Synthesis of Two New Antimony Sulfide Clusters: Structures of $[PPh_4]_2[Sb_6S_6]$ and $[PPh_4]_2[Sb_4S_6]$

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Two new anionic antimony sulfide clusters $[Sb_6S_6]^{2-}$ and $[Sb_4S_6]^{2-}$ have been prepared and structurally characterized from the reduction of Sb_2S_5 with BH_4^- and $[FeH(CO)_4]^-$ respectively.

Investigations into the molecular species of mixed Group 15–Group 16 anionic clusters, in particular those involving the heavier elements, have generally been sporadic but have recently become more intensified.[1] Clusters containing arsenic and the heavier elements of Group 16 have received the most interest. In addition to the well established arsenic sulfide clusters,[2] several arsenic selenides[3] and tellurides[4] have been prepared. However, clusters containing antimony and the chalcogenides have not received much attention. Besides Schlippe's Salt, $Na_3SbS_4{\cdot}9H_2O$,[5] and some derivatives, only a handful of antimony chalcogenide anionic clusters have been reported.[6–8] Although a number of solid-state polymeric antimony sulfide phases are known, the only previously reported molecular antimony sulfide cluster is $Sb_2S_{15}^{2-}$.[6] Here we report the synthesis of two new antimony sulfide anionic clusters, $Sb_4S_6^{2-}$ and $Sb_6S_6^{2-}$, which contain unusual structures. In particular $Sb_6S_6^{2-}$ contains a square Sb_4 unit making it an intermediate between the classical species mentioned above and the true Zintl ion Sb_4^{2-}.[9]

Both anions were prepared by reduction of Sb_2S_5, the only difference being the nature of the reducing agent. The reaction of Sb_2S_5 and a slight excess of $NaBH_4$ led to the formation of orange $Sb_6S_6^{2-}$.† In contrast when $[FeH(CO)_4]^-$ was used as the reducing agent $Sb_4S_6^{2-}$ was isolated in good yield.

The $Sb_6S_6^{2-}$ anion (Fig. 1) was characterized as its PPh_4^+ salt,‡ and consists of a central four-membered ring of antimony atoms in a planar, nearly ideal rectangular arrangement with all the interior angles of the ring *ca.* 90°. The Sb-Sb distances in the ring are 2.829(2) Å and 2.871(2) Å, which are considerably longer than those in the known Sb_4^{2-} square [2.750(1) Å]. This may be due to the presence of the bridging SbS_3 groups. Capping the two faces of the ring are two SbS_3 fragments which bridge opposite edges of the central rectangle. These form two

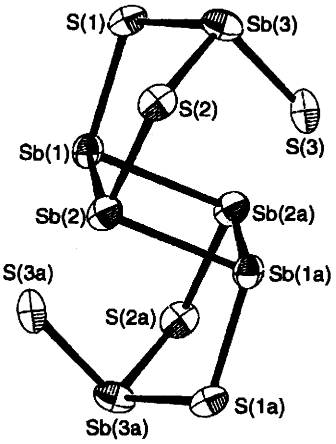

Fig. 1 View of the $Sb_6S_6^{2-}$ anion (35% probability ellipsoids). Selected distances (Å) and angles (°): Sb(1)–Sb(2) 2.829(2), Sb(1)–Sb(2a) 2.871(2), Sb(1)–S(1) 2.478(4), Sb(2)–S(2) 2.509(4), Sb(3)–S(1) 2.427(4), Sb(3)–S(2) 2.406(4), Sb(3)–S(3) 2.360(5), S(3) ··· Sb(2a) 2.934(5), S(3) ··· Sb(1a) 3.114(4); Sb(2)–Sb(1)–Sb(2a) 89.99(5), Sb(1)–Sb(2)–Sb(1a) 90.01(5)

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† Typically Sb_2S_5 (0.30 g, 0.74 mmol) and $NaBH_4$ (0.07 g, 1.89 mmol) were stirred at ambient temperature for 12 h in dry dimethylformamide (dmf) (15 cm³). The orange solution was filtered onto PPh_4Br (0.60 g, 1.4 mmol). Filtration and reduction of the volume to 7 cm³ resulted in precipitation of bright orange cubes in 70% yield based upon Sb. IR (Nujol mull): 525s, 365m, 332m, 300m, 276m, 181w and 135w cm^{-1} (Found: C, 37.35; H, 2.70. Calc. for $C_{48}H_{40}P_2S_6Sb_6$: C, 36.00; H, 2.50%). Similarly $[N(PPh_3)_2][FeH(CO)_4]$ (0.30 g, 0.42 mmol) and Sb_2S_5 (0.18 g, 0.44 mmol) were allowed to react at 60 °C for 2 h in dry dmf (15 cm³). After addition of PPh_4Br (0.38 g, 0.89 mmol) to the brown solution, it was filtered and layered with dry diethyl ether (5 cm³). Storage at 4 °C overnight produced yellow-green plates in 52% yield based upon Sb. IR (Nujol mull): 527s, 385m, 732m, 320(sh), 311s, 157w, 151w and 109w cm^{-1} (Found: C, 42.65; H, 3.10. Calc. for $C_{48}H_{40}P_2S_6Sb_4$: C, 42.45; H, 3.00%).

