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Association and fragmentation of imidotin(II) complexes containing donor-functionalised peripheries; towards new three-dimensional main group metal ligands†

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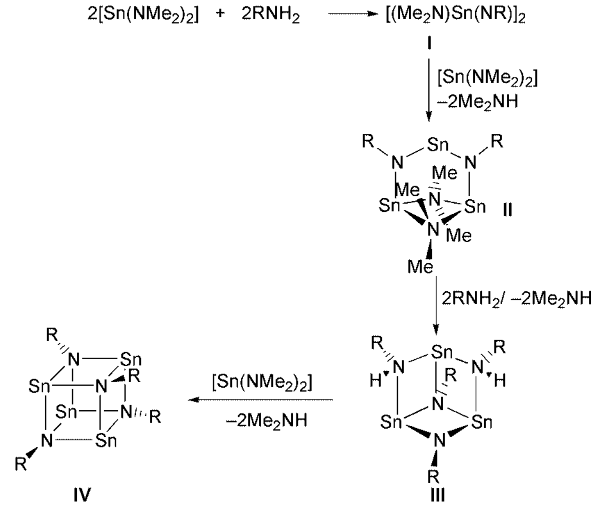
Structural studies of a series of tin(II) imido cubanes, $[SnNR]_4$, containing donor-functionalised organic substituents (R), have allowed the systematic investigation of the factors controlling and affecting association of these architypal tin(II) complexes in the solid state. In addition to steric shielding of the Sn_4N_4 cores, intra- and inter-molecular O and N donation modifies or curtails association *via* Sn···Sn interactions, and can even facilitate fragmentation of the cubane cores.

Introduction

In seminal work, Snaith and co-workers showed that the structural and bonding patterns found in an extensive range of metallo-organic and organometallic alkali metal complexes can simply be understood in terms of 'Ring-stacking' and 'Ring-laddering' principles.[1] Thus, prototypical cubanes such as $[Ph_2C{=}NLi(py)]_4$[2] (py = pyridine) and $[MeLi]_4$[3] can be viewed best as coming about by the association of solvated or unsolvated dimer constituents. Although other p block metal cubanes, such as the tetrameric tin(II) cubanes $[SnNR]_4$,[4–8] are markedly different in terms of the greater covalency and the electron-precise nature of the metal–ligand bonding, the ring-stacking principle provides at least a *conceptual* model for aggregation in these species, and an insight into the potential ways in which Lewis base solvation and the steric requirements of organic substituents (R) can affect the association state.

Tin(II) imido cubanes (which this paper concerns) were first reported by Veith and co-workers[4] in the early 1980s. Since then a number of synthetic strategies have been employed in their preparation.[5–7] However, we have found that reactions of $Sn(NMe_2)_2$ with primary amines (RNH_2) have the advantages that they give clean formation of the cubanes for a broad range of amines, at low temperatures.[8] This has been of particular importance in cases where the imido tin(II) complexes are thermally unstable, such as the cubane $[SnNCH_2(C_5H_4N\text{-}2)]_4$.[8] The isolation of intermediates of the type $[\{Sn(NR)_2\}\{Sn(NMe_2)\}_2]$ (having the 'basket' shaped cage structure **II** in Scheme 1) from the reactions of $Sn(NMe_2)_2$ with sterically demanding amines [such as $DippNH_2$ (Dipp = 2,6-$^iPr_2C_6H_3$)][9] indicates that cubane formation involving acid–base reactions of this type occurs by a common stepwise process (Scheme 1), rather than through the formation then aggregation of discrete :Sn=NR monomers.

We recently embarked on a research programme involving the synthesis of functionalised cubanes $[SnNR]_4$, possessing O and N donor groups within their organic substituents (R). Our primary aims are (*i*) to investigate the stability of the Sn_4N_4 cores to intramolecular solvation, and (*ii*) to explore the factors affecting and controlling intermolecular association.



