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FULL PAPER

Syntheses and structures of the cubanes [PhOSb(μ_3-NCy)]$_4$ and [pyOBi(μ_3-NCy)]$_4$ (Cy = cyclohexyl, py = 2-pyridyl)

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The *in situ* reaction of the Sb(III) imido dimer [Me$_2$NSb(μ-NCy)]$_2$ with PhOH gives the tetrameric cubane [PhOSb(μ_3-NCy)]$_4$ (**3**). The analogous reaction of 2-pyOH (py = 2-pyridyl) gives the related Bi(III) cubane [pyOBi(μ_3-NCy)]$_4$ (**4**). The latter, which is a rare example of a structurally characterised Bi(III) imido compound, exhibits unusual molecular association of the tetrameric units in the solid state and fluxional behaviour in solution.

Introduction

We have shown in the past ten years that the dimethyl amido Group 15 reagents E(NMe$_2$)$_3$ (E = As–Bi) are highly potent bases and can be used to prepare a range of neutral and anionic Group 15 imido frameworks.[1] For example, the 1 : 1 stoichiometric reactions of a broad range of primary amines (RNH$_2$) with E(NMe$_2$)$_3$ give dimers of the type [Me$_2$NE(μ-NR)]$_2$ at low temperatures, irrespective of the presence of conjugative stabilisation within the organic substituent (R) (Scheme 1).[2]

$$2\mathrm{E(NMe_2)_3} + 2\mathrm{RNH_2} \longrightarrow [\mathrm{Me_2NE}(\mu\text{-NR})]_2 + 4\mathrm{Me_2NH}$$

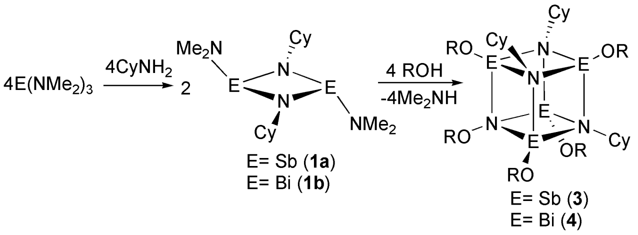
Scheme 1

In the majority of cases these dimers contain planar E$_2$N$_2$ ring units, with the terminal Me$_2$N groups adopting a *trans* conformation with respect to the core.[2a] Only in the case of extremely sterically demanding organic substituents is this arrangement disrupted. For example, the dimer [Me$_2$NSb(μ-NDipp)]$_2$ [Dipp = 2,6-(^{i}Pr)$_2$C$_6$H$_3$] has a highly puckered Sb$_2$N$_2$ ring and a *cis* orientation of the Me$_2$N groups, as a result of the steric confrontation between the Dipp and Me$_2$N groups.[2b] We observed recently that where the Me$_2$N groups in the dimeric unit are replaced by more electronegative substituents further aggregation of the dimeric units into tetrameric 'stack' structures results.[3] In this case the reaction of the dimer [Me$_2$NSb(μ-NCy)]$_2$ (**1a**) (Cy = cyclohexyl) with pyOH (py = 2-pyridyl) gives the tetramer [pyOSb(μ_3-NCy)]$_4$ (**2**) (Fig. 1a). This result can be rationalised in terms of the consequence of increasing the Lewis acidity of the Sb(III) centres, leading to a tendency to increase their coordination number from three in a dimeric unit to four in the tetramer. The formation of a tetramer for **2** has a direct analogue in Sb(V) imido complexes, the organo-Sb(V) imido complex [Ph$_3$Sb(μ-NCH$_2$CH$_2$Ph)]$_2$ being dimeric[4] whereas halide [Cl$_3$Sb(μ_3-NMe)]$_4$ adopts a cubane structure.[5] However, although cubane structures have been observed previously for a few Sb(III) and Sb(V) halides,[6–8] **2** was the first such arrangement to be observed for a simple imido Sb(III) compound.[3]

One interesting feature which we wished to explore in further studies is the effect of electronegative substituents on the pattern of E–N bond lengths found in similar cubane structures. In **2**, the axial disposition of the oxygen substituents leads directly to a pattern of long and short bonds within the Sb$_4$N$_4$ core, and results in an arrangement that can be viewed as a folded, tunnel-shaped Sb$_4$N$_4$ ring (reminiscent of cyclooctetraene) (Fig. 1b). The generality of this observation is demonstrated here by the structural and synthetic studies of the formation of two new examples of Group 15 compounds having similar cubane arrangements, the tetrameric Sb(III) and Bi(III) compounds [PhOSb(μ_3-NCy)]$_4$ (**3**) and [pyOBi(μ_3-NCy)]$_4$ (**4**).

