DALTON COMMUNICATION

Antimony imido and imido–amido compounds: a new route to an imidoantimony macrocycle

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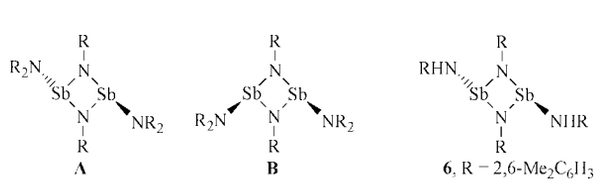
The syntheses of the antimony imido–amido and imido compounds $Sb_2(NH\text{-}2,6\text{-}Me_2C_6H_3)_2(\mu\text{-}N\text{-}2,6\text{-}Me_2C_6H_3)_2$ and $Sb_{12}(NPh)_{18}$ are described.

Compounds of antimony and bismuth incorporating amido and/or imido substituents are important both in terms of the fundamental chemistry of these elements[1] and as starting materials for further synthesis.[2] Well characterised examples in which the antimony and bismuth centres are bonded only to nitrogen are still few in number, however. For antimony these include the tris-amido species $Sb(NR_2)_3$ (R = Me,[3,4] Et,[4] Pr,[4] Bu,[4] $SiMe_3$[1c]) and $Sb(NH\text{-}2,4,6\text{-}Bu^t_3C_6H_2)_3$,[5] dinuclear imido–amido compounds $Sb_2(NMe_2)_2(\mu\text{-}NR)_2$ [R = 4-methylpyridin-2-yl **1**,[6] 3,4,5-$(MeO)_3C_6H_2$ **2**,[6] 2,6-$Pr^i_2C_6H_3$ **3**[2]] and $Sb_2[N(SiMe_3)_2]_2(\mu\text{-}NBu^t)_2$,[7] and a range of species based on the anions $[Sb(NR)_3]^{3-}$ (R = $PhCH_2CH_2$,[8] cyclohexyl[9]), $[Sb_2(NCy)_2(\mu\text{-}NCy)_2]^{2-}$ (Cy = cyclohexyl),[9b,10] $[Sb_3(NMe_2)_2(\mu\text{-}NCy)_4]^-$[8,10c] and $[Sb_3(NHCy)_2(\mu\text{-}NCy)_4]^-$.[9b,10c]† Of particular interest (see below) is the twenty four-membered imidoantimony metallacycle $Sb_{12}[N\text{-}2\text{-}(MeO)C_6H_4]_{18}$ **4**.[11] Bismuth compounds include the tris-amido derivatives $Bi(NR_2)_3$ (R = Me,[12–14] $SiMe_3$,[13,14] Ph[15]) and $Bi(NH\text{-}2,4,6\text{-}Bu^t_3C_6H_2)_3$,[5] the imido–amido compounds $Bi_2(NHR)_2(\mu\text{-}NR)_2$ (R = 2,6-Pr^i_2-C_6H_3) **5**[16] and $Bi_3(NHR)(\mu\text{-}NR)_4$ (R = 2,6-$Me_2C_6H_3$)[17] and the dianion $[Bi_2(NBu^t)_2(\mu\text{-}NBu^t)_2]^{2-}$.[18] We note also the structure of $Bi_2[Me_2Si(NBu^t)_2]_2[\mu\text{-}Me_2Si(NBu^t)_2]$.[19] Herein we describe the synthesis and structure of the dinuclear imido–amido compound $Sb_2(NH\text{-}2,6\text{-}Me_2C_6H_3)_2(\mu\text{-}N\text{-}2,6\text{-}Me_2C_6H_3)_2$ **6** and the imido metallacycle $Sb_{12}(NPh)_{18}$ **7**.

