

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

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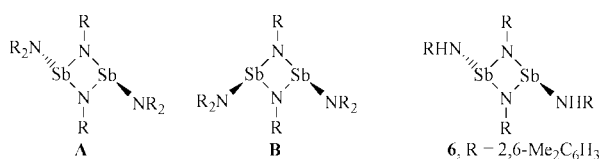
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The syntheses of the antimony imido–amido and imido compounds $\text{Sb}_2(\text{NH}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2(\mu\text{-N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2$ and $\text{Sb}_{12}(\text{NPh})_{18}$ are described.

Compounds of antimony and bismuth incorporating amido and/or imido substituents are important both in terms of the fundamental chemistry of these elements¹ 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 $\text{Sb}(\text{NR}_2)_3$ ($\text{R} = \text{Me},^{3,4} \text{Et},^4 \text{Pr},^4 \text{Bu},^4 \text{SiMe}_3^{1c}$) and $\text{Sb}(\text{NH}-2,4,6\text{-Bu}^t\text{C}_6\text{H}_2)_3$,⁵ dinuclear imido–amido compounds $\text{Sb}_2(\text{NMe}_2)_2(\mu\text{-NR})_2$ [$\text{R} = 4\text{-methylpyridin-2-yl } \mathbf{1}$,⁶ $3,4,5\text{-(MeO)}_3\text{C}_6\text{H}_2$, $\mathbf{2}$,⁶ $2,6\text{-Pr}^i_2\text{C}_6\text{H}_3$, $\mathbf{3}$]⁷ and $\text{Sb}_2[\text{N}(\text{SiMe}_3)]_2(\mu\text{-NBU}^t)_2$,⁷ and a range of species based on the anions $[\text{Sb}(\text{NR})_3]^{3-}$ ($\text{R} = \text{PhCH}_2\text{CH}_2$,⁸ cyclohexyl⁹), $[\text{Sb}_2(\text{NCy})_2(\mu\text{-NCy})_2]^{2-}$ ($\text{Cy} = \text{cyclohexyl}$),^{9b,10} $[\text{Sb}_3(\text{NMe}_2)_2(\mu\text{-NCy})_4]^{-}$,^{8,10c} and $[\text{Sb}_3(\text{NHCy})_2(\mu\text{-NCy})_4]^{-}$.^{9b,10c}† Of particular interest (see below) is the twenty four-membered imidoantimony metallacycle $\text{Sb}_{12}[\text{N}-2\text{-(MeO)C}_6\text{H}_4]_{18}$ $\mathbf{4}$.¹¹ Bismuth compounds include the tris-amido derivatives $\text{Bi}(\text{NR}_2)_3$ ($\text{R} = \text{Me},^{12-14} \text{SiMe}_3,^{13,14} \text{Ph}^{15}$) and $\text{Bi}(\text{NH}-2,4,6\text{-Bu}^t\text{C}_6\text{H}_2)_3$,⁵ the imido–amido compounds $\text{Bi}_2(\text{NHR})_2(\mu\text{-NR})_2$ ($\text{R} = 2,6\text{-Pr}^i_2\text{-C}_6\text{H}_3$) $\mathbf{5}$ ¹⁶ and $\text{Bi}_3(\text{NHR})(\mu\text{-NR})_4$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$)¹⁷ and the dianion $[\text{Bi}_2(\text{NBU}^t)_2(\mu\text{-NBU}^t)]^{2-}$.¹⁸ We note also the structure of $\text{Bi}_2[\text{Me}_2\text{Si}(\text{NBU}^t)]_2[\mu\text{-Me}_2\text{Si}(\text{NBU}^t)]_2$.¹⁹ Herein we describe the synthesis and structure of the dinuclear imido–amido compound $\text{Sb}_2(\text{NH}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2(\mu\text{-N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2$ $\mathbf{6}$ and the imido metallacycle $\text{Sb}_{12}(\text{NPh})_{18}$ $\mathbf{7}$.