Results and discussion

The new compounds **3** and **4** were obtained in a similar way to [pyOSb(μ_3-NCy)]$_4$ (**2**), by the reactions of the dimers [Me$_2$NSb(μ-NCy)]$_2$ (**1a**) and [Me$_2$NBi(μ-NCy)]$_2$ (**1b**) with PhOH and pyOH, respectively (Scheme 2). The dimers **1a** and **1b** were prepared by the 1 : 1 reactions of E(NMe$_2$)$_3$ (E = Sb, Bi) with CyNH$_2$ using toluene as the solvent; the solutions of the dimers being reacted *in situ* with the organic acids without isolating **1a** and **1b**. A range of other reactions involving alkyl- and alkoxy-substituted 2-amino-pyridines and 2-amino-pyrimidines with **1a** and **1b** were also explored. However, the products were either too thermally unstable to be characterised or no solid products could be isolated.



Scheme 2

The preliminary characterisations of **3** and **4**, which are crystallised as the toluene solvates **3**·0.5toluene and **4**·toluene, were made on the basis of elemental analysis and ^{1}H NMR spectroscopy. These data confirmed the empirical formulae of the compounds, and on this basis it seemed probable that they had similar cubane structures to the previously reported cubane **2** (which also crystallises as a toluene solvate). An interesting feature of the ^{1}H NMR spectrum of the Bi(III) compound **4** is the appearance of only two, very broad C–H resonances for the aromatic py groups at room temperature in toluene or benzene [at δ = 7.7 (1H) and 6.3 (3H)]. This is very different to the

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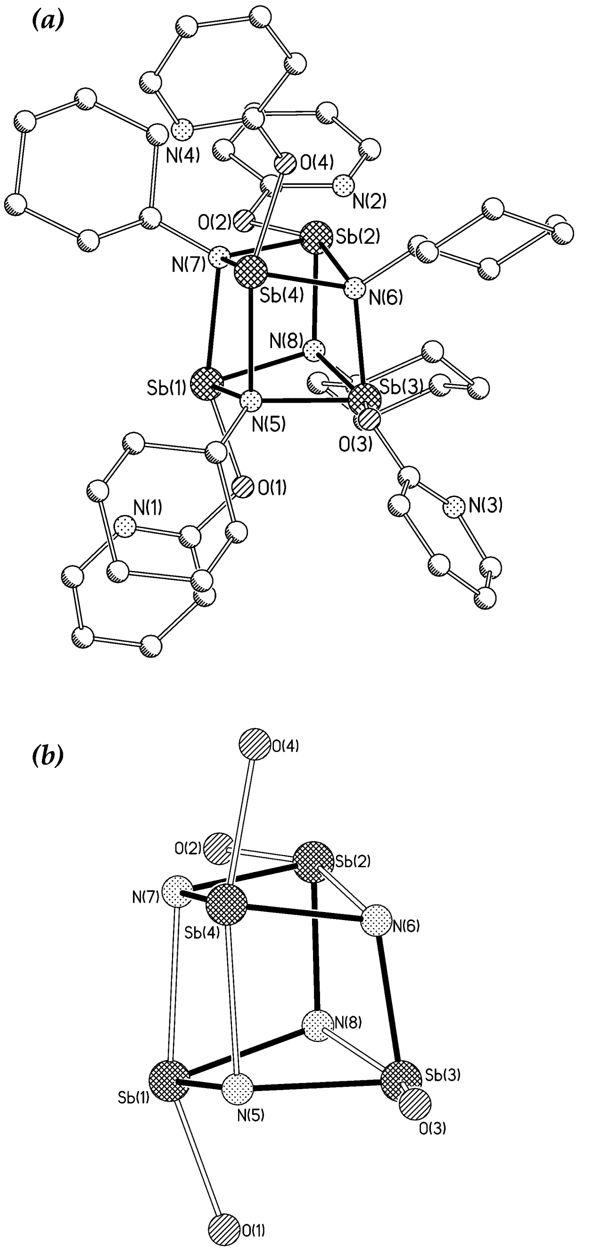