Scheme 1

The second objective is aimed ultimately at the application of these species as novel, three-dimensional Lewis bases for the assembly of a range of heterometallic molecular and extended arrangements. Interestingly, in preliminary studies we found that the reactions of 2-pyridyl and 2-pyrimidinyl amines with $Sn(NMe_2)_2$ do not give the expected cubanes, but instead the mixed-oxidation state double cubanes $[Sn_7(NR)_8]$ are formed.[10] The formation of the latter may be attributed to a combination of the way in which the organic substituents effect the Sn^{IV}–Sn^{II} reduction potential and the presence of intramolecular N···Sn interactions in the double cubanes, which reinforce the cage structure. Prompted by this finding, we present here a study of the reactions of $Sn(NMe_2)_2$ with an extensive series of primary amines containing O-donor functionalities, and of the formation, intermolecular association and de-aggregation of the $[SnNR]_4$ cubane frameworks.

Results and discussion

Structurally characterised $[SnNR]_4$ cubanes reported previously have almost exclusively involved unfunctionalised organic

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† Dedicated to Ron Snaith.

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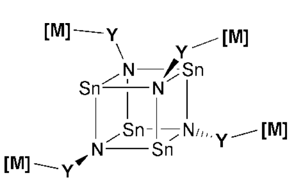
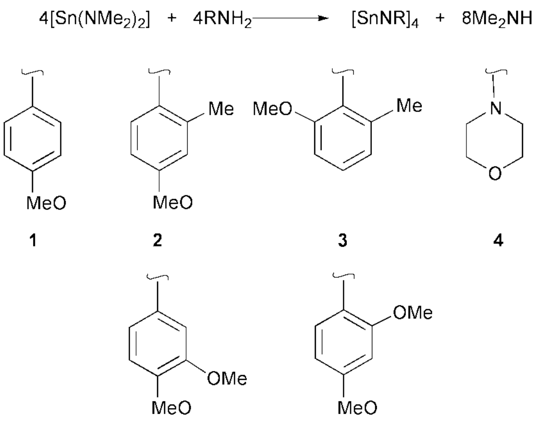


Y = organic group containing donor functionality
[M] = metal fragment

substituents (*e.g.* R = ^{t}Bu,[4] cyclohexyl,[6,8] Ph,[5] 2,6-$^i Pr_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$[7]), notable exceptions being the pyridyl-substituted complex $[SnNCH_2(C_5H_4N\text{-}2)]_4$[8] and the hydrazide $[SnNNMe_2]_4$.[4c] In order to assess the impact of O-donor functionalities on the $[SnNR]_4$ framework, a series of commercially available methoxy- and dimethoxy-substituted arylamines (RNH_2) was selected [R = 4-$MeOC_6H_4$, 2-Me-4-$MeOC_6H_3$, 2-MeO-6-MeC_6H_3, 3,4-$(MeO)_2C_6H_3$ or 2,4-$(MeO)_2C_6H_3$]. For comparison, we also examined reactions of 4-aminomorpholine [R = $N(CH_2CH_2)_2O$]. The 1 : 1 reactions of these amines with $Sn(NMe_2)_2$ in toluene and/or thf all give smooth formation of the corresponding cubanes, which could all be isolated in crystalline form (Scheme 2) (in the cases of **2**, **4** and **5** these were obtained in crystalline form as their solvates **2**·1.5C_6H_5Me, **4**·thf and **5**·2C_6H_5Me). However, during attempts to prepare **3** by this method, the complex $[\{SnN(2\text{-}MeO\text{-}6\text{-}MeC_6H_3)\}_2Sn(NMe_2)_2]$ **7** was isolated, presumably as a result of incomplete reaction of the amine. Repeating the reaction using the appropriate stoichiometry gave **7** more reproducibly (Scheme 3).