The reaction between $SbCl_3$ and three equivalents of the primary amide salt $Li[NH\text{-}2,6\text{-}Me_2C_6H_3]$ in thf/Et_2O (thf = tetrahydrofuran) afforded, after work-up, yellow crystals of the imido–amido compound $Sb_2(NH\text{-}2,6\text{-}Me_2C_6H_3)_2(\mu\text{-}N\text{-}2,6\text{-}Me_2C_6H_3)_2$ **6**‡ the structure of which was established by X-ray crystallography (Fig. 1).§ Compound **6**, which resides on a crystallographic centre of inversion, comprises two trigonal pyramidal antimony centres each carrying a terminal primary amido group and bridged by two imido units. The disposition of the amido groups with respect to the central Sb_2N_2 unit is *trans* (**A**) (required by the crystallographic inversion centre) as



A **B** **6**, R = 2,6-$Me_2C_6H_3$

found in the related structures of **1**, **2** and **5** although in contrast to the *cis* (**B**) configuration observed for **3**.¶ The Sb–N bond distances (terminal and bridging) are all similar [Sb(1)–N(1) 2.042(4), Sb(1)–N(2) 2.033(4), Sb(1)–N(2A) 2.057(4) Å] and are comparable to those observed in **1** and **2** although the Sb–amide bond lengths in **1** and **2** [2.019(5) and 2.013(5) Å respectively] are shorter than the Sb–imido nitrogen distances in these structures [**1**, 2.052(5), 2.068(5); **2**, 2.048(4), 2.060(4) Å].[6] In all

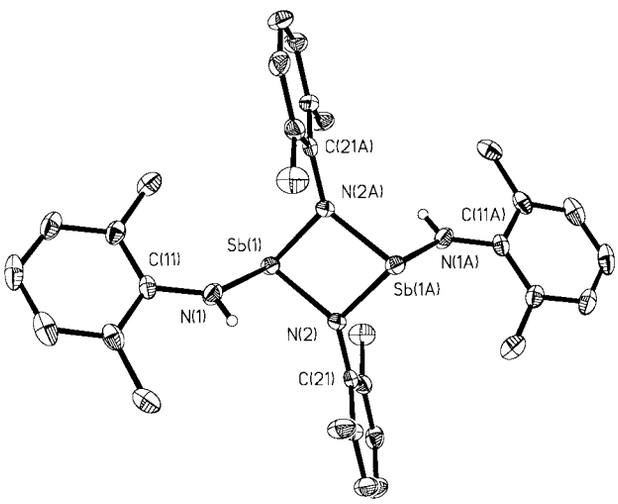


Fig. 1 A view of the molecular structure of **6** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Ellipsoids are drawn at the 40% level. Selected bond lengths (Å) and angles (°) include: Sb(1)–N(1) 2.042(4), Sb(1)–N(2) 2.033(4), Sb(1)–N(2A) 2.057(4), N(1)–C(11) 1.403(6), N(2)–C(21) 1.427(6); N(1)–Sb(1)–N(2) 92.2(2), N(1)–Sb(1)–N(2A) 98.8(2), N(2)–Sb(1)–N(2A) 77.5(2), Sb(1)–N(1)–C(11) 136.2(4), Sb(1)–N(2)–Sb(1A) 102.5(2), Sb(1)–N(2)–C(21) 129.7(3), Sb(1A)–N(2)–C(21) 126.2(3). Symmetry transformations used to generate equivalent atoms: A, $-x$, $-y$, $-z$.

examples the nitrogen atoms are very close to trigonal planar and the antimony atoms are highly pyramidal. The orientation of the imido aryl groups with respect to the Sb_2N_2 units range from almost perpendicular in **6** to nearly coplanar in **1**; in both **1** and **2**, however, these orientations are influenced by significant intermolecular interactions[6] which are absent in the solid state structure of **6**. Further metric data for **6** is given in the caption to Fig. 1.

