Intramolecular *versus* Intermolecular Bonding in Amidoantimony Dimers; Syntheses and Structures of $\{Sb(NMe_2)[\mu\text{-}N(mpy)]\}_2$ (mpy = 4-methylpyridin-2-yl) and $[Sb(NMe_2)\{\mu\text{-}N[C_6H_2(OMe)_3\text{-}3,4,5]\}]_2$†

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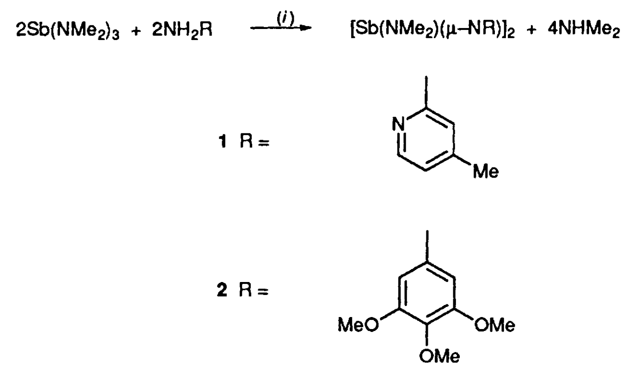
The reaction of $Sb(NMe_2)_3$ with 2-amino-4-methylpyridine (1:1 ratio) produced $\{Sb(NMe_2)[\mu\text{-}N(mpy)]\}_2$ (mpy = 4-methylpyridin-2-yl) which forms unassociated dimers in which relatively weak intramolecular Sb···N interactions are present [2.891(5) Å], whereas a similar reaction with 3,4,5-trimethoxyaniline produced $[Sb(NMe_2)\{\mu\text{-}N[C_6H_2(OMe)_3\text{-}3,4,5]\}]_2$ in which the dimer units are associated into a loosely linked polymer by intermolecular chelating MoO···Sb interactions [3.500(5) Å].

Reagents of the form $ECl_x(NMe_2)_{3-x}$ (E = As, Sb or Bi; x = 0–2) have been known for some time although they have only been employed in a few organic and inorganic syntheses.[1,2] Recently we embarked on a reinvestigation of the use of these species as metallating reagents in the syntheses of Group 15 heteroatom complexes (containing N, P, O, S, *etc.*). None of the antimony complexes previously prepared in this manner had been characterised by single-crystal X-ray analysis or by NMR spectroscopy.[1,2] It was with surprise then that we observed $NHMe_2$, produced as a gaseous by-product in these reactions (b.p. +7 °C), as a stable ligand to Sb in the dimers $[SbCl_2(NHMe_2)(\mu\text{-}OEt)]_2$ and $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$ both in the solid state and in solution.[3] The latter complexes also exhibit intricate association *via* Sb···Cl interactions in their solid-state structures. More recently we have employed the 'mixed-metallation' reaction of $Sb(NMe_2)_3$ with the anionic antimony complex $Li^+Sb[NH(C_6H_{11})]_4^-$ in the synthesis of the unusual 'deck-chair' complex $Li[Sb_3(NMe_2)_2\{N(C_6H_{11})\}_6]$, the first compound to contain a polynuclear amidoantimony anion, and the similar reaction of $Sb(NMe_2)_3$ with the neutral amidolithium complex $[Li(NHCH_2CH_2Ph)]_n$ in the synthesis of the cage complex $[Sb(LiNCH_2CH_2Ph)_3\cdot thf]_2$ (thf = tetrahydrofuran), containing an $Sb(NR)_3{}^{3-}$ trianion.[4]

We now report the syntheses and structures of the related dimeric amidoantimony complexes $\{Sb(NMe_2)[\mu\text{-}N(mpy)]\}_2$ **1** (mpy = 4-methylpyridin-2-yl) and $[Sb(NMe_2)\{\mu\text{-}N[C_6H_2(OMe)_3\text{-}3,4,5]\}]_2$ **2** in which two similar, though differently substituted, aromatic primary amine bridges are present. Complexes **1** and **2** were prepared by the metallation reactions of 2-amino-4-methylpyridine and 3,4,5-trimethoxyaniline, respectively, with $Sb(NMe_2)_3$. In **1** intramolecular Sb···N interactions occur between the pyridyl nitrogen centres and each Sb. In **2**, where the MeO groups are at the periphery of the Sb_2N_2 dimer core, the molecules associate (by chelating intermolecular MeO···Sb interactions) in the solid state.