Scheme 2

$$3[Sn(NMe_2)_2] + 2RNH_2 \longrightarrow [\{Sn(\mu\text{-}NR)\}_2Sn(NMe_2)_2] + 4Me_2NH$$
$$R = 2\text{-}MeO\text{-}6\text{-}MeC_6H_3\ (\mathbf{7})$$

Scheme 3

A combination of elemental analysis and IR and ^{1}H NMR spectroscopy confirmed that compounds **1**–**6** have the expected compositions (the cubane structures later being proved by their structural characterisation). In the cases of **2**, **4** and **5**, complete or partial desolvation of the lattices by thf or toluene results during isolation of their solvates under vacuum prior to analysis. The ^{1}H NMR spectrum of **7** revealed the presence of Me_2N ligands as well as 2-MeO-6-MeC_6H_3 groups (ratio 1 : 1), indicating that it is a co-complex of an imido tin(II) fragment with $Sn(NMe_2)_2$. As noted in the Introduction, the reactions of sterically demanding primary amines with $Sn(NMe_2)_2$ (1 : 1) led previously to the complexes $[\{Sn(NR)\}_2\{Sn(NMe_2)_2\}]$ [R = 2,6-$^i Pr_2C_6H_3$ (Dipp) or 2,4,6-$Me_3C_6H_2$ (Mes)] which have the same composition as **7**. Prior to the X-ray crystallographic study of **7** it was assumed that the same 'basket-like' cage structure would be observed for this complex. However, although no indication was given by the preliminary spectroscopic studies of the complex, it transpired that **7** is in fact a '*nido*-cubane' isomer (the structure is discussed in detail later).

