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Tetrakis(N-Ethyl-9-Oxo-4-Azonia-5-Aza-9H-Fluorene) Tetra- μ_3 -Iodo-Hexa- μ_2 -Iodo-Dodecaiodohexabismuthate

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Tetrakis(*N*-ethyl-9-oxo-4-azonia-5-aza-9*H*-fluorene) tetra- μ_3 -iodo-hexa- μ_2 -iodo-dodecaiodohexabismuthate

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The new iodobismuthate compound (C₁₃H₁₁N₂O)₄[Bi₆I₂₂] has been synthesized solvothermally by reacting BiI₃, Zn(NO₃)₂·6H₂O and 4,5-diazafluoren-9-one in a water/ethanol solvent mixture. The asymmetric unit of the compound contains two independent [*N*-ethyl-4,5-dafo]⁺ cations and one-half of a centrosymmetric [Bi₆I₂₂]^{4−} anion. The average terminal Bi—I, Bi— μ_2 -I and Bi— μ_3 -I bond lengths in the anion are 2.8923 (2), 3.1403 (2) and 3.3022 (2) Å, respectively.

Key indicators

Single-crystal X-ray study

T = 150 K

Mean σ (C—C) = 0.013 Å

R factor = 0.035

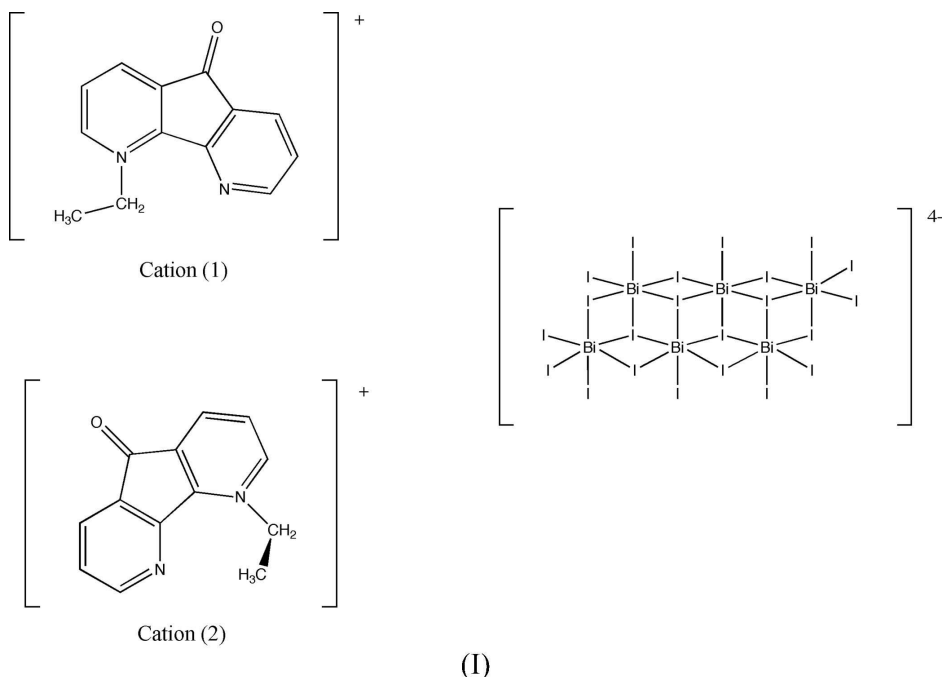
wR factor = 0.076

Data-to-parameter ratio = 23.0

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

Comment

[*N*-Ethyl-4,5-dafo]₄[Bi₆I₂₂] (*N*-ethyl-4,5-dafo = *N*-ethyl-9-oxo-4-azonia-5-aza-9*H*-fluorene) was synthesized solvothermally from BiI₃, zinc nitrate hexahydrate and 4,5-diazafluoren-9-one using a 3:1:3 molar ratio. This reaction was performed in an attempt to produce an iodobismuthate compound containing a charge-balancing, tris-chelate coordination cation of the formula [Zn(dafo)₃]²⁺, but instead an *N*-ethylated cation formed between the 4,5-diazafluoren-9-one and the ethanol reaction solvent. While both the cation and the anion of the title compound, (I), are formed *in situ*, no zinc from the zinc nitrate starting material is incorporated into either species.