Results and Discussion

The complexes **1** and **2** are prepared in relatively low, though reproducible, first batch yields by the reactions of $Sb(NMe_2)_3$ with 2-amino-4-methylpyridine and 3,4,5-trimethoxyaniline



Scheme 1 (*i*) Toluene

(1:1 ratio), respectively. The metallation agent $Sb(NMe_2)_3$ was prepared by the literature route from $SbCl_3$ and $Li(NMe_2)$ and is conveniently stored as a standardised toluene solution.[1] The syntheses of **1** and **2** are rapid and little or no decomposition into Sb metal occurs. However, the use of predried solvents (thf and toluene) is essential in order to avoid decomposition (apparently into Sb metal and metal oxides).

Prior to the X-ray characterisations of the complexes, they were basically characterised by elemental analyses and IR and ^1H NMR spectroscopy. Although both are thermally stable, some problems were experienced with **2** which appears to be unstable to prolonged storage at room temperature, and fresh samples of the complex were used in all the analytical and spectroscopic investigations. The results confirm that both reactions result in the retention of one of the Me_2N groups of the precursor $Sb(NMe_2)_3$, and in complete deprotonation of the primary amines, giving species with empirical formulae $[Sb(NMe_2)(NR)]_n$. The reactivity of $Sb(NMe_2)_3$ with primary amines is therefore similar to that of $SbCl(NMe_2)_2$ with NH_2Bu^t {producing $[SbCl(NHMe_2)(\mu\text{-}NBu^t)]_2$}.[3] However, in contrast to the latter, there is no incorporation of the gaseous by-product $NHMe_2$ as a Lewis base to the antimony centres in **1** and **2**. It is particularly noteworthy that the Me_2N groups in the ^1H NMR spectra occur at almost identical chemical shifts (δ 2.99 for **1** and 3.01 for **2**), thus implying that these groups have very similar chemical environments and providing an indication of the similar structures of the two complexes.

Low-temperature X-ray crystallographic studies were under-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

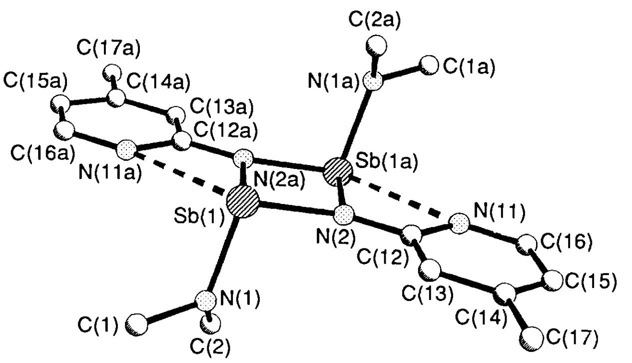

Fig. 1 The dimer structure of molecules of complex **1**

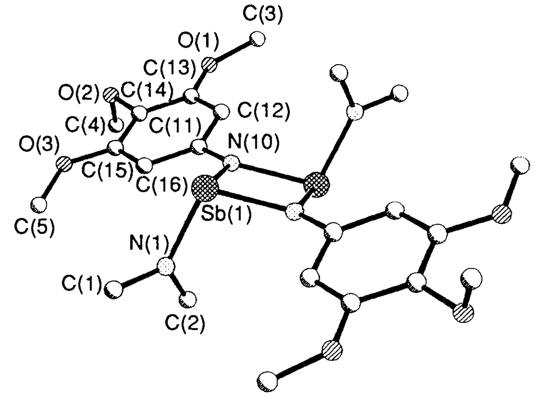

Fig. 2 The dimer structure of molecules of complex **2**

Table 1 Crystal data and structure solutions of $\{Sb(NMe_2)[\mu\text{-N-(mpy)}]\}_2$ **1** and $[Sb(NMe_2)\{\mu\text{-N}[C_6H_2(OMe)_3\text{-}3,4,5]\}]_2$ **2***

	1	**2**
Empirical formula	$C_8H_{12}N_3Sb$	$C_{11}H_{17}N_2O_3Sb$
M	271.96	347.02
Crystal size/mm	0.38 × 0.35 × 0.32	0.37 × 0.31 × 0.24
a/Å	7.206(1)	7.953(2)
b/Å	8.829(2)	9.028(2)
c/Å	9.632(2)	11.262(1)
α/°	115.91(3)	89.38(3)
β/°	110.35(3)	70.68(3)
γ/°	92.76(3)	67.82(3)
U/Å^3	502.0(2)	700.6(3)
D_c/Mg m^{-3}	1.799	1.645
θ range/°	3.57–22.46	3.87–22.50
Reflections collected	1401	1913
Independent reflections	1307 (R_{int} = 0.0092)	1812 (R_{int} = 0.0173)
Goodness of fit	1.392	1.218
*wR*1, *wR*2 [$F > 4\sigma(F)$]	0.026, 0.073	0.031, 0.091
(all data)	0.031, 0.098	0.034, 0.109
Final difference peak and hole/e Å^{-3}	0.925, −1.649	1.104, −1.912

* Details in common: 153(2) K; λ 0.710 73 Å; triclinic, space group $P\bar{1}$; $Z = 2$; $wR1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = F_o^2 + (2F_c^2/3)$.