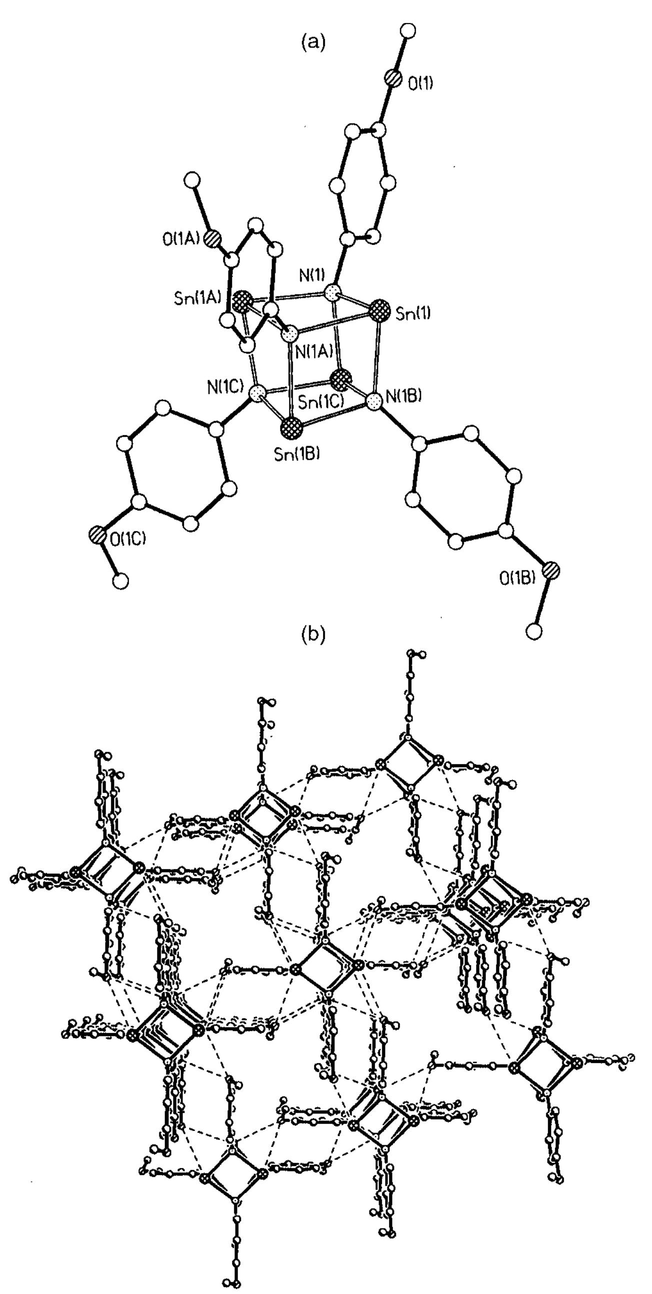


Fig. 1 (a) The cubane structure of $[SnN\{4\text{-}MeOC_6H_4\}]_4$ **1**, which has crystallographic S_4 symmetry. (b) Association of **1** in the crystal lattice through 'face' Sn ··· (μ-O) ··· Sn interactions.

Table 1 Selected bond lengths (Å) and angles (°) for the cubane $[SnN\{4\text{-}MeOC_6H_4\}]_4$ **1**

Sn(1)–N(1)	2.207(3)	Sn(1) ··· O(1A)	3.366(5)
Sn(1)–N(1A)	2.182(3)	Sn(2) ··· O(1A)	3.441(5)
Sn(1)–N(1B)	2.226(3)		
N–Sn–N	80.4(1)–80.8(1)	Sn–N–Sn	98.3(1)–99.9(1)

The low-temperature crystal structures of compounds **1**–**7** were obtained, the molecular structures of which are illustrated in Figs. 1–7, respectively (with H atoms and lattice solvation by toluene and thf omitted for clarity). Tables 1–7 list key bond lengths and angles.

The structures of $[SnN\{4\text{-}MeOC_6H_4\}]_4$ **1** (Fig. 1a), $[SnN\{2\text{-}Me\text{-}4\text{-}MeOC_6H_3\}]_4$·1.5$C_6H_5Me$ **2**·C_6H_5Me (Fig. 2), $[SnN\{2\text{-}MeO\text{-}6\text{-}MeC_6H_3\}]_4$ **3** (Fig. 3), $[SnN\{N(CH_2CH_2)_2O\}]_4$·thf **4**·thf

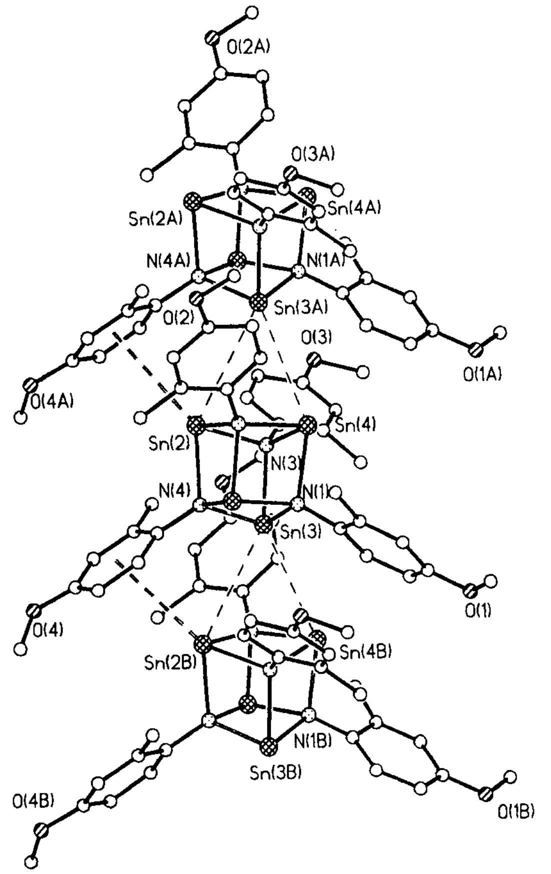


Fig. 2 Association of compound **2** in the crystal lattice into polymers *via* Sn···Sn and Sn···η^6-aryl interactions between neighboring molecules related by *c*-glide symmetry.