The title compound contains a centrosymmetric [Bi₆I₂₂]^{4−} anion (Fig. 1) and two crystallographically independent [*N*-ethyl-4,5-dafo]⁺ cations, which will subsequently be referred to

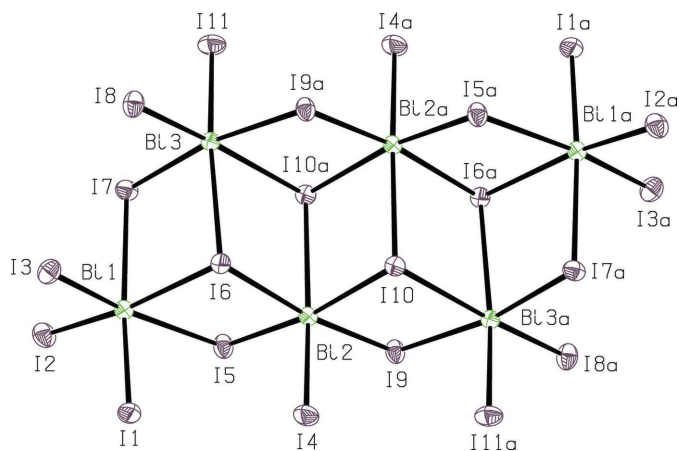


Figure 1
The structure of the $[\text{Bi}_6\text{I}_{22}]^{4-}$ anion of $[N\text{-ethyl-4,5-dafo}]_4[\text{Bi}_6\text{I}_{22}]$, showing 50% probability displacement ellipsoids. [Symmetry code: (a) $1 - x, 1 - y, 1 - z$.]

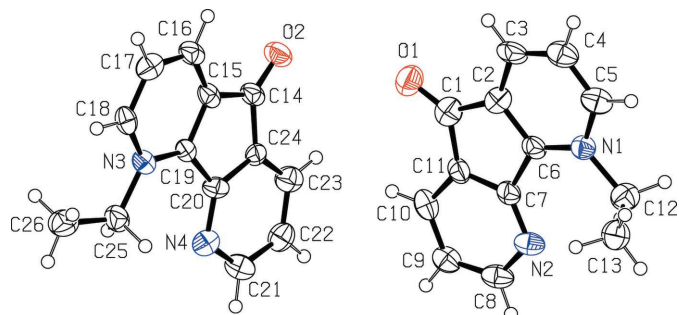


Figure 2
The two independent $[N\text{-ethyl-4,5-dafo}]^+$ cations of $[N\text{-ethyl-4,5-dafo}]_4[\text{Bi}_6\text{I}_{22}]$; (1), left and (2), right. Displacement ellipsoids are drawn at the 50% probability level.

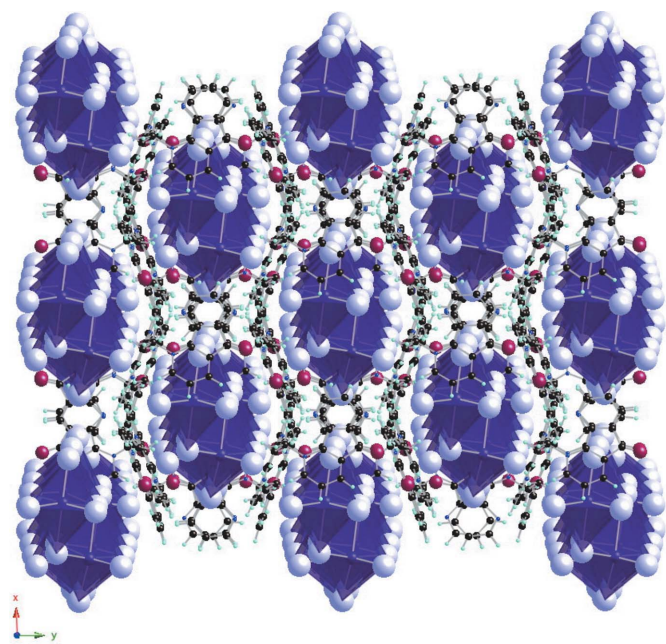


Figure 3
A view along [001] of the crystal packing in $[N\text{-ethyl-4,5-dafO}]_4[\text{Bi}_6\text{I}_{22}]$. Bi atoms are in the center of dark purple polyhedra. I atoms are shown as pale purple spheres; C atoms, black spheres; N atoms, blue spheres; O atoms, maroon spheres; H atoms, pale-green spheres.