Table 2 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Sb(1)	618(1)	6 470(1)	4 514(1)
N(1)	−1 959(7)	7 314(6)	3 969(6)
N(2)	482(7)	6 135(6)	6 475(6)
N(11)	994(7)	6 212(6)	8 986(6)
C(1)	−2 163(11)	8 172(9)	2 944(9)
C(2)	−3 888(9)	6 270(9)	3 571(8)
C(12)	1 183(8)	7 117(7)	8 207(7)
C(13)	2 008(8)	8 931(7)	9 101(7)
C(14)	2 590(8)	9 819(8)	10 833(7)
C(15)	2 325(9)	8 873(9)	11 610(8)
C(16)	1 569(10)	7 099(9)	10 678(8)
C(17)	3 440(9)	11 762(8)	11 799(8)

Table 3 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Sb(1)	3858(1)	1325(1)	6258(1)
O(1)	3066(6)	2988(6)	576(4)
O(2)	−636(6)	4845(5)	1883(4)
O(3)	−2240(5)	4679(5)	4386(4)
N(1)	1506(7)	841(6)	7136(5)
N(10)	4062(6)	980(5)	4413(4)
C(1)	192(17)	1645(14)	8319(9)
C(2)	1071(11)	−322(9)	6588(7)
C(3)	5097(10)	2281(11)	−119(6)
C(4)	−1601(11)	4129(10)	1381(7)
C(5)	−3130(8)	4532(7)	5689(5)
C(11)	2851(8)	1915(6)	3795(5)
C(12)	3627(8)	1942(7)	2489(5)
C(13)	2436(8)	2890(7)	1853(5)
C(14)	492(8)	3818(7)	2513(5)
C(15)	−294(7)	3773(6)	3816(5)
C(16)	871(7)	2815(6)	4456(5)

taken on complexes **1** (Fig. 1) and **2** (Fig. 2). Details of the structural refinements of both complexes are given in Table 1, Tables 2 and 3 list the atomic coordinates and selected bond lengths and angles are given in Table 4. Both complexes form similar dimer molecules in the solid state in which almost symmetrical planar Sb_2N_2 cores are present (average Sb–N 2.060 in **1**, 2.054 Å in **2**). There have been comparatively few structurally characterised examples of such dimetallated frameworks as are present in **1** and **2**. Similarly to the Sb_2N_2 core of $[SbCl(NHMe_2)(\mu\text{-NBu}^t)]_2$, the cores of both **1** and **2** are rhombic and have extremely acute angles at Sb {73.6(2) in **1**, 75.8(2)° in **2**; *cf.* 78.4(1)° in $[SbCl(NHMe_2)(\mu\text{-NBu}^t)]_2$[3]}. In both complexes terminal (unreacted) *trans* substituted NMe_2 groups are attached to Sb [Sb–N 2.019(5) in **1**, 2.013(5) Å in **2**]. It is intriguing that, in contrast to $[SbCl_2(NHMe_2)(\mu\text{-OEt})]_2$ and $[SbCl(NHMe_2)(\mu\text{-NBu}^t)]_2$,[3] no further complexation of the Sb in **1** and **2** by $NHMe_2$, produced during their syntheses, has occurred. As indicated by the structures of antimony halide complexes[5] which (unlike antimony amides[6]) are commonly associated by intermolecular interactions in the solid state, the main reason for this difference lies in the greater Lewis acidity of the metal centres in $[SbCl_2(NHMe_2)(\mu\text{-OEt})]_2$ and $[SbCl(NHMe_2)(\mu\text{-NBu}^t)]_2$. However, the solubility of $NHMe_2$ in the reaction solvent used {toluene for **1** and **2**, and diethyl ether for $[SbCl_2(NHMe_2)(\mu\text{-OEt})]_2$ and $[SbCl(NHMe_2)(\mu\text{-NBu}^t)]_2$[3]} may be an additional factor.