Table 2 Selected bond lengths (Å) and angles (°) for $[SnN\{2\text{-}Me\text{-}4\text{-}MeOC_6H_3\}]_4\cdot1.5C_6H_5Me$ **2**

Sn(1)–N(1)	2.21(1)	Sn(3)–N(4)	2.18(1)
Sn(1)–N(2)	2.23(1)	Sn(4)–N(1)	2.22(1)
Sn(1)–N(4)	2.22(1)	Sn(4)–N(2)	2.19(1)
Sn(2)–N(2)	2.21(1)	Sn(4)–N(3)	2.22(1)
Sn(2)–N(3)	2.25(1)	Sn(2)···Sn(3A)	3.87(1)
Sn(2)–N(4)	2.24(1)	Sn(4)···Sn(3A)	3.86(1)
Sn(3)–N(1)	2.22(1)	$aryl_{centroid}$···Sn(2)	3.74
Sn(3)–N(3)	2.21(1)		
N–Sn–N	80.0(4)–83.3(4)	Sn–N–Sn	96.4(4)–100.6(5)

(Fig. 4), $[SnN\{3,4\text{-}(MeO)_2C_6H_3\}]_4\cdot2C_6H_5Me$ **5**·$2C_6H_5Me$ (Fig. 5), and $[SnN\{2,4\text{-}(MeO)_2C_6H_3\}]_4$ **6** (Fig. 6) reveal that all of these species adopt cubane structures in the solid state. Although the Sn–N bond lengths [2.182(3)–2.262(5) Å] and the internal angles at the Sn [77.1(2)–83.3(4)°] and N [95.0(4)–102.4(2)°] fall over a fairly large range, these values are typical of structurally characterised cubanes of this type [Sn–N range 2.15(1)–2.34(2) Å, N–Sn–N mean 81.9 and Sn–N–Sn mean 98.4°].[4–8] A significant feature in the structures of $[SnN\{2\text{-}MeO\text{-}6\text{-}MeC_6H_3\}]_4$ **3** and $[SnN\{2,4\text{-}(MeO)_2C_6H_3\}]_4$ **6** is the presence of intramolecular Sn···O interactions. The 2-Me-6-$MeOC_6H_3$ and 2,4-$(MeO)_2C_6H_3$ groups of both pivot towards four of the ('equatorial') Sn_2N_2 faces of the cubane cores in these species, with their 6-MeO groups μ_2-bridging the tin centres [Sn(1)···O(61B) 2.776(7), Sn(3)···O(61B) 2.967(7) in **3**; O(6)···Sn(1,2) 3.10(1) and 3.00(1) and O(8)···Sn(1,4) 2.97(1), 3.08(1) Å in **6**]. The disposition of the MeO groups in **3** and **6** can be compared to that of the 2-Me groups in $[SnN\{2\text{-}Me\text{-}4\text{-}MeOC_6H_3\}]_4\cdot1.5C_6H_5Me$ **2**·$1.5C_6H_5Me$ in which no distortion of the Me groups towards the Sn_2N_2 faces occurs. The large C···Sn contact distances between the 2-Me substituents and the tin centres of the Sn_2N_2 cubane faces in **2** (*ca.* 3.32–3.71 Å) provides good evidence that the facial MeO···Sn bridgings in **3** and **6** are real interactions. Although the intramolecular Sn···O interactions in **3** and **6** are considerably longer than conventional donor–acceptor bonds, *e.g.* as occur in polymeric $SnBr_2\cdot1,4\text{-}C_4H_8O_2$ [Sn–O 2.527(5)–2.549(9) Å],[11] they are well within the distance estimated for van der Waals interactions (*ca.* 3.70 Å[12]) and are similar to the intermolecular Sn···O interactions linking the oxocubane $[Sn_4(N^tBu)_3O]$ in the solid state (2.90–3.32 Å).[4c] In view of the distortional effects of intramolecular interactions on the cubane cores of the latter, the presence of extensive intermolecular interactions (discussed later) and the varying steric demands of the organic substituents present in these complexes, it is not possible to discern any overall relationships between the electronic influence of the substituents and the pattern of bond lengths and angles present in the Sn_4N_4 cores of **1**–**6**. However, it seems reasonable to assume that the distinctly different range and pattern of bond lengths and angles found in $[SnN\{N(CH_2CH_2)_2O\}]_4\cdot thf$ **4**·thf (which is similar to that observed in the previously characterised hydrazide $[SnNNMe_2]_4$[4c]) stems from the effect of the morpholine N on the hybridisation of the N atoms of the Sn_4N_4 core.

