Crystal Structure of $Me_3Sb{\cdot}SbI_2Me$, an Adduct with a Short Dative Sb–Sb Bond

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A crystal structure determination of the adduct $Me_3Sb{\cdot}SbI_2Me$ has shown it to consist of pyramidal Me_3Sb bound to T-shaped SbI_2Me through a short (286 pm) Sb–Sb bond.

The ability of antimony and its lighter congeners to exhibit both nucleophilic and electrophilic activity gives rise to the possibility of the formation of dative element–element bonds. Such bonds have been realized in adducts of $SbMe_3$ with SbI_3[1] or SbI_2Me[2] and related phosphorus or arsenic compounds.[1] Little is known of the structures of these adducts. Reports on Sb···Sb interactions between stibane molecules or inorganic antimony(III) compounds consider only weak contacts with distances in the range 350–400 pm.[3] We report here on the X-ray crystal structure determination† of $Me_3Sb{\cdot}SbI_2Me$ **1**, a molecular adduct with Sb–Sb distances that correspond to single-bond lengths.

The synthesis of **1** is achieved by the known[2] scrambling reaction of $SbIMe_2$. For the preparation of single crystals of **1** the procedure[2] has been modified. Instead of working in solution the crystals were allowed to grow at −20 °C in a sample of $SbIMe_2$ in the absence of solvent.

The crystals of **1** contain two types of Me_3SbSbI_2Me molecules (**1a**, **1b**) of similar geometry but with different environments. The structure of one of the adducts (**1a**) is shown in Fig. 1. The molecules consist of pyramidal Me_3Sb donors attached to T-shaped SbI_2Me acceptors. The resulting coordination of the acceptor Sb may be described as distorted trigonal-bipyramidal with the two iodines in axial positions and trimethylstibane, the methyl group and the lone pair in equatorial positions. This description implies the presence of a stereochemically active lone pair that is responsible for the considerable deviations of bond angles from regular trigonal-bipyramidal values. Alternative models using p orbitals for bonding and the s orbital as the lone pair at antimony would also be in accord with the bond angles at the acceptor atom. The Sb–Sb bond lengths [**1a** 285.9(1), **1b** 286.8(1) pm] and the Sb–C distances (**1a** 211.7 - 214.3, **1b** 211.8 - 217.6 pm] compare well with the corresponding single-bond lengths (*cf.* $Me_2SbSbMe_2$,[4] Sb–Sb 283.8(1), Sb–C 211.8 – 219.0 pm). Also the Sb–I bond distances [**1a** 291.3(1), 309.3(1); **1b** 289.4(1), 313.2(1)] are not unusual. Similar bond lengths have been found in other hypervalent antimony(III) iodides with linear I–Sb–I units.[2,5,6] They may be described by three-centre–four electron bond models[7] rather than by partially ionic bonding as proposed by Summers and Sisler.[1] The formation of only four bonds by Sb^{III} is unusual but has been realized in the $[SbCl_2Ph_2]^-$ anion[8,9] in antimony(III) tartrates and in the distorted trigonal-bipyramidal SbF_4^- ion that form part of the structure of KSb_2F_7.[6] Complex antimony halides of the type $MSbX_4$ however form polymers where antimony is six-coordinate.[6] In these halides the Sb–X bond lengths are not equal but form three sets of different distances. If for instance only the four shorter bonds in $(SbI_4)_n{}^{n-}$ are considered the resulting geometry is similar to the structure of the adducts **1**, which obviously also have a tendency to enhance their coordination. The resulting intermolecular interactions are shown in Fig. 2 and are the main discriminating features between **1a** and **1b**. The adduct **1a** forms dimers through Sb···I bridges of length 348.0(1) pm *trans* to the Sb–Sb bond. If this interaction is considered, the coordination of the acceptor may be described as tetragonal pyramidal. Further association of the dimers of **1a** through Sb···I contacts of 390.3(1) and 397.0(1) pm lead to tetrameric units. The intermolecular interactions are however not primarily responsible for the geometry of the adducts since **1b** with essentially the same