Inspection of the geometry of the bridging 4-methylpyridin-2-ylimide ligands of complex **1** indicates that there is a weak intramolecular Sb • • • N interaction between the pyridyl ring nitrogen and each Sb [Sb(1a) • • • N(11) 2.891(5) Å; *cf.* sum of van der Waals radii[7] of Sb and N 3.70 Å]. Thus, the transoid imide ligands have their aromatic rings in the same plane as that of the Sb_2N_2 core of **1** and are pivoted about their μ-N atoms so as to bring the pyridyl N atoms into closer contact with each Sb [C(12)–N(2)–Sb(1a) 115.9(4), C(12)–N(2)–Sb(1) 136.9(4)°]. The antimony centres therefore have a highly distorted four-coordinate geometry.

In contrast to the coplanar conformation of the bridging aromatic groups in complex **1**, the 3,4,5-trimethoxyphenyl groups of **2** are tilted out of the plane of the Sb_2N_2 core by *ca.* 37.1° and are not pivoted towards either of the Sb atoms. These rings have an eclipsed conformation with respect to each other. A major difference between the structures of **1** and **2** is seen in their solid-state packing. Whereas the molecules of **1** are not

Table 4 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1		**2**	
Sb(1)–N(1)	2.019(5)	Sb(1)–N(1)	2.013(5)
Sb(1)–N(2)	2.068(5)	Sb(1)–N(10)	2.048(4)
Sb(1)–N(2a)	2.052(5)	Sb(1)–N(10a)	2.060(4)
C(12)–N(2)	1.378(8)	C(11)–N(10)	1.394(7)
N(11) ··· Sb(1a)	2.891(5)	Intermolecular Sb ··· O	3.500(5) (average)
Sb(1)–N(2)–Sb(1a)	106.4(2)	Sb(1)–N(10)–Sb(1a)	104.2(2)
N(2)–Sb(1)–N(1a)	73.6(2)	N(10)–Sb(1)–N(10a)	75.8(2)
N(1)–Sb(1) ··· Sb(1a)	102.4(1)	N(1)–Sb(1) ··· Sb(1a)	102.6(1)
C(12)–N(2)–Sb(1)	136.9(4)	C(11)–N(10)–Sb(1)	129.1(4)
C(12)–N(2)–Sb(1a)	115.9(4)	C(11)–N(10)–Sb(10a)	125.6(3)

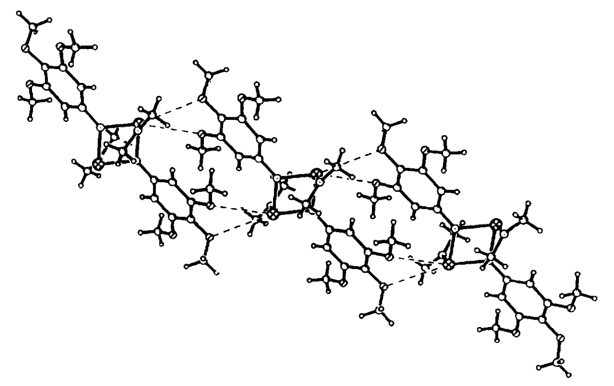

Fig. 3 Association of molecules of complex **2**

associated since the inward-facing pyridyl N atoms are bonded intramolecularly, those of **2** are associated by intermolecular MeO ··· Sb interactions (Fig. 3). Two MeO groups from each bridging trimethoxyphenyl ring of **2** chelate one Sb atom of two neighbouring dimers [average Sb ··· O 3.500(5) Å; *cf.* sum of van der Waals radii[7] of Sb and O *ca.* 3.60 Å]. Thus, overall the structure is that of a loosely linked polymeric sheet in which each Sb has an identical (highly distorted) five-co-ordinate geometry. The co-operative tilting of the aromatic rings of **2** with respect to the Sb_2N_2 ring plane not only brings the MeO groups and the neighbouring antimony centres into more favourable contact, but presumably also aids the packing of the trimethoxyphenyl rings. The intermolecular association of molecules of **2** is a very rare feature in an amido complex of Sb or Bi.

It is clear that the key factor directing the association of complex **2**, as compared to **1**, is the accessibility of the donating heteroatomic groups involved. Only in **2** are these groups at the periphery of the dimer. In contrast to the shielded pyridyl nitrogen centres within **1** which bond intramolecularly, the MeO groups of **2** can therefore induce intermolecular association of the dimers.