‡ Crystal data for $[PPh_4]_2[Sb_6S_6]$. $C_{48}H_{40}P_2S_6Sb_6$, $M = 1601.7$, triclinic, space group $P\bar{1}$, $a = 11.173(4)$, $b = 13.177(5)$, $c = 10.922(4)$ Å, $\alpha = 91.49(4)$, $\beta = 118.29(2)$, $\gamma = 110.02(3)$°, $U = 1295(1)$ Å³, $D_c = 2.053$ g cm^{-3}, μ(Mo-Kα) = 3.416 mm^{-1}, $Z = 1$, $\lambda = 0.7107$ Å, orange polyhedron, dimensions 0.05 × 0.10 × 0.15 mm, $2\theta_{max} = 50°$. Data were collected at 173 K on a Rigaku AFC7R four-circle diffractometer; and the structure was solved and refined using TEXSAN;[10] absorption correction (ψ scans, 0.924–1.000) applied, 4825 unique reflections of which 2357 were observed [$I > 3\sigma(I)$]. Full-matrix least-squares refinement with hydrogens constrained to chemically reasonable positions. Final $R = 0.0468$, $R' = 0.0446$ for all Sb, S, P and C atoms anisotropic with 280 variables and 8.4 reflections per refined parameter. Crystal data for $[PPh_4]_2[Sb_4S_6]$. $C_{48}H_{40}P_2S_6Sb_4$, $M = 1358.15$, monoclinic, space group $P2_1/a$, $a = 18.588(2)$, $b = 14.100(5)$, $c = 21.492(2)$ Å, $\beta = 115.137(7)$°, $U = 5091(1)$ Å³, $D_c = 1.772$ g cm^{-3}, μ(Mo-Kα) = 2.438 mm^{-1}, $Z = 4$, $\lambda = 0.7107$ Å, crystal yellow parallelopipeds, dimensions 0.34 × 0.20 × 0.20 mm, $2\theta_{max} = 50°$, data collected at 295.2 K, the structure solved and refined as above. Absorption correction (ψ scans 0.929–1.000), 9675 unique reflections of which 6159 were observed [$I > 3\sigma(I)$]. Refined as above to $R = 0.0342$, $R' = 0.0453$ for all Sb, S, P and C atoms anisotropic with 541 variables and 11.4 reflections per refined parameter. Atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

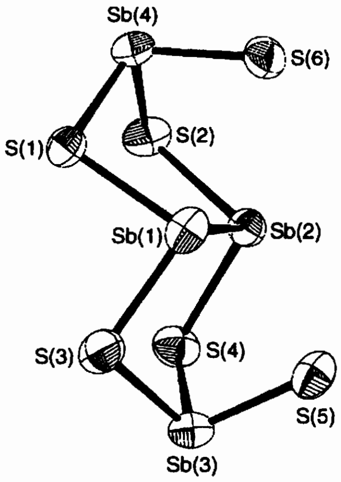
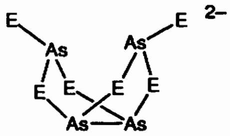


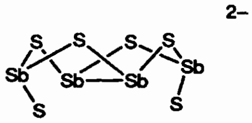
Fig. 2 View of the $Sb_4S_6^{2-}$ anion (35% probability ellipsoids). Selected distances (Å): Sb(1)–Sb(2) 2.8597(9), Sb(1)–S(1), 2.474(2), Sb(1)–S(3) 2.477(2), Sb(2)–S(2) 2.468(2), Sb(2)–S(4), 2.450(2), Sb(3)–S(3) 2.440(3), Sb(3)–S(4) 2.464(2), Sb(3)–S(5) 2.327(2), Sb(4)–S(1) 2.448(2), Sb(4)–S(2) 2.449(2), Sb(4)–S(6) 2.349(2)

five-membered rings with the central core of the molecule, with each face of the ring having an exocyclic sulfur atom directed inward toward the central antimony ring. It is interesting that the exocyclic sulfurs do not bisect the Sb–Sb bonds. Instead, the sulfur atoms are preferentially oriented toward one Sb atom of the ring as shown by the distances S(3) ··· Sb(2a) 2.934(5) *versus* 3.114(4) Å for S(3) ··· Sb(1a). Thus the dianion possesses an inversion centre, but not a mirror plane.

All of the Sb atoms are in a three-co-ordinate apical geometry with the negative charges formally located on the terminal sulfides. The Sb–S distances [2.406(4)–2.509(4) Å] compare favourably to those in $Sb_2S_{15}^{2-}$ [2.412(3)–2.667(4) Å]. The terminal Sb-S distance is shorter at 2.360(5) Å, as expected. The extensive Sb–Sb bonding gives the molecule true Zintl-anion character, not unlike the recently reported antimony tellurides $Sb_4Te_4^{4-}$ and $Sb_9Te_6^{3-}$.[8] The presence of the SbS_3 capping groups makes it a conceptual intermediate between a Zintl ion and a classical main group polyatomic anion.

If the alternative reducing agent $[FeH(CO)_4]^-$ is used the dianion $Sb_4S_6^{2-}$ is obtained as its PPh_4^+ salt (see Fig. 2). The compound is isoelectronic with the well known $As_4E_6^{2-}$ (E = S or Se),[2e,4b] but its conformation is different. In $As_4E_6^{2-}$ the molecule is in a basket-type arrangement with two As-E exocyclic bonds. However, in the $Sb_4S_6^{2-}$ dianion the cyclic Sb-S fragments are inverted. Thus, the two terminal sulfur atoms are pointing downward and slightly toward the Sb–Sb bond.





The Sb–S bond distances of the dianion are similar to those in $Sb_6S_6^{2-}$ and $Sb_2S_{15}^{2-}$. Those in $Sb_4S_6^{2-}$ average 2.46(1) Å and the two exocyclic Sb–S bond distances [Sb(4)–S(6) and Sb(3)–S(5)] are considerably shorter at 2.34(1) Å, indicating some double-bond character. All the Sb atoms in the dianion are trivalent and are in a trigonal-pyramidal environment. There is one Sb-Sb bond in the hinge [2.859 7(9) Å]. The packing in the unit cell appears to be unexceptional, so there is no obvious reason for the choice of conformation of the antimony compound relative to the arsenic analogue.

Acknowledgements

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