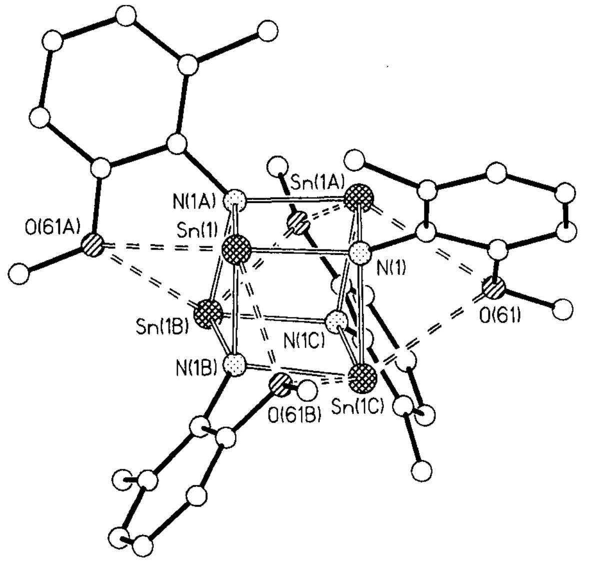


Fig. 3 The cubane structure of $[SnN\{2\text{-}MeO\text{-}6\text{-}MeC_6H_3\}]_4$ **3**.

Table 3 Selected bond lengths (Å) and angles (°) for $[SnN\{2\text{-}MeO\text{-}6\text{-}MeC_6H_3\}]_4$ **3**

Sn(1)–N(1)	2.213(6)	Sn(1)···O(61B)	2.776(7)
Sn(1)–N(1A)	2.235(7)	Sn(3)···O(61B)	2.967(7)
Sn(1)–N(1B)	2.246(7)		
N–Sn–N	79.8(3)–82.9(3)	Sn–N–Sn	96.0(3)–101.1(3)

The structural characterisation of compounds **1**–**6** provides a unique opportunity to examine not only the possibility of intramolecular co-ordination of the Sn_4N_4 cores (as realised in the structures of **3** and **6**), but also the formation and modification of intermolecular interactions in a related series of donor functionalised cubanes. In $[SnN\{4\text{-}MeOC_6H_4\}]_4$ **1**, in which the MeO groups are directed *exo* to the cubane core, all four of the MeO groups of a cubane are involved in identical intermolecular μ-O bonding modes, co-ordinating a Sn_2N_2 face of a neighbouring cubane [Sn···O 3.441(5) and 3.366(5) Å; *cf. ca.* 3.70 Å estimated for a van der Waals interaction[12]] (Fig. 1b). This produces an intricate network structure in which the cubanes are stacked into infinite columns with each being coordinated (as in **3** and **6**) 'equatorially' at four of the six Sn_2N_2 faces by neighbouring MeO groups. Interestingly, the presence of the Me substituent in the 2-Me-4-$MeOC_6H_3$ groups of $[SnN\{2\text{-}Me\text{-}4\text{-}MeOC_6H_3\}]_4\cdot1.5C_6H_5Me$ **2**·$1.5C_6H_5Me$ results