Fig. 1 (a) Cubane structure of [pyOSb(μ_3-NCy)]$_4$ (**2**), and (b) view of the core of **2** as a folded Sb_4N_4 ring.

behaviour of **2** in the same solvents, for which distinct and sharp resonances are observed for the four py proton environments of the pyO ligands [at δ = 8.21 (mult.), 7.25 (mult.), 6.75 (apparent d.), 6.51 (mult.)].[3] This feature provided an initial indication of the unexpected involvement of the py-N donor centres in intramolecular bonding to the Bi(III) atoms in **4**. A variable-temperature ^{1}H NMR study of **4** in toluene shows that as the temperature is lowered to −45 °C, three distinct singlet resonances of approximately equal intensity are resolved (at δ = 8.12, 6.74 and 6.3) (with the expected fourth resonance being masked by the multiplet of the toluene solvent). We ascribe this observation tentatively to a fluxional process in which the weakly bonded py-N donor centres disengage their respective Bi(III) centres within the cubane structure of **4**, and are then free to re-engage other Bi(III) atoms of the Bi_4N_4 core (Scheme 3). Unfortunately, attempts to investigate the nature of **2**, **3** and **4** in benzene using cryoscopic molecular mass measurements proved fruitless as a result of the low solubility of the compounds once isolated.

In order to confirm the preliminary characterisations of **3** and **4**, low-temperature (180 K) X-ray crystallographic studies of both compounds were undertaken. Details of the data collections and refinements of both are given in Table 3. Tables 1and 2 list key bond lengths and angles for **3** and **4**, respectively.

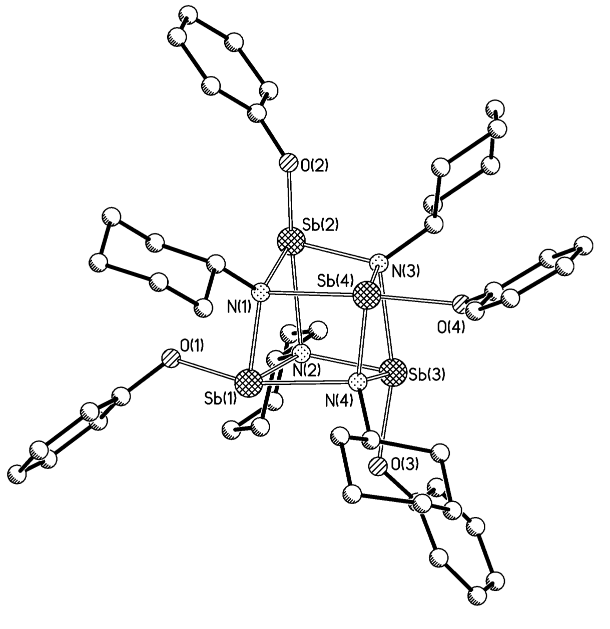
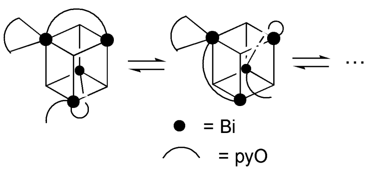


Fig. 2 (a) Structure of cubane molecules of [PhOSb(μ_3-NCy)]$_4$ (**3**).



Scheme 3

Two crystallographically independent, though chemically identical, cubane molecules are found in the solid-state structure of **3** (only one of which is shown in Fig. 2). In addition, half a toluene molecule is found in the crystal lattice for each cubane molecule. Since the two, independent molecules of **3** differ little in terms of the observed bond lengths and angles within them, the discussion of the structure of the compound will involve the average and ranges of the metric parameters between both. Overall, the cubane units of **3** are very similar to those observed previously in the structure of [pyOSb(μ_3-NCy)]$_4$ (**2**).[3] In particular, all of the Sb(III) centres in the cubane molecules of **3** have ten-electron, pseudo-trigonal bipyramidal geometries in which a lone pair of electrons occupies a fifth, equatorial position. The other four-coordination sites are occupied by two equatorial and one axial μ_3-NCy imido N centres within the Sb_4N_4 core and by an axial PhO ligand. This arrangement results in a pattern of Sb–N bond lengths within the core similar to that in **2**, in which the Sb–N bonds which are in axial positions and *trans* with respect to the electronegative PhO groups are severely elongated [range 2.478(3)–2.574(3) Å in **3**; *cf.* 2.475(6)–2.543(6) Å in **2** [3]] compared to the other (equatorial) Sb–N bonds of the core [2.071(3)–2.090(3) Å in **3**; *cf.* 2.075(6)–2.087(6) Å in **2** [3]]. Thus, as in the case of the previously characterised cubane **2**, the structure of the cubane units of **3** can be regarded as arising from the folding of an eight-membered Sb_4N_4 ring (rather than occurring *via* stacking of two dimeric Sb_2N_2 ring units).

