

## 4,4'-Bipyridyl adduct of an iodoantimonate anion linked by a 4,4'-bipyridinium cation

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### Key indicators

Single-crystal X-ray study

$T = 173\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$

Disorder in main residue

$R$  factor = 0.041

$wR$  factor = 0.079

Data-to-parameter ratio = 21.5

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

The crystal structure of the title iodoantimonate complex, 4,4'-bipyridinium(2+) di- $\mu$ -iodo-bis[(4,4'-bipyridyl)triiodoantimony(III)], formulated as  $[4,4'\text{-H}_2\text{bipy}]^{2+}[\text{Sb}_2\text{I}_8(4,4'\text{-bipy})_2]^{2-}$  or  $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{Sb}_2\text{I}_8(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ , contains layers of hydrogen-bonded ribbon polymers in which anionic dimetal complexes are linked through hydrogen bonding with 4,4'- $\text{H}_2\text{bipy}$  cations. The complex is isostructural with its bismuth analogue.

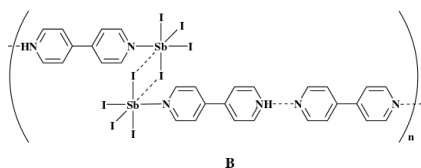
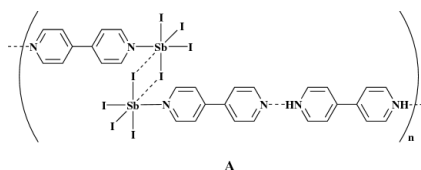
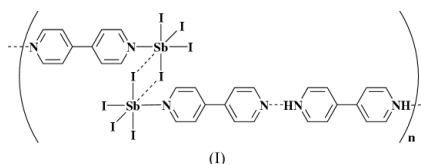
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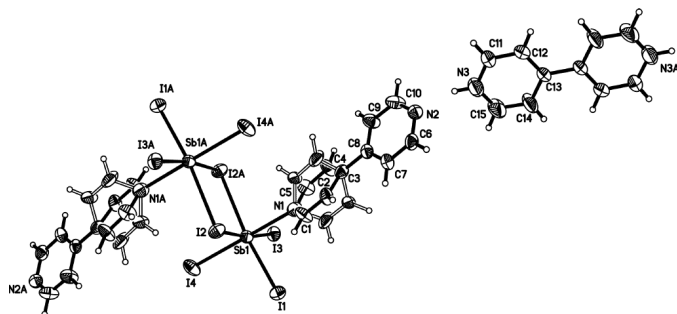
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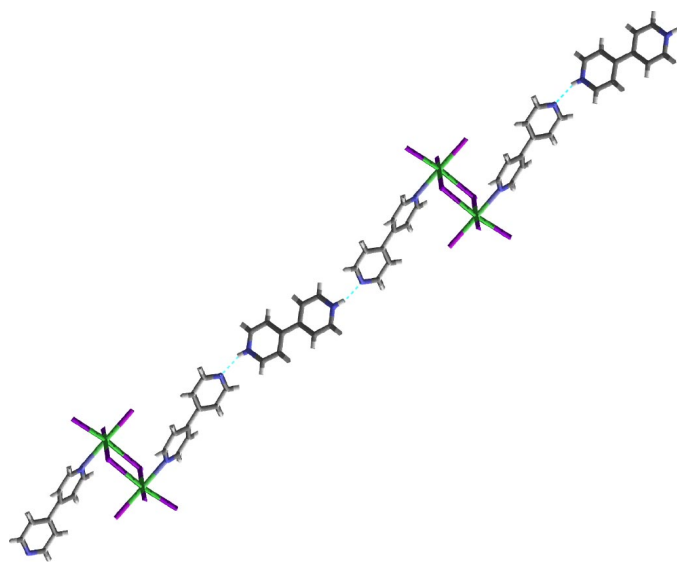
### Comment

Halogeno anions containing antimony(III) and bismuth(III) adopt a wide variety of structures including polymeric forms (Fisher & Norman, 1994). A small subset of these halogeno anions incorporate neutral two-electron donor ligands coordinated to one or more  $\text{Sb}^{\text{III}}$  or  $\text{Bi}^{\text{III}}$  centres in a similar fashion to the many known coordination complexes of neutral antimony and bismuth trihalides (Carmalt *et al.*, 1996). Examples of anionic species include  $[\text{BiX}_5\text{L}]^{2-}$  ( $X = \text{Cl}, \text{Br}; L = \text{pyridine}, 4\text{-picoline}$ ) (James *et al.*, 2000; Raston *et al.*, 1981; Bharadwaj *et al.*, 1994),  $[\text{Bi}_2\text{I}_8(\text{SMe}_2)_2]^{2-}$  (Clegg *et al.*, 1993),  $[\text{Bi}_2\text{Cl}_8(\text{thf})_2]^{2-}$  (James *et al.*, 1997),  $[\text{Bi}_2\text{I}_8(\text{thf})_2]^{2-}$  (Krautscheid, 1995),  $[\text{Sb}_2\text{Br}_7(\text{PEt}_3)_2]^-$  (Clegg *et al.*, 1994),  $[\text{Bi}_4\text{I}_{14}(\text{thf})_2]^{2-}$  (Krautscheid, 1994),  $[\text{Bi}_4\text{I}_{14}(\text{thf})_4]^{2-}$  (Krautscheid, 1995) and  $\{[\text{Bi}_2\text{Br}_7(\text{PMe}_3)_2]^- \}_n$  (Clegg *et al.*, 1991). Here we describe the structure of the 4,4'-bipyridyl (4,4'-bipy) adduct  $[\text{Sb}_2\text{I}_8(4,4'\text{-bipy})_2]^{2-}$ , (I), where the cation is 4,4'-bipyridinium  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  (structure A, see discussion below) and in which cations and anions are linked by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds.



