Bis(2-amino-3,5-dibromo-4,6-dimethylpyridinium) hexabromidostannate(IV)

Rawhi Al-Far[a] **and Basem Fares Ali**[b]*

[a]Faculty of Science and Information Technology, Al-Balqa'a Applied University, Salt, Jordan, and [b]Department of Chemistry, Al al-Bayt University, Mafraq 25113, Jordan
Correspondence e-mail: bfali@aabu.edu.jo

In the title compound, $(C_7H_9Br_2N_2)_2[SnBr_6]$, the cations and centrosymmetric anions are stacked in alternating layers that show no significant intermolecular interactions within each stack. Extensive cation$\cdots[SnBr_6]^{2-}$ interactions are found, represented by short Br$\cdots$Br interactions, along with different Br$\cdots$HN (pyridine and amine) and weaker Br$\cdots$HCH$_2$ hydrogen-bonding motifs.

Comment

There has been a surge of research activity in the development of specific structural architectures that involve the self-assembly of molecules or ions into well defined supramolecular arrays. Non-covalent interactions play an important role in organizing structural units in both natural and artificial systems (Desiraju, 1997, and references therein). Several studies report the X-ray structures of complexes containing cationic pyridine derivatives with bromido–metal(II) anions, and their structures have been investigated in terms of non-covalent interactions (Luque *et al.* 2001; Haddad, AlDamen & Al-Far, 2004; Haddad & Al-Far, 2003; Haddad *et al.*, 2003; Willett *et al.*, 2003; Al-Far *et al.*, 2006; Ali *et al.*, 2007). In the present work, we report the crystal structure of the title complex, (I), prepared from the reaction of 2-amino-4,6-dimethylpyridine with tin metal in the presence of HBr and Br$_2$. The introduction of the 2-amino group facilitates electrophilic substitution of Br atoms at the 3- and 5-positions, and increases the nucleophilicity at the ring N atom (Place & Willett, 1987). Therefore, protonation of the brominated 2-amino-4,6-dimethylpyridine takes place on the pyridine N atom rather than on the amino group. The presence of the amino group and the bromination and protonation were expected to create many important centres of interaction with the $[SnBr_6]^{2-}$ anion, *e.g.* Br$\cdots$Br, NH$\cdots$Br, and possibly Br$\cdots$aryl and aryl$\cdots$aryl interactions.

The pyridine rings of the starting cation have undergone bromination during the synthesis process. This is ascribed to the fact that the resonance effect of the 2-amino group

increases the basicity of the pyridine N atom, while the amino group lone pair interacts with the π system of the aryl group. Halogenation of the pyridine rings of substituted pyridinium cations has been observed previously (Liu *et al.*, 2001, and references therein).
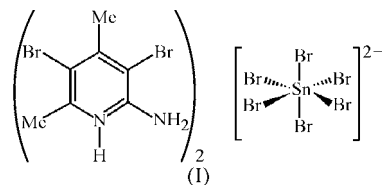
The asymmetric unit of the structure of (I) was found to contain two independent cationic 2-amino-3,5-dibromo-4,6-dimethylpyridinium ligands and $[SnBr_6]^{2-}$ anions. The two anions lie on centres of symmetry (Fig. 1). The $[SnBr_6]^{2-}$ anions exhibit a distorted octahedral arrangement about the Sn atoms (Table 1). The Sn—Br distances are similar, but Sn1—Br1 and Sn2—Br5 are significantly longer than the others. The Sn—Br distances are in the range 2.5606 (6)–2.6443 (6) Å for the Sn1 anion, with a mean value of 2.6001 (6) Å, and in the range 2.5699 (6)–2.6326 (6) Å for the Sn2 anion, with a mean value of 2.6013 (6) Å. These bond lengths fall within the range of Sn—Br distances reported previously for compounds containing $[SnBr_6]^{2-}$ anions (Willey *et al.*, 1998; Tudela & Khan, 1991).