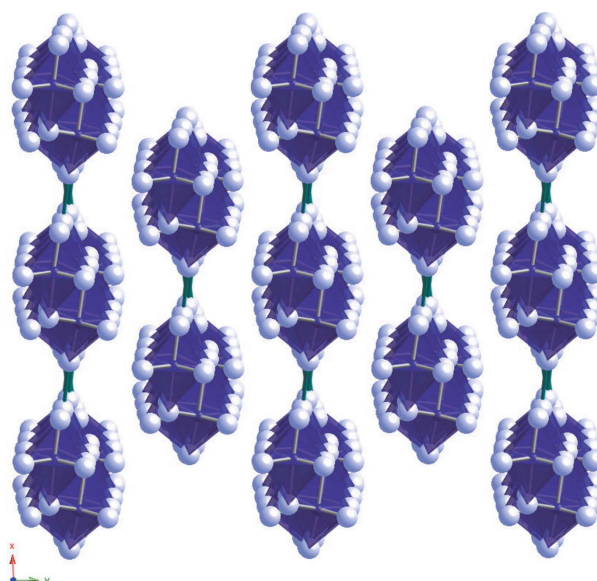


Figure 4
A view along [001] of $[N\text{-ethyl-4,5-dafO}]_4[\text{Bi}_6\text{I}_{22}]$ highlighting the one-dimensional anionic chains formed by weak $\text{I} \cdots \text{I}$ interactions (green lines). Bi atoms are in the center of dark-purple polyhedra; I atoms, pale-purple spheres. Cations are not shown.

as [N-ethyl-4,5-dafo]⁺(1) and [N-ethyl-4,5-dafo]⁺(2) (Fig. 2). The anion consists of two sets of three *trans* edge-sharing BiI₆ octahedra, which additionally share five *cis* edges. This is the typical arrangement of the [Bi₆I₂₂]⁴⁻ anion (Eickmeier *et al.*, 1999; Goforth *et al.*, 2005; Krautscheid, 1994), although we have recently published an alternative arrangement (Goforth *et al.*, 2006). The average terminal Bi—I, Bi—μ₂-I, and Bi—μ₃-I bond lengths in the anion of the title compound [2.8923 (2), 3.1403 (2), and 3.3022 (2), respectively] are comparable to those of the same type in other iodobismuthate compounds (Feldmann, 2003). When viewed along [001], rows of anions surrounded by the organic cations are observed (Fig. 3).

Pairs of $[N\text{-ethyl-4,5-daf}]^+(1)$ cations separate the anion clusters along the b -axis direction and thereby create undulating rows that extend in the a -axis direction (Fig. 3). Pairs of $[N\text{-ethyl-4,5-daf}]^+(2)$ cations, which are oriented nearly perpendicular to the pairs of $[N\text{-ethyl-4,5-daf}]^+(1)$ cations, separate the anion clusters along the c -axis direction. Other than their orientations, the two crystallographically independent cations also differ significantly in the lengths of their N -ethyl carbon bonds. The N1—C12 bond distance [1.52 (1) Å] in $[N\text{-ethyl-4,5-daf}]^+(2)$ is longer than the corresponding N3—C25 distance in $[N\text{-ethyl-4,5-daf}]^+(1)$ [1.47 (1) Å]. The difference in bond lengths in the two cations is likely the result of the different orientations of the ethyl groups relative to the plane of the ring system. In cation (2), the ethyl group is roughly perpendicular to the ring system plane, while in cation (1), it is coplanar. Therefore, the differences in orientation likely arise as a result of steric considerations with respect to the crystal packing. The roughly orthogonal geometry of cation (2) puts H12 and its symmetry-equivalent atom H12A closer than the sum of their van der Waals radii (2.05 Å;

symmetry code: $-x + 2, y, -z + \frac{1}{2}$; vdW radius for H = 1.20 Å).