The fact that the cage arrangements of **2** and **3** are almost identical in terms of the pattern of Sb–N bond lengths and of the internal N–Sb–N [range 73.0(1)–84.8(1)° in **3**; range 74.1(2)–84.3(2)° in **2** [3]] and Sb–N–Sb [range 91.3(1)–107.4(1)° in **3**; range 92.8(2)–106.6(2)° in **2** [3]] angles within their Sb_4N_4 units, testifies to the lack of involvement of the pyridyl-N atoms in secondary interactions in **2**. Such interactions are likely to lead to a greater distortion of the core geometry in the complex.

Table 1 Key bond lengths (Å) and angles (°) for **3**

Molecule 1		Molecule 2	
Sb(1)–O(1)	2.060(3)	Sb(5)–O(5)	2.046(3)
Sb(1)–N(1)	2.083(3)	Sb(5)–N(5)	2.081(4)
Sb(1)–N(2)	2.081(4)	Sb(5)–N(6)	2.071(3)
Sb(1)–N(4)	2.478(3)	Sb(5)–N(7)	2.574(3)
Sb(2)–O(2)	2.058(3)	Sb(6)–O(6)	2.051(3)
Sb(2)–N(1)	2.082(3)	Sb(6)–N(5)	2.550(3)
Sb(2)–N(2)	2.511(3)	Sb(6)–N(6)	2.089(3)
Sb(2)–N(3)	2.076(3)	Sb(6)–N(8)	2.077(3)
Sb(3)–O(3)	2.059(3)	Sb(7)–O(7)	2.069(3)
Sb(3)–N(2)	2.073(3)	Sb(7)–N(5)	2.071(3)
Sb(3)–N(3)	2.533(3)	Sb(7)–N(7)	2.075(4)
Sb(3)–N(4)	2.090(4)	Sb(7)–N(8)	2.509(3)
Sb(4)–O(4)	2.056(3)	Sb(8)–O(8)	2.064(3)
Sb(4)–N(1)	2.506(3)	Sb(8)–N(6)	2.543(3)
Sb(4)–N(3)	2.082(3)	Sb(8)–N(7)	2.072(3)
Sb(4)–N(4)	2.083(3)	Sb(8)–N(8)	2.078(3)
N–Sb–N range	73.6(1)–84.3(1)	N–Sb–N range	73.0(1)–84.8(1)
Sb–N–Sb range	92.2(1)–106.6(1)	Sb–N–Sb range	91.3(1)–107.4(1)
O–Sb–N range[a]	86.6(1)–91.0(1)	O–Sb–N range[a]	85.3(1)–91.4(1)
O–Sb–N range[b]	157.8(1)–160.0(1)	O–Sb–N range[b]	154.6(1)–157.2(1)

[a] Between equatorial NCy groups and O. [b] Between axial NCy groups and O.