Finally, the presence of reactive Me_2N groups in complexes **1** and **2** should provide the opportunity for introducing further functionality into both, *e.g.* by treatment with other acids (amines, alcohols, phosphines, *etc.*) it should be possible to prepare mixed-ligand complexes. Additionally, we have recently confirmed that dimers similar to **1** and **2** can be used, in place of $Sb(NMe_2)_3$, as reagents for 'mixed metallation'. Thus, the reaction of $\{Sb(NMe_2)[\mu\text{-}N(C_6H_{11})]\}_2$ with $\{Li[NH(C_6H_{11})]\}_n$ (1 : 1 monomer equivalents) gives the heterometallic complex $\{Sb_2Li_2[N(C_6H_{11})]_4\}_2$ which contains a core of two interlocked 'broken' cubes.[8]

Experimental

The compound $Sb(NMe_2)_3$[1] and the products **1** and **2** are air- and/or moisture-sensitive. They were handled on a vacuum line using standard inert-atmosphere techniques[9] and under dry oxygen-free Ar. The toluene solvent was dried using sodium–benzophenone and degassed prior to the reactions. The $Sb(NMe_2)_3$ was prepared as described in the literature from $SbCl_3$ and $Li(NMe_2)$ (Aldrich) in Et_2O, and purified by distillation.[1] No purification of the primary amine starting materials was required. Complexes **1** and **2** were isolated and characterised with the aid of an Ar-filled glove-box (Faircrest Mark 4A) fitted with an oxygen and water recirculation system (type B). Melting points were determined by using a conventional apparatus and sealing samples in capillaries under Ar. Infrared spectra were recorded as Nujol mulls using NaCl windows and were run on a Perkin-Elmer 2400 spectrophotometer. Elemental analyses were performed by first sealing samples under Ar in air-tight aluminium boats (1–2 mg). The analyses C, H and N were carried out using a Perkin-Elmer 240 elemental analyser. Proton NMR spectra were recorded on a Bruker WH 250 MHz spectrometer in dry C_6D_6 (using the solvent resonances as the internal reference).

Syntheses.—Complex **1**. A solution of 2-amino-4-methylpyridine (0.27 g, 2.5 mmol) in toluene (15 cm^3) was treated at 0 °C with $Sb(NMe_2)_3$ (0.64 g, 2.5 mmol). The reaction mixture was then stirred at 60 °C (15 min). Reduction of the volume of the colourless solution to 6 cm^3 afforded a trace of white precipitate. Warming led to complete dissolution and subsequent storage at 5 °C (48 h) yielded colourless crystalline blocks of complex **1** in 32% yield (first batch), m.p. 160–162 °C, decomp. 190 °C; ^1H NMR (+25 °C), δ 7.94 [d, 1 H, C^6H], 6.30 [s, 1 H, C^3H], 6.13 [d, 1 H, C^5H], 2.99 (s, 6 H, Me_2N) and 1.80 [s, 3 H, MeC^4] (Found: C, 35.3; H, 4.4; N, 15.2. Calc.: C, 35.3; H, 4.4; N, 15.4%).

Complex **2**. A solution of 3,4,5-trimethoxyaniline (0.46 g, 2.5 mmol) in toluene (30 cm^3) was treated at 0 °C with $Sb(NMe_2)_3$ (0.64 g, 2.5 mmol). The reaction mixture was then stirred at 60 °C for 15 min to yield an intense orange solution. This was filtered through Celite and reduction in its volume to 15 cm^3 afforded a yellow precipitate. Warming led to complete dissolution and subsequent storage at room temperature for 24 h yielded yellow crystalline blocks of complex **2** in 34% yield (first batch); m.p. 183–185 °C; ^1H NMR (+25 °C), δ 5.90 [s, 2 H, $C^{2,6}H$], 3.87 [s, 3 H, C^4OMe], 3.53 [s, 6 H, $C^{3,5}OMe$] and 3.01 (s, 6 H, Me_2N) (Found: C, 37.9; H, 5.0; N, 8.0. Calc.: C, 38.0; H, 4.9; N, 8.0%).

Structure Determinations of Complexes **1** *and* **2**.—Crystals were mounted directly from solution under Ar using a perfluorocarbon oil which protected them from atmospheric O_2 and moisture.[10] The oil 'freezes' at reduced temperatures and holds the crystals static in the X-ray beam. Data were collected on a Stoe-Siemens AED diffractometer by the θ–ω method. Semiempirical absorption corrections based on ψ-scans were employed for both complexes. Details of the structure solutions and refinements of both complexes are shown in Table 1. Both structures were solved by direct methods (SHELXTL PLUS)[11] and refined by full-matrix least squares on F^2 (SHELXL 93).[12]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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