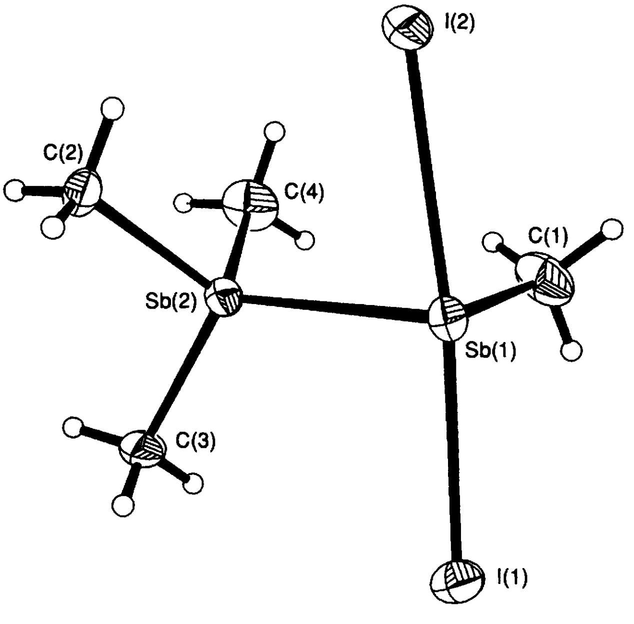

Fig. 1 The structure of one of the adducts Me_3SbSbI_2Me **1a**. Important bond distances (pm) and angles (°): Sb(1)–Sb(2) 285.9(1), Sb(1)–I(1) 291.3(1), Sb(1)–I(2) 309.3(1), Sb(1)–C(1) 214.3(11); I(1)–Sb(1)–I(2) 169.7(1), C(1)–Sb(1)–Sb(2) 92.3(3), C(1)–Sb(1)–I(1) 90.1(2), I(1)–Sb(1)–Sb(2) 90.5(1), I(2)–Sb(1)–Sb(2) 80.4(1), C(1)–Sb(1)–I(2) 85.3(3).

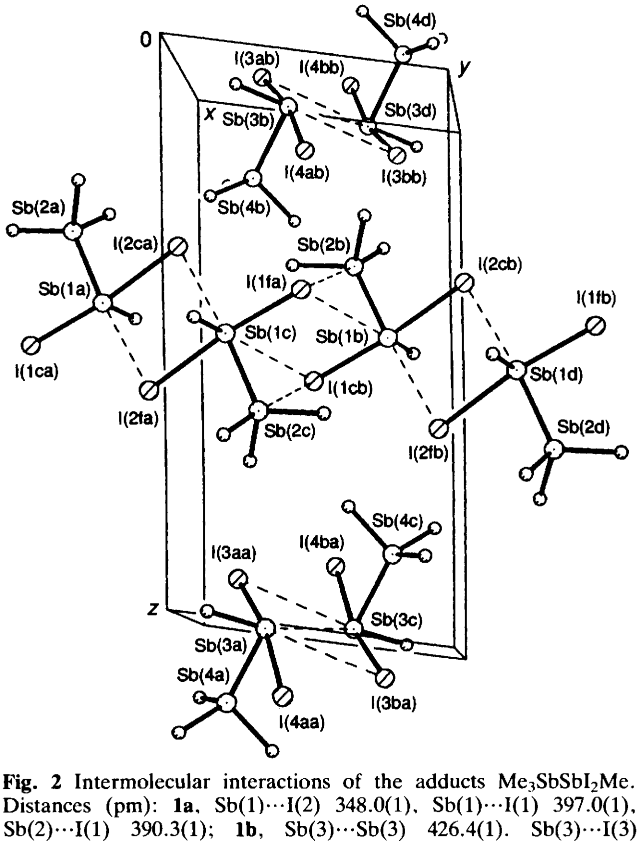

Fig. 2 Intermolecular interactions of the adducts Me_3SbSbI_2Me. Distances (pm): **1a**, Sb(1)···I(2) 348.0(1), Sb(1)···I(1) 397.0(1), Sb(2)···I(1) 390.3(1); **1b**, Sb(3)···Sb(3) 426.4(1). Sb(3)···I(3) 423.4(1).

geometry as **1a**, is much less associated with neighbouring molecules, the shortest Sb–I distances between two adducts being 423.4(1) pm, close to the sum of van der Waals radii of Sb and I (*ca.* 420 pm).[10]

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Footnote

† *Crystal data* for **1**: $C_4H_{12}I_2Sb_2$, $M = 557.4$, triclinic, space group $P\bar{1}$, $a = 7.267(2)$, $b = 9.325(2)$, $c = 18.659(4)$ Å, $\alpha = 81.93(3)$, $\beta = 79.33(3)$, $\gamma = 81.77(3)°$, $T = 173$ K, $V = 1221.3(5)$ Å^3, $Z = 4$, $D_c = 3.032$ g cm^{-3}, μ(Mo-Kα) = 94.17 cm^{-1}. The structure was solved by direct methods, using 5578 independent reflections ($R_{\rm Int} = 0.0004$). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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