The reaction between $SbCl_3$ and three equivalents of lithium anilide Li[NHPh] also afforded a yellow crystalline material‖ which was identified by X-ray crystallography as the twenty four-membered imidoantimony metallacycle $Sb_{12}(NPh)_{18}$ **7** analogous to the previously characterised species $Sb_{12}[N\text{-}2\text{-}(MeO)C_6H_4]_{18}$ **4**.[11] Crystals of **7** were of very poor quality, however, and no metric or crystallographic data is given here but the structure determination ** was sufficient to establish the atom connectivities beyond reasonable doubt. The structure is illustrated below. Molecules of **7** have approximate C_{6h} symmetry with antimony centres alternating between being on the outside and inside of the twenty four-membered ring and alternately bridged by $(\mu\text{-}NPh)_2$ and $(\mu\text{-}NPh)$ units. The structure may also be described as containing linked *trans*-related $(NPh)Sb(\mu\text{-}NPh)_2Sb(NPh)$ moieties (*i.e.* type **A** above) of similar form to **6** but having the terminal amido hydrogens replaced by the next antimony in the macrocycle. Thus, the gross structure of **7** is the same as found in **4** although the molecular symmetry of **4** is reduced to S_6 due to the presence

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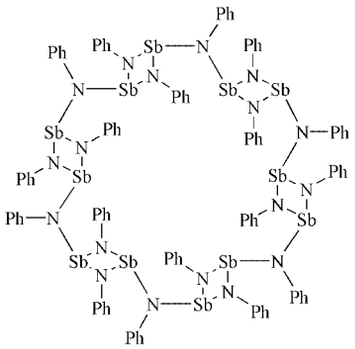

7

and disposition of the imido OMe groups. Clearly the intramolecular O · · · Sb interactions present in **4** are not found in **7** which is interesting in light of the conjecture in ref. 11 indicating that such intramolecular interactions might favour the observed metallacyclic structure over alternative polymeric forms. The basic $Sb_{12}N_{18}$ cyclic structure found in **4** and **7** may now be seen as a more general structural type not critically dependent on the nature of the R group and any associated secondary bonding interactions.

The formation of **6** and **7** may be thought to occur formally according to eqns. (1)–(3) as discussed for related examples by Burford *et al.*[5] and Roesky *et al.*[16]

$$SbCl_3 + 3\ Li[NHR] \longrightarrow Sb(NHR)_3 + 3\ LiCl \quad (1)$$

$$2\ Sb(NHR)_3 \longrightarrow Sb_2(NHR)_2(\mu\text{-}NR)_2 + 2\ NH_2R \quad (2)$$

$$12\ Sb(NHR)_3 \longrightarrow Sb_{12}(\mu\text{-}NR)_{18} + 18\ NH_2R \quad (3)$$

In conclusion, these results show that the structure of the product obtained from reactions between $SbCl_3$ and lithium primary amides is strongly dependent on the amido R group but that formation of the twenty four-membered imidoantimony macrocycles is not dependent on intramolecular secondary bonding interactions. The high yield synthesis of macrocyclic **7** will also enable a study of its host–guest chemistry, the potential for which was also discussed for **4**.[11]

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Notes and references

† For a more detailed discussion of the anionic imido and imido–amido compounds of antimony, see refs. 1*a*,*b* and 2.

‡ A solution of $SbCl_3$ (0.050 g, 2.19 mmol) dissolved in thf (10 cm^3) was added to a stirred solution of Li[NH-2,6-$Me_2C_6H_3$], prepared from 1-NH_2-2,6-$Me_2C_6H_3$ (0.81 cm^3, 6.57 mmol) and Bu^nLi (4.1 cm^3 of a 1.6 M solution in hexanes), in Et_2O (10 cm^3) at 0 °C which resulted in an immediate colour change from colourless to yellow-orange and formation of a white precipitate. After warming to room temperature, all volatiles were removed by vacuum and the remaining solid redissolved in CH_2Cl_2 (30 cm^3). Filtration afforded a clear yellow filtrate which was reduced in volume by vacuum to about 5 cm^3. Addition of an overlayer of hexane (20 cm^3) followed by solvent diffusion at −30 °C over a period of days afforded yellow needle-like crystals of **6** (25% recrystallised yield) one of which was used for X-ray diffraction. ^{1}H NMR (C_6D_6) δ 7.20–6.55 (m, Ph), 2.85 (s, Me), 2.80 (s, Me), 2.30 (s, Me), 2.25 (s, Me). $C_{32}H_{38}Sb_2N_4$ requires C, 53.20; H, 5.30; N, 7.75. Found C, 50.35; H, 5.00; N, 7.10%.