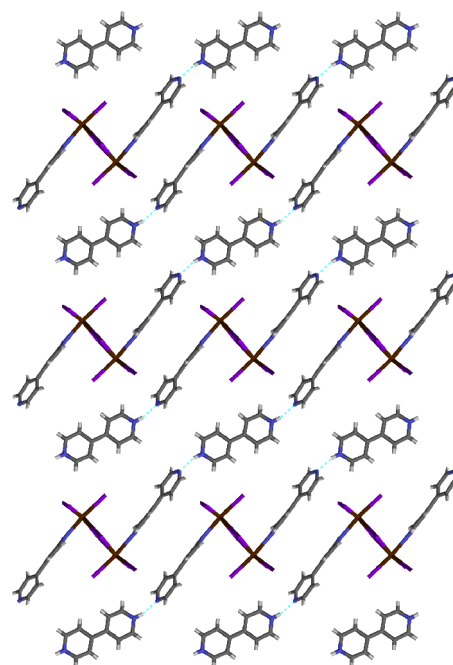


**Figure 1**  
The structure of a cation-anion pair of (I). Displacement ellipsoids are drawn at the 50% probability level, and the suffix A denotes an atom generated by inversion symmetry.



**Figure 2**  
The hydrogen-bonded ribbon polymer structure of (I).

Species with the general formula  $[E_2X_8(L)_2]^{2-}$  (see above) adopt an edge-shared bioctahedral centrosymmetric structure in which the ligands  $L$  are *trans* to a terminal halide. The iodoantimonate species formulated as  $[4,4'\text{-H}_2\text{bipy}]^{2+}[\text{Sb}_2\text{I}_8(4,4'\text{-bipy})_2]^{2-}$ , (I), shown in Fig. 1, adopts this same structure, wherein one of the N atoms of each 4,4'-bipy ligand acts as the donor site to the antimony centre. The other N atom forms a hydrogen bond with one end of a diprotonated 4,4'-bipyridinium cation, resulting in hydrogen-bonded ribbons, as illustrated in Fig. 2. A diagrammatic representation, *A*, for this formulation is shown in the scheme, but an alternative arrangement, *B*, must be considered which contains a monoprotonated ligand, giving a neutral complex that acts as a hydrogen-bond donor to neutral 4,4'-bipy molecules. For the purposes of discussion, the structure is assigned to be *A*, but it has proved impossible to distinguish crystallographically between the two possibilities *A* and *B* owing to the difficulty of locating H atoms in a structure rich in heavy atoms. The N...N separation [2.71 (2) Å] in the structure clearly shows the strength of the hydrogen bonding present. The hydrogen-bonded ribbon polymers pack into layers



**Figure 3**  
The packing of hydrogen-bonded ribbons for compound (I). The layer shown is parallel to the  $bc$  plane.

(illustrated in Fig. 3). Adjacent layers are related to each other through the  $n$ -glide operation of the space group, so that simultaneous translation of the layer in the  $a$  and  $c$  directions followed by reflection in the  $ac$  plane places the  $[\text{Sb}_2\text{I}_8(4,4'\text{-bipy})_2]^{2-}$  complexes directly above the uncoordinated 4,4'-bipyridinium cations. An isostructural bismuth analogue has also been characterized (Charmant *et al.*, 2003). The antimony centre deviates only slightly from a regular octahedral geometry with respect to the interbond angles, but we note that the terminal Sb—I distances are significantly shorter than the bridging Sb—I bond lengths. The Sb—N distance is also long, such that the overall disposition of bond lengths around the antimony centre is three short and three long, with a *fac* rather than the *mer* arrangement seen previously (Clegg *et al.*, 1994; James *et al.*, 1997).

## 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.  $\text{SbI}_3$  (99.99%) was procured from Aldrich and generally used without further purification (filtration to remove insoluble  $\text{SbOI}$  was occasionally necessary). 4,4'-Bipyridyl was also obtained from Aldrich. Equimolar quantities of  $\text{SbI}_3$  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

(C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>)[Sb<sub>2</sub>I<sub>8</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 1629.26  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 9.6444 (19) Å  
*b* = 12.678 (2) Å  
*c* = 18.097 (2) Å  
 $\beta$  = 95.570 (16)°  
*V* = 2202.3 (6) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 2.608 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5693 reflections  
 $\theta$  = 2–27°  
 $\mu$  = 6.86 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, red–orange  
 0.20 × 0.10 × 0.05 mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans (0.3° frames)  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.528, *T*<sub>max</sub> = 0.710  
 13744 measured reflections

5038 independent reflections  
 3230 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.049  
 $\theta$ <sub>max</sub> = 27.5°  
*h* = –12 → 5  
*k* = –15 → 16  
*l* = –23 → 23

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR* (*F*<sup>2</sup>) = 0.079  
*S* = 0.97  
 5038 reflections  
 234 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.35 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -1.56 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXTL  
 Extinction coefficient: 0.00028 (5)

Table 1

Selected geometric parameters (Å).

Sb1–N1	2.588 (7)	Sb1–I4	2.9283 (8)
Sb1–I3	2.8687 (8)	Sb1–I2	3.2334 (9)
Sb1–I1	2.8741 (8)	Sb1–I2 <sup>i</sup>	3.2381 (9)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N3–H3···N2	0.88	1.87	2.71 (2)	160

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. 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 (1.35 e Å<sup>-3</sup>) and lowest hole (–1.56 e Å<sup>-3</sup>) in the electron density difference map were found close (0.83 and 0.87 Å, respectively) to I4.

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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