The reaction between SbCl_3 and three equivalents of the primary amide salt $\text{Li}[\text{NH}-2,6\text{-Me}_2\text{C}_6\text{H}_3]$ in $\text{thf}/\text{Et}_2\text{O}$ ($\text{thf} = \text{tetrahydrofuran}$) afforded, after work-up, yellow crystals of the imido–amido compound $\text{Sb}_2(\text{NH}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2(\mu\text{-N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2$ $\mathbf{6}$ ‡ the structure of which was established by X-ray crystallography (Fig. 1).§ Compound $\mathbf{6}$, 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 $\mathbf{1}$, $\mathbf{2}$ and $\mathbf{5}$ although in contrast to the *cis* (**B**) configuration observed for $\mathbf{3}$.¶ The $\text{Sb}-\text{N}$ bond distances (terminal and bridging) are all similar [$\text{Sb}(1)-\text{N}(1)$ 2.042(4), $\text{Sb}(1)-\text{N}(2)$ 2.033(4), $\text{Sb}(1)-\text{N}(2A)$ 2.057(4) Å] and are comparable to those observed in $\mathbf{1}$ and $\mathbf{2}$ although the Sb –amide bond lengths in $\mathbf{1}$ and $\mathbf{2}$ [2.019(5) and 2.013(5) Å respectively] are shorter than the Sb –imido nitrogen distances in these structures [$\mathbf{1}$, 2.052(5), 2.068(5); $\mathbf{2}$, 2.048(4), 2.060(4) Å].⁶ In all

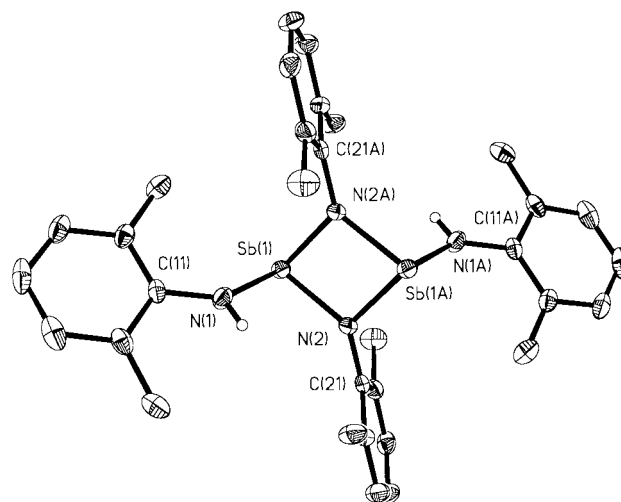
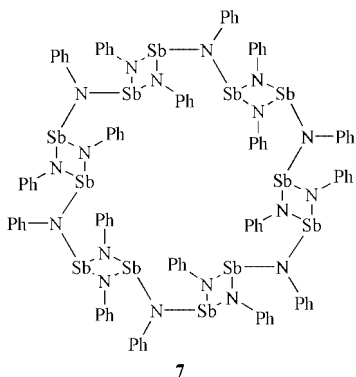


Fig. 1 A view of the molecular structure of $\mathbf{6}$ showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Ellipsoids are drawn at the 40% level. Selected bond lengths (Å) and angles ($^\circ$) include: $\text{Sb}(1)-\text{N}(1)$ 2.042(4), $\text{Sb}(1)-\text{N}(2)$ 2.033(4), $\text{Sb}(1)-\text{N}(2A)$ 2.057(4), $\text{N}(1)-\text{C}(11)$ 1.403(6), $\text{N}(2)-\text{C}(21)$ 1.427(6); $\text{N}(1)-\text{Sb}(1)-\text{N}(2)$ 92.2(2), $\text{N}(1)-\text{Sb}(1)-\text{N}(2A)$ 98.8(2), $\text{N}(2)-\text{Sb}(1)-\text{N}(2A)$ 77.5(2), $\text{Sb}(1)-\text{N}(1)-\text{C}(11)$ 136.2(4), $\text{Sb}(1)-\text{N}(2)-\text{Sb}(1A)$ 102.5(2), $\text{Sb}(1)-\text{N}(2)-\text{C}(21)$ 129.7(3), $\text{Sb}(1A)-\text{N}(2)-\text{C}(21)$ 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 $\mathbf{6}$ to nearly coplanar in $\mathbf{1}$; in both $\mathbf{1}$ and $\mathbf{2}$, however, these orientations are influenced by significant intermolecular interactions⁶ which are absent in the solid state structure of $\mathbf{6}$. Further metric data for $\mathbf{6}$ is given in the caption to Fig. 1.

