
123 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 14.444P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.02$ e Å^{-3}
$\Delta\rho_{min} = -1.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Bi1—I1	3.0785 (7)	Bi1—I2	2.9151 (6)
Bi1—I1^i	3.2645 (6)		
I2—Bi1—I2^{ii}	92.87 (3)	Bi1—I1—Bi1^i	92.61 (2)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$n\cdots$N1^{iii}	0.86	1.87	2.71 (1)	165

Symmetry code: (iii) $-x, y, -z-\frac{1}{2}$.

H atoms were placed at calculated positions (C—H = 0.93 Å for the aromatic H atoms and 0.97 Å for the aliphatic H atoms; N—H = 0.86 Å) and were refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C,N)$. Crystal symmetry results in the H atom associated with N1 being disordered over two positions, resulting in superimposed N—H$\cdots$N and N$\cdots$H—N hydrogen bonds. Its fractional site occupancy was fixed at 0.5. The highest and deepest difference peaks are about 1 Å from I2.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC,
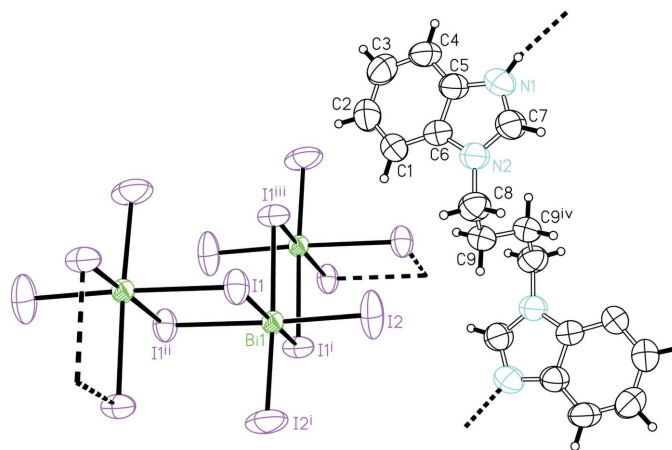

Figure 1
View of a portion of the polymeric structure of (I). Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radii. Dashed lines represent bonds to adjacent symmetry-generated atoms in the anion, and hydrogen bonds in the cation. Only one position for H1n is shown. [Symmetry codes: (i) $1-x, y, \frac{3}{2}-z$; (ii) $1-x, 1-y, 2-z$; (iii) $x, 1-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, \frac{3}{2}-y, -z$.]

2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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