Table 2 Key bond lengths (Å) and angles (°) for **4**

Bi(1)–N(4)	2.738(6)	Bi(2)–O(2)	2.443(5)
Bi(1)–N(6)	2.427(6)	Bi(3)–N(5)	2.180(6)
Bi(1)–N(7)	2.212(6)	Bi(3)–N(6)	2.317(6)
Bi(1)–N(8)	2.311(6)	Bi(3)–N(8)	2.193(6)
Bi(1)–O(1)	2.381(5)	Bi(3)–O(3)	2.434(5)
Bi(2)–N(2)	2.705(5)	Bi(4)–N(5)	2.481(6)
Bi(2)–N(3)	2.609(6)	Bi(4)–N(6)	2.201(6)
Bi(2)–N(5)	2.217(6)	Bi(4)–N(7)	2.206(5)
Bi(2)–N(7)	2.462(6)	Bi(4)–O(4)	2.301(5)
Bi(2)–N(8)	2.479(6)	Bi(4) ··· O(4A)[a]	3.323(6)
N(4)–Bi(1)–N(6)	78.8(2)	O(2)–Bi(2)–N(8)	141.2(2)
N(4)–Bi(1)–N(7)	82.6(2)	N(5)–Bi(3)–N(6)	78.7(2)
N(6)–Bi(1)–N(7)	76.7(2)	N(5)–Bi(3)–N(8)	83.0(2)
N(7)–Bi(1)–N(8)	82.6(2)	N(6)–Bi(3)–N(8)	80.0(2)
O(1)–Bi(1)–N(6)	149.2(2)	O(3)–Bi(3)–N(6)	162.1(2)
N(2)–Bi(2)–N(5)	90.2(2)	N(5)–Bi(4)–N(6)	74.8(2)
N(2)–Bi(2)–N(7)	125.4(2)	N(5)–Bi(4)–N(7)	79.6(2)
N(2)–Bi(2)–N(8)	154.0(2)	N(6)–Bi(4)–N(7)	81.7(2)
N(3)–Bi(2)–N(7)	154.6(2)	O(4)–Bi(4)–N(5)	162.0(2)
N(5)–Bi(2)–N(7)	79.8(2)	Bi–N–Bi[b]	94.9(2)–105.4(2)
N(5)–Bi(2)–N(8)	76.0(2)	Bi(4) ··· O(4) ··· Bi(4A)[a]	106.3(2)
N(7)–Bi(2)–N(8)	74.4(2)	O(4)–Bi(4)–O(4A)	73.7(2)

[a] Atoms labelled A are at $-x, 1-y, -z$. [b] Within the Bi_4N_4 core.

This effect is strikely apparent in the solid-state structure of the Bi(III) compound **4** (Fig. 3a), the direct analogue of the Sb(III) system **2**. Again the structure of **4** is composed of cubane units (with one toluene molecule found in the lattice for each cubane unit). However, owing to the greater Lewis acidity of Bi(III) the pyridyl-N centre of the pyO ligands are now involved in extensive donor intramolecular interactions [range 2.609(6)–2.738(6) Å]. The latter bond lengths are typical of donor interactions found in Bi–N bonded complexes previously characterised (*ca.* 2.30–2.95 Å).[9] In **4**, the two pyO ligands associated with N(3)/O(3) and N(4)/O(4) bridge across opposite Bi_2N_2 faces of the Bi_4N_4 core of **4**, while the ligand associated with N(2)/O(2) adopts a chelating mode, with both donor atoms being bonded exclusively to Bi(2). The remaining pyO ligand bonds to Bi(1) solely by its O centre [O(1)], with the associated N centre [N(1)] remaining uncoordinated. These secondary interactions lead to a broad range of coordination numbers for the Bi(III) centres in the cubane core of **4**. Bi(3) and Bi(4) have similar four-coordinate, pseudo-trigonal bipyramidal coordination geometries, Bi(1) has a five-coordinate, pseudo-octahedral geometry and Bi(2) has a six-coordinate, pseudo-pentagonal bipyramidal geometry [with the vacant sites in each case being occupied by a lone pair of electrons].

The overall result of the irregular pattern of intramolecular coordination of the metal centres in **4** is the highly irregular pattern of Bi–N bond lengths now observed in the cubane core [range Bi–N 2.180(6)–2.481(6) Å]. These Bi–N bond lengths fall over a broader range than normally anticipated for bonds between Bi(III) and amido (R_2N^-) or imido (RN^{2-}) N centres (*ca.* 2.08–2.30 Å [9]). Nonetheless, the pattern of core Bi–N bonds in **4** can be partly attributed to the influence of electronegative O centres on the Bi–N bonds *trans* to them, in a similar way to the pattern observed in **2** and **3**. Thus, three of the longest Bi–N bonds [Bi(1)–N(6) 2.427(6), Bi(2)–N(8) 2.479(6), Bi(4)–N(5) 2.481(6) Å] occur at positions which are approximately *trans* to the coordinating O centres of the pyO ligands. However, although the Bi(3)–N(6) bond is also *trans* to the coordinating O centre O(3), this bond is far shorter [2.317(6) Å]