The arrangement of the cations in the title compound does not completely encapsulate the anions, and certain I atoms of neighboring anions are closer to one another than twice the van der Waals radius of I [vdW (I) = 1.98 Å, $I \cdots I \leq 3.96$ Å; Bondi, 1964]. These $I \cdots I$ interactions [$I(4) \cdots I(11)^i = 3.947$ (7) Å; symmetry code: (i) $x + 1, y, z$] serve to link the discrete anions into weakly bonded one-dimensional anionic chains extending along [100] (Fig. 4).

Experimental

All solvents, bismuth triiodide (99.999%, Alfa Aesar), 4,5-diazafluoren-9-one (98%, Aldrich), and $Zn(NO_3)_2 \cdot 6H_2O$ (reagent grade, Fisher) were purchased from commercial sources and used without further purification. BiI_3 (0.3 mmol, 177 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 30 mg), and 4,5-diazafluoren-9-one (0.3 mmol, 54 mg) were weighed and placed in a 15 ml glass pressure vessel (Ace Glass) with 5 ml of water and 5 ml of ethanol as the reaction solvent. The glass tube was sealed with a threaded Teflon plug (having a back seal FETFE *o*-ring) and heated upright at a rate of 1 K min^{-1} to 413 K. The temperature was held at 413 K for three days before it was decreased, at a rate of 0.1 K min^{-1} to 343 K where it was then held for 6 h. Finally, the temperature was decreased at a rate of 0.1 K min^{-1} to room temperature. Orange plate crystals were isolated from the reaction and a suitable single crystal was selected for the X-ray structure determination.

Crystal data

$(C_{13}H_{11}N_2O)_4[Bi_6I_{22}]$	$Z = 4$
$M_r = 4890.63$	$D_x = 3.492\text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 13.3944$ (10) Å	$\mu = 18.65\text{ mm}^{-1}$
$b = 17.0764$ (12) Å	$T = 150$ (1) K
$c = 40.710$ (3) Å	Plate, orange
$\beta = 92.589$ (1)°	$0.14 \times 0.08 \times 0.04\text{ mm}$
$V = 9302.1$ (12) Å ³	

Data collection

Bruker SMART APEX CCD diffractometer	48604 measured reflections
ω scans	9574 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	8178 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.180, T_{\max} = 0.474$	$R_{\text{int}} = 0.046$
	$\theta_{\max} = 26.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 84.5173P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 1.08$	$\Delta\rho_{\max} = 1.13\text{ e \AA}^{-3}$
9574 reflections	$\Delta\rho_{\min} = -0.92\text{ e \AA}^{-3}$
417 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Bi1—I1	2.8820 (7)	Bi3—I8	2.8783 (6)
Bi1—I3	2.9169 (7)	Bi3—I7	3.0022 (6)
Bi1—I2	2.9445 (7)	Bi3—I9 ⁱ	3.1881 (6)
Bi1—I6	3.2533 (6)	Bi3—I10 ⁱ	3.3479 (6)
Bi1—I7	3.3257 (7)	Bi3—I6	3.4156 (6)
Bi1—I5	3.3304 (6)	I9—Bi3 ⁱ	3.1881 (6)
Bi2—I4	2.8632 (7)	I10—Bi3 ⁱ	3.3479 (6)
Bi2—I5	2.9718 (6)	I10—Bi2 ⁱ	3.4024 (6)
Bi2—I9	3.0237 (6)	C12—C13	1.467 (13)
Bi2—I6	3.1887 (6)	C12—N1	1.518 (12)
Bi2—I10	3.2053 (6)	C14—O2	1.198 (10)
Bi2—I10 ⁱ	3.4025 (6)	C25—N3	1.470 (11)
Bi3—I11	2.8687 (7)	C25—C26	1.512 (13)
I2—Bi1—I6	167.845 (19)	I4—Bi2—I10 ⁱ	176.323 (19)
I1—Bi1—I7	175.988 (19)	I7—Bi3—I9 ⁱ	170.583 (18)
I3—Bi1—I5	171.314 (19)	I8—Bi3—I10 ⁱ	172.718 (18)
I9—Bi2—I6	172.594 (18)	I11—Bi3—I6	171.880 (19)
I5—Bi2—I10	171.609 (18)		

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

H atoms were placed in geometrically idealized positions and included as riding atoms [$C-H = 0.95-0.99$ Å and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ or $1.5U_{\text{eq}}(C)$]. The highest residual electron density map peak is located 0.85 Å from Bi2.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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