Crystal structure of tris(tetramethylammonium) dibismuth nonaiodide, $[N(CH_3)_4]_3Bi_2I_9$

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Experimental details

The hydrogen atoms were not localized.

Discussion

The crystal structure of $[N(CH_3)_4]_3Bi_2I_9$ is characterized by two face-sharing BiI_6 octahedra forming dimeric $[Bi_2I_9]^{3-}$ anions as in $Cs_3Bi_2I_9$ [2,3]. Bond lengths are $d(Bi—I)_{endo} = 3.27(1)$ Å and $d(Bi—I)_{exo} = 2.95(1)$ Å. The unidirectional orientation of the tetramethylammonium cations causes a symmetry reduction compared to $Cs_3Bi_2I_9$ ($P6_3/mmc$). Bond lengths and angles in the cation are: $d(N—C) = 1.45$ Å – $1.47(2)$ Å, $\angle C—N—C = 104^\circ$ – $114(2)^\circ$.

Table 1. Data collection and handling.

Crystal:	orange hexagonal plate, size $0.08 \times 0.20 \times 0.20$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	158.08 cm $^{-1}$
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	44.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13041, 1755
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1556
$N(param)_{refined}$:	62
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Abstract

$C_{12}H_{36}Bi_2I_9N_3$, trigonal, $P31c$ (No. 159), $a = 9.908(1)$ Å, $c = 23.420(1)$ Å, $V = 1991.1$ Å 3 , $Z = 2$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.112$, $T = 293$ K.

Source of material

The title compound was obtained by reaction of equimolar amounts of $[N(CH_3)_4]I$ and BiI_3 in diethylene glycol at 413 K for 2 days [1].

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

Atom	Site	x	y	z	U_{iso}
C(1)	6c	0.485(4)	−0.203(6)	−0.082(2)	0.24(2)
C(2)	2b	1/3	2/3	−0.003(2)	0.28(6)
C(3)	6c	0.798(6)	0.481(5)	0.770(2)	0.27(3)
C(4)	2b	2/3	1/3	0.691(1)	0.29(3)
C(5)	6c	1.131(4)	−0.022(5)	0.109(1)	0.19(2)
C(6)	2a	0	0	0.032(1)	0.18(1)

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	2b	2/3	1/3	0.1830(1)	0.067(1)	U_{11}	0.050(1)	$U_{11}/2$	0	0
Bi(2)	2b	2/3	1/3	−0.0004(1)	0.067(1)	U_{11}	0.050(1)	$U_{11}/2$	0	0
I(1)	6c	0.5408(2)	0.0462(1)	0.0912(1)	0.081(1)	0.058(1)	0.070(1)	0.031(1)	0.000(1)	0.000(1)
I(2)	6c	0.3782(2)	0.1695(2)	0.9319(1)	0.084(1)	0.102(1)	0.084(1)	0.038(1)	−0.026(1)	−0.011(1)
I(3)	6c	0.3782(2)	0.1693(2)	0.2507(1)	0.086(1)	0.102(1)	0.083(1)	0.038(1)	0.025(1)	0.011(1)
N(1)	2b	1/3	2/3	−0.066(1)	0.06(1)	U_{11}	0.06(2)	$U_{11}/2$	0	0
N(2)	2b	2/3	1/3	0.753(1)	0.07(1)	U_{11}	0.03(1)	$U_{11}/2$	0	0
N(3)	2a	0	0	0.094(1)	0.05(1)	U_{11}	0.07(1)	$U_{11}/2$	0	0

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