As far as the cations of (I) are concerned, the bond distances and angles in the brominated cation are the same as
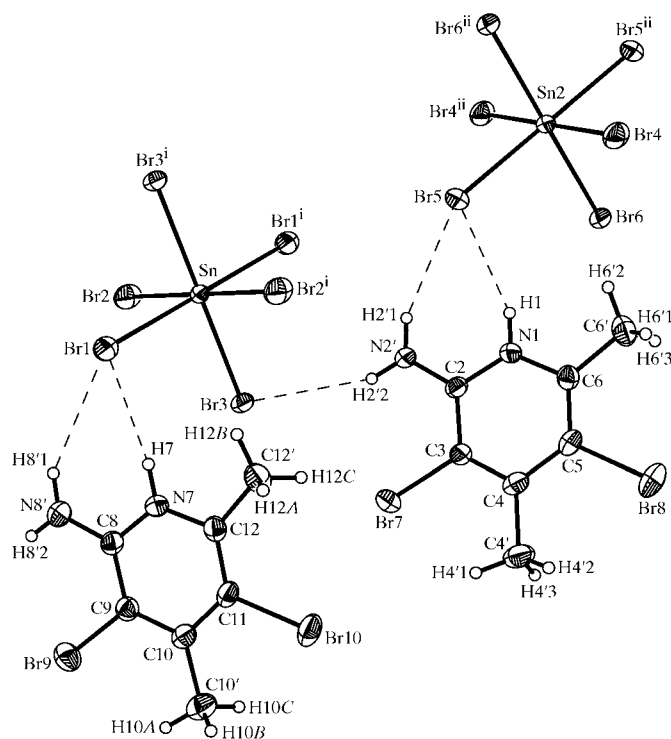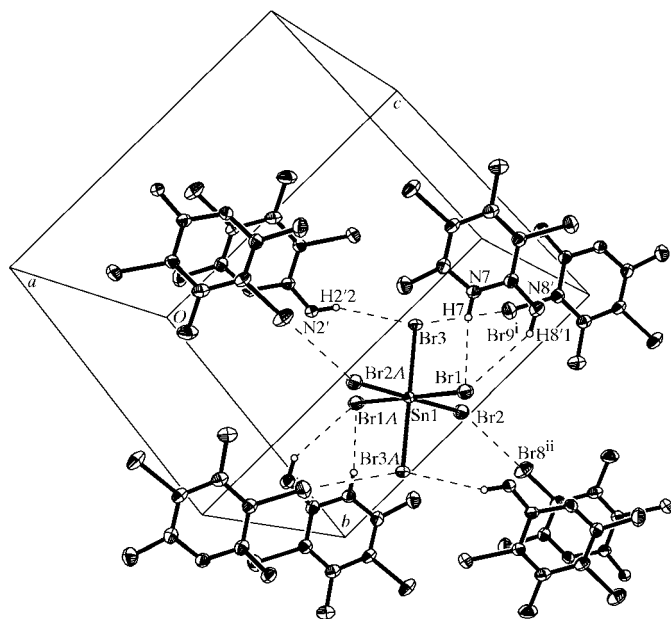

Figure 1
A view of asymmetric unit of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. The complete coordination about Sn1 and Sn2 has been included in the drawing. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z$.]

metal-organic compounds

Figure 2
Part of the cell contents of (I), showing some of the short N—H···Br and Br···Br intermolecular interactions (dashed lines) for one $[SnBr_6]^{2-}$ anion. Br atoms related by the centre of symmetry at the Sn1 atom at $(\frac{1}{2}, 1, \frac{1}{2})$ have an additional A label. [Symmetry codes: (i) $-x+1$, $-y+2$, $-z+2$; (ii) $x-1$, $y+1$, z.]

those reported previously, within experimental error (Place & Willett, 1987; Liu *et al.*, 2001; Albrecht *et al.*, 2003; Prince *et al.*, 2003). The cations are nearly planar, with the largest deviation from the cation plane 1 (N1/C2/C3/C4/C5/C6) being for atom Br7, which lies 0.131 (1) Å out of this plane. This is probably due to steric repulsion with the adjacent NH₂ and methyl groups (Willett *et al.*, 2000). Atoms Br8 and N2′ deviate from plane 1 by 0.027 (1) and 0.062 (1) Å, respectively. For cation plane 2 (N7/C8/C9/C10/C11/C12), the deviations from planarity are smaller for the substituents: amino atom N8′ deviates by 0.029 (2) Å and atom Br10 by 0.052 (2) Å.

The molecules of (I) pack in stacks of discrete anions that are separated by stacks of cations. The anion stacks are parallel to the cation stacks, with an Sn···Sn distance of 9.857 (11) Å (the lattice translation) and no significant interactions between the $[SnBr_6]^{2-}$ anions. The anions and cations interact not only through Br···Br interactions but also through extensive N—H···Br and C—H···Br hydrogen bonds involving the Br atoms of the $[SnBr_6]^{2-}$ anion and the NH₂ and CH₃ H atoms of the cations (Table 2). These interactions link the anions and cations together into two-dimensional layers approximately normal to the crystallographic *a* axis (Fig. 2). In each layer, the anions are surrounded by eight cations interacting *via* four equatorial Br···Br short interactions [two of 3.4422 (10) Å and two of 3.3869 (10) Å] and six N—H···Br (amino and pyridine) short interactions (two of 2.63 Å, two of 2.76 Å and two of 2.74 Å) in the case of the Sn2 anion, and correspondingly [two of 3.4668 (11) Å and two of 3.5724 (10) Å, and two each of 2.50, 2.93 and 2.82 Å] in the case of anion Sn1.