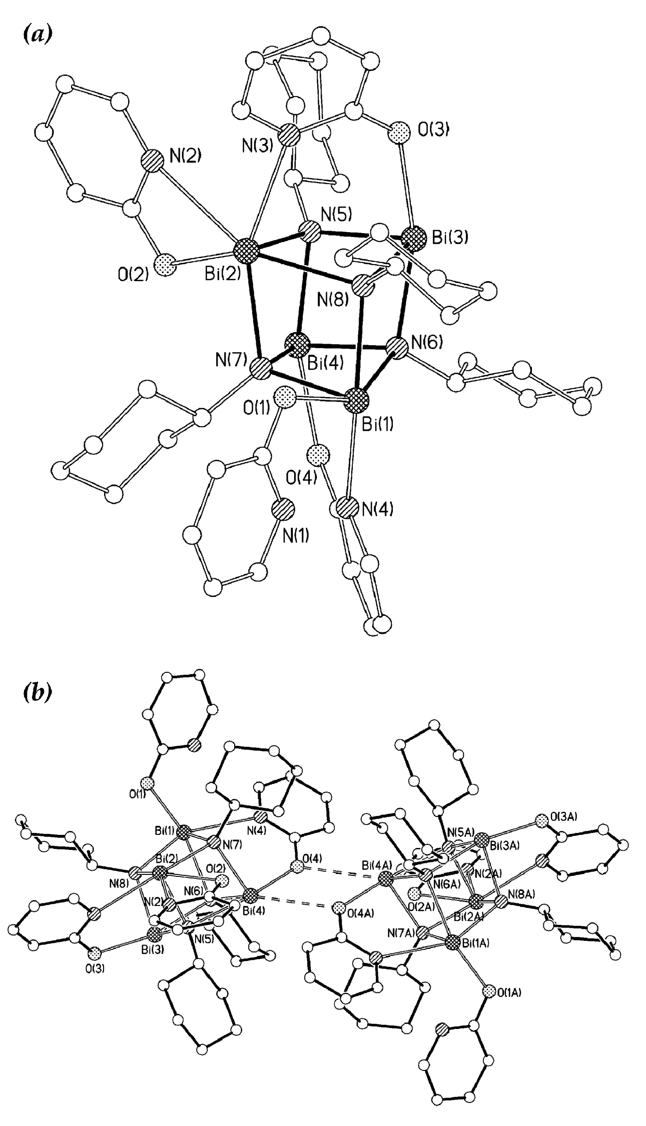


Fig. 3 (a) Structure of cubane molecules of [pyOBi(μ_3-NCy)]$_4$ (**4**), and (b) association of molecules of **4** in the crystal lattice into loosely-linked polymer strands.

than expected on the basis of the pattern observed previously in **2** and **3**. This behaviour can be compared to that found for Bi(4) which has the same coordination geometry as Bi(3) but which exhibits the expected elongation in the *trans* Bi(4)–N(5) bond. The reason for this anomaly lies in the difference in the extent of O and N bonding for the two Bi_2N_2 face-bridging pyO ligands. The Bi(3)–O(3) [2.434(5) Å] bond for the pyO ligand associated with O(3)/N(3) is far longer than the corresponding Bi(4)–O(4) bond [2.301(5) Å] for the ligand associated with O(4)/N(4). This leads directly to a lower *trans* influence on Bi(3). Associated with this is the greater strength of the Bi–N interaction for the O(3)/N(3)–pyO ligand [Bi(2)–N(3) 2.609(6) Å] as compared to that for the O(4)/N(4)–pyO ligand [Bi(1)–N(4) 2.738(6) Å]. Interestingly, the pyridyl-N centres N(3) and N(4) therefore exhibit different *trans* influences on the Bi_4N_4 core, Bi(2)–N(7) [2.462(6) Å] (*trans* to the stronger Bi(2)–N(3) bond) being significantly longer than Bi(1)–N(8) [2.311(6) Å] (*trans* to the weaker Bi(1)–N(4) bond). The remaining Bi–N bonds in **4**, which are not subject to the *trans* influences of O and N centres, are much shorter [range 2.180(6)–2.217(6) Å] than the other bonds of the core.

