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

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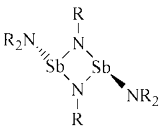
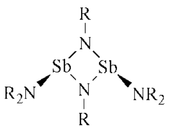
The syntheses of the antimony imido–amido and imido compounds $Sb_2(NH\text{-}2,6\text{-}Me_2C_6H_3)_2(\mu\text{-}N\text{-}2,6\text{-}Me_2C_6H_3)_2$ and $Sb_{12}(NPh)_{18}$ are described.

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-$Pr^i_2C_6H_3$) **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**.

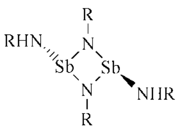
The reaction between $SbCl_3$ and three equivalents of the primary amide salt $Li[NH\text{-}2,6\text{-}Me_2C_6H_3]$ in thf/Et_2O (thf = tetrahydrofuran) afforded, after work-up, yellow crystals of the imido–amido compound $Sb_2(NH\text{-}2,6\text{-}Me_2C_6H_3)_2(\mu\text{-}N\text{-}2,6\text{-}Me_2C_6H_3)_2$ **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 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 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.



A



B



6, R = 2,6-$Me_2C_6H_3$

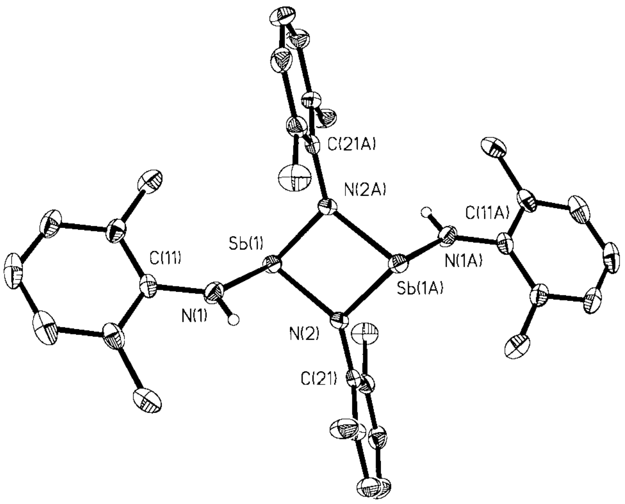


Fig. 1 A view of the molecular structure of **6** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Ellipsoids are drawn at the 40% level. Selected bond lengths (Å) and angles (°) include: Sb(1)–N(1) 2.042(4), Sb(1)–N(2) 2.033(4), Sb(1)–N(2A) 2.057(4), N(1)–C(11) 1.403(6), 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, $-x$, $-y$, $-z$.

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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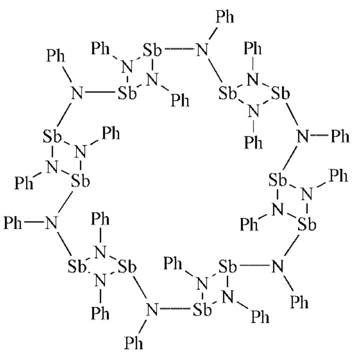

7

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]

Acknowledgements

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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. ^1H 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 $Sb_2(NH\text{-}2,6\text{-}Me_2C_6H_3)_2(\mu\text{-}N\text{-}2,6\text{-}C_6H_3)_2$ **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, $\alpha = 101.00(2)$, $\beta = 110.705(14)$, $\gamma = 107.892(14)°$, $U = 736.9(4)$ 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 $E_2(NR_2)_2$-(μ-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 ^1H 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, $\alpha = 84.085(16)$, $\beta = 79.647(19)$, $\gamma = 61.340(17)°$, $U = 2566(2)$ 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.

1 (*a*) M. A. Paver, C. A. Russell and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1545; (*b*) M. A. Beswick, M. E. G. Mosquera and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 2437; (*c*) M. F. Lappert, A. R. Sanger, R. C. Srivastava and P. P. Power, *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1979.

2 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373.

3 K. Moedritzer, *Inorg. Chem.*, 1964, **3**, 609.

4 A. Kiennemann, G. Levy, F. Schué and C. Taniélian, *J. Organomet. Chem.*, 1972, **35**, 143.

5 N. Burford, C. L. B. Macdonald, K. N. Robertson and T. S. Cameron, *Inorg. Chem.*, 1996, **35**, 4013.

6 A. J. Edwards, M. A. Paver, M.-A. Rennie, P. R. Raithby, C. A. Russell and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1994, 2963.

7 B. Ross, J. Belz and M. Nieger, *Chem. Ber.*, 1990, **123**, 975.

8 A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1277.

9 (*a*) D. Barr, A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1012; (*b*) M. A. Beswick, N. L. Cromhout, C. N. Harmer, M. A. Paver, P. R. Raithby, M.-A. Rennie, A. Steiner and D. S. Wright, *Inorg. Chem.*, 1997, **36**, 1740; (*c*) A. Bashall, M. A. Beswick, C. N. Harmer, M. McPartlin, M. A. Paver and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 517.

10 (*a*) D. Barr, A. J. Edwards, S. Pullen, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1875; (*b*) R. A. Alton, D. Barr, A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1994, 1481; (*c*) A. Bashall, M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. McPartlin, M. A. Paver, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 1389; (*d*) A. Bashall, M. A. Beswick, H. Ehlenberg, S. J. Kidd, M. McPartlin, J. S. Palmer, P. R. Raithby, J. M. Rawson and D. S. Wright, *Chem. Commun.*, 2000, 749.

11 M. A. Beswick, M. K. Davies, M. A. Paver, P. R. Raithby, A. Steiner and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1508.

12 F. Ando, T. Hayashi, K. Ohashi and J. Koketsu, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2011.

13 W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, M. E. Green, D. C. R. Hockless and N. C. Norman, *Inorg. Chem.*, 1991, **30**, 4680.

14 C. J. Carmalt, N. A. Compton, R. J. Errington, G. A. Fisher, I. Moenandar and N. C. Norman, *Inorg. Synth.*, 1996, **31**, 98.

15 W. Clegg, N. A. Compton, R. J. Errington, N. C. Norman and N. Wishart, *Polyhedron*, 1989, **8**, 1579.

16 U. Wirringa, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 1994, **33**, 4607.

17 S. C. James, N. C. Norman, A. G. Orpen, M. J. Quayle and U. Weckenman, *J. Chem. Soc., Dalton Trans.*, 1996, 4159.

18 A. J. Edwards, M. A. Beswick, J. R. Galsworthy, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell, K. L. Verhorevoort and D. S. Wright, *Inorg. Chim. Acta.*, 1996, **248**, 9.

19 M. Veith and B. Bersch, *Z. Anorg. Allg. Chem.*, 1988, **557**, 7.

20 G. M. Sheldrick SHELXL97, Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1997.