§ Crystal data for Sb_2(NH-2,6-$Me_2C_6H_3)_2(\mu$-N-2,6-$C_6H_3)_2$ **6**: M = 722.16, triclinic, space group $P\bar{1}$ (no. 2), a = 7.929(2), b = 10.012(3), c = 11.075(4) Å, α = 101.00(2), β = 110.705(14), γ = 107.892(14)°, U = 736.9(4) Å^3, T = 173(2) K, Z = 1, μ(Mo-Kα) = 1.860 mm^{-1}, 3491 reflections measured, 2479 unique (R_{int} = 0.0297), final $R1$ = 0.0417 (all data). Data for **6** were collected on a Bruker SMART-CCD detector and the structure was solved and refined against F^2 using SHELXL97.[20] Hydrogen atoms were attached in idealised positions. CCDC reference number 186/2229. See http://www.rsc.org/suppdata/dt/b0/b007020n/ for crystallographic files in .cif format.

¶ The factors affecting whether a *trans* or *cis* geometry is observed in the solid state for imido–amido compounds of the type $E_2(NR_2)_2(\mu\text{-}NR)_2$ (E = Sb, Bi) have been discussed by Wright and Beswick[2] although it is likely that both isomers of such species are present in solution. In the case of **6**, the ^{1}H NMR spectrum reveals four methyl signals of equal intensity consistent with the presence of equal amounts of both isomers in C_6D_6 solution.

‖ A solution of $SbCl_3$ (0.050 g, 2.19 mmol) dissolved in thf (10 cm^3) was added to a stirred solution of Li[NHPh], prepared from $PhNH_2$ (0.59 cm^3, 6.57 mmol) and Bu^nLi (4.1 cm^3 of a 1.6 M solution in hexanes), in Et_2O (10 cm^3) at 0 °C which resulted in an immediate colour change from colourless to yellow-orange and formation of a white precipitate. After warming to room temperature, filtration afforded a clear yellow filtrate which yielded yellow feather-like crystals of **7** (85% recrystallised yield) on cooling to 4 °C. One of these was used for X-ray diffraction although it was of poor quality. Repeated attempts to grow better quality crystals from this and other (*e.g.* CH_2Cl_2/hexane) solvent systems met with no success. $C_{108}H_{90}Sb_{12}N_{18}$ requires C, 41.85; H, 2.95; N, 8.15. Found C, 41.60; H, 2.70; N, 9.00%. Mass spectrum (EI): the following antimony–imido fragments were observed, *m/z* 943 [$Sb_4(NPh)_5$], 820 [$Sb_3(NPh)_5$], 729 [$Sb_3(NPh)_4$], 638 [$Sb_3(NPh)_3$], 426 [$Sb_2(NPh)_2$].

** Despite repeated attempts, good quality crystals of **7** could not be obtained and only a weak and poor quality data set was collected. The data is not of sufficient quality to warrant deposition although the unit cell dimensions are given here; triclinic, space group $P\bar{1}$, a = 17.538(5), b = 17.596(5), c = 27.431(7) Å, α = 84.085(16), β = 79.647(19), γ = 61.340(17)°, U = 2566(2) Å^3. The possibility of the presence of solvent of crystallisation in **7** cannot be ruled out although the microanalytical data on bulk samples ‖ are consistent with unsolvated crystals.

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