A further feature of **4** is the association of the cubanes into loosely-linked dimeric units in the crystal lattice (Fig. 3b). Bi(4) and O(4) interact with the symmetry-related atoms of an adjacent molecule, forming centrosymmetric Bi_2O_2 ring units [Bi(4) ··· O(4A) 3.323(6) Å, Bi(4) ··· O(4) ··· B(4A) 106.3(2), Bi(4) ··· O(4) ··· Bi(4A) 73.7(2)°]. There are no other significant interactions between the cubane units, the closest Bi ··· Bi interactions being between symmetry-related Bi(3) atoms [*ca.* 4.95 Å] is probably too long to be considered significant. The presence of the additional intermolecular Bi–O interaction in **4** may provide the underlying reason for the different extents of intramolecular O and N interactions observed for the face-bridging pyO ligands, noted above.

As noted in the introduction to this paper, the cubane structural motif has been observed previously in a few Sb(III) halide complexes, such as the cation [$Cl_3Sb(\mu_3$-Cl)]$_4^+$ [6] and the heterometallic [$Cl_3Sb(\mu_3$-Cl{Fe(CO)$_3$})].[7] In addition, cubane arrangements are observed for the imido/nitrido Sb(III) complex [{ClSb(μ_3-NSiMe$_3$)}$_2${Sb(μ_3-NSbCl$_2$)}{ClSb(μ_3-NSbCl$_3$)}][8] and the imido Sb(V) complex [$Cl_3Sb(\mu_3$-NMe)]$_4$.[5] However, the structures of the new compounds **3** and **4** are rare examples of simple imido Group 15 compounds of this type, the only other being the Sb(III) complex **2** which we reported previously. Also of note is the rarity of structurally characterised Bi(III) imido compounds. Indeed, only three examples have been characterised previously, [$Bi_2(N^tBu)_4$(Li·thf)$_2$] (containing a [$Bi_2(N^tBu)_4]^{2-}$ dianion),[10] the dimer [DippNHBi(μ-NDipp)]$_2$[11] and the trinuclear ring compound [Bi_3{N(2,6-Me$_2C_6H_4$)}$_4$-{NH(2,6-Me$_2C_6H_4$)}].[12] Thus compound **4** represents the highest nuclearity Bi(III) imido compound to be reported so far.

Experimental

General experimental

Compounds **3** and **4** are air- and moisture-sensitive. They were handled on a vacuum line (in an efficient cupboard) using standard inert-atmosphere techniques[13] and under dry/oxygen-free argon. Sb(NMe$_2$)$_3$ and Bi(NMe$_2$)$_3$ were prepared using the literature routes, by transmetallation of $SbCl_3$ or $BiCl_3$ with $LiNMe_2$ (1 : 3 equiv).[14] They were purified by distillation in the case of Sb(NMe$_2$)$_3$ and by crystallisation in the case of Bi(NMe$_2$)$_3$. Sb(NMe$_2$)$_3$ was stored as a standardised solution in toluene and Bi(NMe$_2$)$_3$ as a standardised solution in hexane. $CyNH_2$ was distilled over CaH_2 and stored over molecular sieve prior to use. PhOH and pyOH (Aldrich) were used as supplied. Solvents were dried by distillation over sodium/benzophenone prior to the reactions. The products were isolated and characterized with the aid of an argon-filled glove box fitted with a Belle Technology O_2 and H_2O internal recirculation system. Melting points were determined by using a conventional apparatus and sealing samples in capillaries under argon. IR spectra were recorded as Nujol mulls using NaCl plates and were run on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer. Elemental analyses were performed by first sealing the samples under argon in air-tight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440 Elemental Analyser. Proton NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in dry deuterated benzene or toluene (using the solvent resonances as the internal reference standard).

