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Key indicators

Single-crystal X-ray study
 $T = 173\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.025\text{ \AA}$
Disorder in main residue
 R factor = 0.072
 wR factor = 0.212
Data-to-parameter ratio = 41.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4,4'-Bipyridyl adduct of an iodobismuthate
anion linked by a 4,4'-bipyridinium cation

The crystal structure of the title iodobismuthate complex, 4,4'-bipyridinium(2+) di- μ -iodo-bis[(4,4'-bipyridyl)triiodobismuth(III)], formulated as $[4,4'\text{-H}_2\text{bipy}]^{2+}[\text{Bi}_2\text{I}_8(4,4'\text{-bipy})_2]^{2-}$ or $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{Bi}_2\text{I}_8(\text{C}_{10}\text{H}_8\text{N}_2)_2]$, has been determined. The compound is isostructural with its antimony analogue, each containing layers of hydrogen-bonded ribbon polymers in which anionic dinuclear complexes are linked through hydrogen bonding with 4,4'- H_2bipy cations.

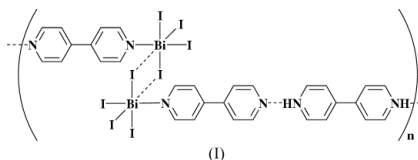
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Comment

The solid-state structure of the title compound, (I), is essentially identical to that reported for the antimony analogue (Charmant *et al.*, 2003).



Diffraction data for the crystal are poor due to the combined effects of disorder and non-merohedral twinning; because of these effects, the atomic displacement parameters of the light atoms, and the distances between them, should not be considered reliable. This said, the distance between N2 and N3 of 2.69 (4) Å provides some evidence for a hydrogen-bond interaction involving these atoms that leads to the hydrogen-bonded polymeric arrangement of ions observed in this structure.

Experimental

Reactions were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk or dry-box techniques and oven-dried glassware. All solvents used were distilled under nitrogen and dried over appropriate drying agents. BiI_3 (99.99%) was procured from Aldrich and generally used without further purification (filtration to remove insoluble BiOI was occasionally necessary). 4,4'-Bipyridyl was also obtained from Aldrich. Equimolar quantities of BiI_3 and 4,4'-bipyridyl were dissolved in tetrahydrofuran, resulting in a dark-orange solution from which an orange solid was obtained after solvent diffusion with an overlayer of hexane at room temperature over a period of days. Redissolution in hot (373 K) tetraglyme afforded a dark-red solution from which a small crop of red-orange crystals of (I) were obtained after slow cooling to room temperature. Compound (I) is not the major product of this reaction. It presumably arises due to partial hydrolysis.

Crystal data

(C₁₀H₁₀N₂)[Bi₂I₈(C₁₀H₈N₂)₂]
M_r = 1903.72
 Monoclinic, *P*2₁/*n*
a = 9.637 (4) Å
b = 12.751 (4) Å
c = 18.173 (7) Å
 β = 95.01 (5)°
V = 2224.39 (6) Å³
Z = 2

D_x = 2.842 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7961 reflections
 θ = 2–27°
 μ = 13.48 mm⁻¹
T = 173 (2) K
 Block, red–orange
 0.20 × 0.10 × 0.05 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans (0.3° frames)
 Absorption correction: none
 10 596 measured reflections
 10 596 independent reflections

7484 reflections with *I* > 2σ(*I*)
 θ_{\max} = 24.0°
h = –11 → 9
k = –14 → 14
l = –20 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.072
wR(*F*²) = 0.212
S = 1.04
 10 596 reflections
 255 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1215P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.08 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -4.26 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å).

Bi1–N1	2.67 (2)	Bi1–I4	2.9782 (13)
Bi1–N1′	2.80 (4)	Bi1–I2′	3.2458 (12)
Bi1–I1	2.9408 (12)	Bi1–I2	3.2497 (13)
Bi1–I3	2.9551 (13)		

Symmetry code: (i) 2 – *x*, 1 – *y*, –*z*.

The crystal shows disorder in the 2- (C1), 3- (C2), 5- (C4) and 6-positions (C5) of the metal-bound pyridyl ring of the bipy ligand. Calculated intensities showed consistently poor agreement with their observed counterparts for reflections with *h* = 3*n*. This is a classic indicator of non-merohedral twinning. A suitable twinning matrix was found: $(\bar{1}00 \ 0\bar{1}0 \ \frac{1}{3}0\bar{1})$. This matrix is in accord with the twin components being related by twofold rotation about the *a* axis of the unit cell. Using a simple in-house Fortran77 program, a new reflection intensity data file was produced that contained flags marking all of the overlapping reflections. During refinement the observed intensity for each overlapping reflection was fitted to the sum of calculated intensities for each twin component. The twin-component ratio refined to a value of 0.202 (2). No absorption correction was applied, as at the time that this experiment was performed no integration

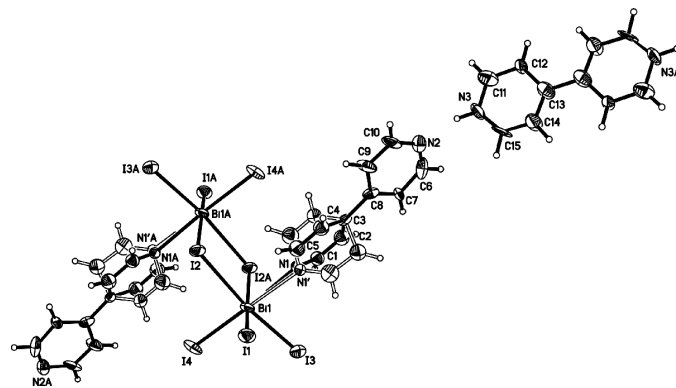


Figure 1

The structure of a cation–anion pair of (I). Displacement ellipsoids are drawn at the 50% probability level, and the suffix A denotes an atom generated by inversion symmetry.

software and absorption correction program existed for dealing with the non-merohedrally twinned intensity data collected. A preliminary version of this software now exists (Ruf & Sheldrick, 2003), but unfortunately the original frame data for the structure were deleted some time ago. Merging of symmetry and ψ -equivalent data was not performed due to the non-merohedral twinning present. All H atoms were constrained to ideal geometries and assigned isotropic displacement parameters equal to 1.2 times that of their parent atom. The highest peak (2.09 e Å⁻³) and lowest hole (–4.26 e Å⁻³) in the electron density difference map were found close (1.18 and 1.05 Å, respectively) to Bi1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SHELXTL* (Siemens, 1996); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

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