These interactions are expected to play a major role in the assembly of cations and anions in supramolecular arrays, along with less significant interactions (longer) that also exist (Fig. 2). These (N—)H···Br distances are in the range 2.74–2.93 Å for the amino N atom, and in the range 2.50–2.63 Å for the pyridine N atom, which are comparable with interactions reported in previous structures of tetrahalocuprate(II) salts, where the amino and pyridine (N—)H···Br distances are in the ranges 2.65–2.89 and 2.57–2.58 Å, respectively (Haddad *et al.*, 2006, and references therein; Haddad, AlDamen, Willett & Twamley, 2004).

It is noteworthy that hydrogen-bond lengths involving amino H atoms are, in general, observed to be similar to those involving methyl H atoms, but longer than those involving pyridine H atoms (Table 2). This might be attributed to the fact that the electronic lone pair in the atomic orbital of the amino N atoms is not involved in hydrogen bonding, but rather is in resonance with the pyridine ring (Haddad *et al.*, 2006), which would weaken the hydrogen bonding.

Experimental

For the preparation of (I), tin metal (1.0 mmol), dissolved in 48% HBr (10 ml) followed by liquid Br₂ (2 ml), was added dropwise to a stirred hot ethanol solution (20 ml) of 2-amino-4,6-dimethylpyridine (2 mmol). After heating for *ca* 3 h, the mixture was filtered and allowed to stand undisturbed at room temperature. The salt crystallized from the filtrate over a period of 2 d as yellow needles. Crystals of (I) were filtered off, washed with diethyl ether and dried under vacuum.

Crystal data

$(C_7H_9Br_2N_2)_2[SnBr_6]$	$\gamma = 93.898\,(2)°$
$M_r = 1160.11$	$V = 1378.8\,(3)$ Å³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.8574\,(11)$ Å	Mo $K\alpha$ radiation
$b = 11.4847\,(13)$ Å	$\mu = 15.43$ mm⁻¹
$c = 12.5957\,(14)$ Å	$T = 297\,(2)$ K
$\alpha = 94.245\,(2)°$	$0.20 \times 0.11 \times 0.06$ mm
$\beta = 103.258\,(2)°$	

Data collection

Bruker SMART APEX diffractometer	20574 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	4979 independent reflections
	4034 reflections with $I > 2\sigma(I)$
$T_{min} = 0.129$, $T_{max} = 0.398$	$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	269 parameters
$wR(F^2) = 0.076$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.96$ e Å⁻³
4979 reflections	$\Delta\rho_{min} = -0.58$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Br1—Sn1	2.6443 (6)	Br4—Sn2	2.5699 (6)
Br2—Sn1	2.5606 (6)	Br5—Sn2	2.6326 (6)
Br3—Sn1	2.5954 (6)	Br6—Sn2	2.6013 (6)
Br2—Sn1—Br3	88.993 (19)	Br4—Sn2—Br6	90.581 (19)
Br2—Sn1—Br1	89.27 (2)	Br4—Sn2—Br5	89.81 (2)
Br3—Sn1—Br1	91.50 (2)	Br6—Sn2—Br5	91.18 (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$\cdots$Br5	0.86	2.62	3.419 (4)	154
N7—H7$\cdots$Br1	0.86	2.50	3.346 (4)	170
N2$'$—H2$'$1$\cdots$Br5	0.86	2.76	3.525 (4)	149
N2$'$—H2$'$2$\cdots$Br3	0.86	2.82	3.635 (4)	158
N8$'$—H8$'$1$\cdots$Br1	0.86	2.93	3.683 (5)	147
N8$'$—H8$'$2$\cdots$Br6^i	0.86	2.74	3.542 (5)	155
C4$'$—H4$'$3$\cdots$Br1^{ii}	0.96	2.82	3.622 (7)	142

Symmetry codes: (i) $x, y + 1, z + 1$; (ii) $x, y - 1, z$.

All H atoms were initially located in a difference Fourier map and were subsequently refined using a riding model, with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms, C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for pyridine H atoms, and N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(N)$ for the pyridinium H atom and the H atoms of the amino groups. The methyl groups were allowed to rotate freely about their local threefold axes.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 2004); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3039). Services for accessing these data are described at the back of the journal.

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