Synthesis of 3

To a solution of $CyNH_2$ (0.23 ml, 2.0 mmol) in toluene (20 ml) was added Sb(NMe$_2$)$_3$ (2.0 ml, 2.0 mmol, 1.0 mol dm^{-3} solution in hexane) at −78 °C. Warming the reaction mixture to room temperature gave a yellow solution of the dimer [Me$_2$NSb-(μ-NCy)]$_2$. Phenol (0.18 g, 2.0 mmol) was added at room temperature and the resulting solution stirred for 20 min yielding a cloudy yellow solution. After filtering through Celite, the solvent was reduced in volume under vacuum until a yellow precipitate was formed. This was heated into solution. Storage at room temperature gave yellow crystals of **3**·0.5toluene. Yield

Table 3 Crystal data and refinements of [PhOSb(μ$_3$-NCy)]$_4$·0.5toluene (**3**·0.5toluene) and [pyOBi(μ$_3$-NCy)]$_4$·toluene (**4**·toluene)[a]

	3·0.5toluene	**4**·toluene
Empirical formula	$C_{51.50}H_{68}N_4O_4Sb_4$	$C_{51}H_{68}Bi_4N_8O_4$
FW	1294.10	1693.05
T/K	213(2)	180(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	15.208(2)	14.4053(4)
b/Å	18.556(3)	14.7360(5)
c/Å	19.837(3)	14.8018(5)
α/°	86.902(18)	94.740(2)
β/°	75.876(17)	116.155(2)
γ/°	73.847(17)	103.563(2)
V/Å^3	5213.9(13)	2678.7(2)
Z	4	2
ρ_{calc}/Mg m^{-3}	1.649	2.099
μ/mm^{-1}	2.096	13.149
Independent reflections	15421	9425
R_{int}	0.057	0.061
R indices $[I > 2\sigma(I)]$[16]	$R_1 = 0.039$	$R_1 = 0.035$
	$wR_2 = 0.095$	$wR_2 = 0.072$
R indices (all data)[16]	$R_1 = 0.044$	$R_1 = 0.053$
	$wR_2 = 0.097$	$wR_2 = 0.078$

[a] $\lambda = 0.71071$ Å.

0.55 g (42.5%). Mp. 175 °C. ^{1}H NMR (400.16 MHz, +25 °C, C_6D_6), δ = 6.8–7.4 (mult., 28H, aromatic H of Ph group and toluene), 2.19 (s., 1.5H, Me of toluene), 0.80–1.75 (mult., 44H, Cy group). Elemental analysis, found: C 47.6, H 5.2, N 5.3; calc. for **3**·0.5toluene: C 47.8, H 5.2, N 4.3.

Synthesis of 4

To a solution of $CyNH_2$ (0.23 ml, 2.0 mmol) in toluene was added $Bi(MMe_2)_3$ (2.0 ml, 2.0 mmol, 1.0 mol dm^{-3} solution in hexane) at −78 °C. Warming of the reaction mixture to room temperature produced an orange solution of the dimer $[Me_2NBi(\mu\text{-NCy})]_2$. 2-Hydroxypyridine (0.19 g, 2.0 mmol) was added and the mixture was stirred for 1 h, giving a cloudy yellow solution. After filtering through Celite, the solvent was reduced in volume under vacuum until a yellow precipitate appeared which was heated gently into solution. Storage at room temperature gave yellow crystals of **4**·toluene. Yield 0.91 g (11%). Decomp. 144 °C. ^{1}H NMR (400.16 MHz, +25 °C, C_6D_6), δ = 8.0 (br. s., *ca.* 1H C–H py), 7.03–7.40 (mult., 5H, C–H toluene), 6.2 (br. s., *ca.* 3H C–H py), 2.10 (mult., 4H, C(*a*)–H of Cy), 2.19 (s., Me of toluene), 0.80–1.75 (mult., 40H, $-CH_2-$ of Cy), 2.19 (s., 1.5H, Me of toluene), 0.80–1.75 (mult., 44H, Cy group). Elemental analysis, found: C 33.0, H 3.8, N 7.0; calc. for **3**·0.5toluene: C 33.3, H 3.6, N 6.0. Despite repeated attempts we were unable to obtain more satisfactory N analyses of **3** and **4**. The reason for this is unclear, although this may be due to the formation of metal nitrides at the combustion temperature used.

X-Ray crystallographic studies

Data collection for 3 and 4. Crystals of **3** and **4** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture.[15] X-ray intensity data for **3** were collected with a Bruker-AXS Smart APEX CCD diffractometer and for **4** using a Nonius Kappa 4 CCD diffractometer. Details of the data collection, refinement and crystal data are listed in Table 3.

CCDC reference numbers 192356–192357.

See http://www.rsc.org/suppdata/dt/b2/b208302g/ for crystallographic data in CIF or other electronic format.

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