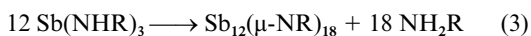
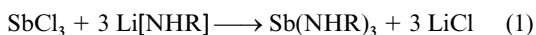
The reaction between SbCl_3 and three equivalents of lithium anilide $\text{Li}[\text{NHPH}]$ also afforded a yellow crystalline material|| which was identified by X-ray crystallography as the twenty four-membered imidoantimony metallacycle $\text{Sb}_{12}(\text{NPh})_{18}$ $\mathbf{7}$ analogous to the previously characterised species $\text{Sb}_{12}[\text{N}-2\text{-(MeO)C}_6\text{H}_4]_{18}$ $\mathbf{4}$.¹¹ Crystals of $\mathbf{7}$ 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 $\mathbf{7}$ 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 $(\text{NPh})\text{Sb}(\mu\text{-NPh})_2\text{Sb}(\text{NPh})$ moieties (*i.e.* type **A** above) of similar form to $\mathbf{6}$ but having the terminal amido hydrogens replaced by the next antimony in the macrocycle. Thus, the gross structure of $\mathbf{7}$ is the same as found in $\mathbf{4}$ although the molecular symmetry of $\mathbf{4}$ is reduced to S_6 due to the presence



7

and disposition of the imido OMe groups. Clearly the intramolecular $O \cdots Sb$ 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



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. 1a,b and 2.

‡ A solution of $SbCl_3$ (0.050 g, 2.19 mmol) dissolved in thf (10 cm³) was added to a stirred solution of $Li[NH-2,6-Me_2C_6H_3]$, prepared from 1-NH₂-2,6-Me₂C₆H₃ (0.81 cm³, 6.57 mmol) and BuⁿLi (4.1 cm³ of a 1.6 M solution in hexanes), in Et₂O (10 cm³) 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 CH₂Cl₂ (30 cm³). Filtration afforded a clear yellow filtrate which was reduced in volume by vacuum to about 5 cm³. Addition of an overlayer of hexane (20 cm³) 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 (C₆D₆) δ 7.20–6.55 (m, Ph), 2.85 (s, Me), 2.80 (s, Me), 2.30 (s, Me), 2.25 (s, Me). C₃₂H₃₈Sb₂N₄ 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, $\alpha = 101.00(2)$, $\beta = 110.705(14)$, $\gamma = 107.892(14)^\circ$, $U = 736.9(4)$ Å³, $T = 173(2)$ K, $Z = 1$, $\mu(Mo-K\alpha) = 1.860$ 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 $E_2(NR_2)_2(\mu-NR)_2$ ($E = Sb, Bi$) have been discussed by Wright and Beswick² 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 C₆D₆ solution.

|| A solution of $SbCl_3$ (0.050 g, 2.19 mmol) dissolved in thf (10 cm³) was added to a stirred solution of $Li[NHPh]$, prepared from $PhNH_2$ (0.59 cm³, 6.57 mmol) and BuⁿLi (4.1 cm³ of a 1.6 M solution in hexanes), in Et₂O (10 cm³) 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.* CH₂Cl₂/hexane) solvent systems met with no success. C₁₀₈H₉₀Sb₁₂N₁₈ 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 [Sb₄(NPh)₃], 820 [Sb₃(NPh)₃], 729 [Sb₃(NPh)₄], 638 [Sb₃(NPh)₃], 426 [Sb₂(NPh)₃].

** 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, $\alpha = 84.085(16)$, $\beta = 79.647(19)$, $\gamma = 61.340(17)^\circ$, $U = 2566(2)$ Å³. 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.

- (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.
- M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373.
- K. Moedritzer, *Inorg. Chem.*, 1964, **3**, 609.
- A. Kiennemann, G. Levy, F. Schué and C. Taniélian, *J. Organomet. Chem.*, 1972, **35**, 143.
- N. Burford, C. L. B. Macdonald, K. N. Robertson and T. S. Cameron, *Inorg. Chem.*, 1996, **35**, 4013.
- 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.
- B. Ross, J. Belz and M. Nieger, *Chem. Ber.*, 1990, **123**, 975.
- 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.
- (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.
- (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. Ehlberg, S. J. Kidd, M. McPartlin, J. S. Palmer, P. R. Raithby, J. M. Rawson and D. S. Wright, *Chem. Commun.*, 2000, 749.
- 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.
- F. Ando, T. Hayashi, K. Ohashi and J. Koketsu, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2011.
- 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.
- 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.