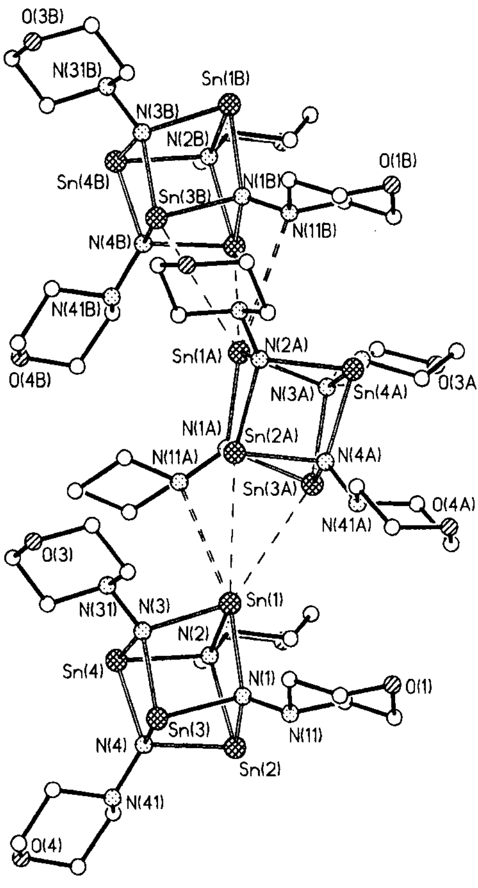


Fig. 4 Association of compound **4** in the crystal lattice into polymers *via* Sn···Sn and Sn···N interactions between molecules related by the 2_1 axis.

Table 4 Selected bond lengths (Å) and angles (°) for $[SnN\{N(CH_2CH_2)_2O\}]_4$·thf **4**·thf

Sn(1)–N(1)	2.250(5)	Sn(3)–N(4)	2.197(5)
Sn(1)–N(2)	2.196(5)	Sn(4)–N(2)	2.208(5)
Sn(1)–N(3)	2.201(5)	Sn(4)–N(3)	2.194(5)
Sn(2)–N(1)	2.207(5)	Sn(4)–N(4)	2.211(5)
Sn(2)–N(2)	2.262(5)	N(11)···Sn(1A)	3.426(5)
Sn(2)–N(4)	2.204(5)	Sn(1)···Sn(2B)	3.677(5)
Sn(3)–N(1)	2.210(5)	Sn(1)···Sn(3B)	3.655(5)
Sn(3)–N(3)	2.252(5)		
N–Sn–N	77.1(2)–81.2(2)	Sn–N–Sn	96.2(2)–102.4(2)

in major modification of the pattern of association found in **1**. Now, the four equatorial Sn_2N_2 faces of each cubane are 'masked' by the 2-Me groups, which reside above these faces (Fig. 2). Thus association of the cubanes in a manner similar to that of **1** is prevented. Instead, molecules of **2** form loosely linked polymer strands (Fig. 2), in which the cubanes are associated by two Sn···Sn interactions [Sn(2)···Sn(3A) 3.87(1), Sn(4)···Sn(3A) 3.86(1) Å]. This type of association is common in imido tin(II) complexes (values in the range 3.41–4.40 Å being observed previously).[4–8] The pattern of Sn···Sn association in **2** is similar to that observed in $[SnNNMe_2]_4$,[4c] although the Sn···Sn distances involved in this complex are clearly considerably more significant (Sn···Sn 3.53 and 3.50 Å[4c]). However, the close approach of molecules of **2** also results in a π interaction between one of the tin centres and the benzene ring of a 2-Me-4-$MeOC_6H_3$ group of the nearest neighbour within the polymer [$aryl_{centroid}$···Sn(2) 3.74 Å]. Of course, considerable care should be taken in the assignment of this close contact as a significant interaction and the $aryl_{centroid}$···Sn distance found in **2** is considerably longer than those observed in $[(arene)SnCl]^+ECl_4^-$ complexes (E = Ga or Al; $aryl_{centroid}$···Sn *ca.* 2.62–2.90 Å).[13] However, in the only reported example involving such a π interaction with a formally *neutral* tin(II) centre, the dimer $[SnS_2(OCH_2Ph)_2]_2$, the contact distance involved ($aryl_{centroid}$···Sn *ca.* 3.66 Å[14]) is extremely similar to that found in **2**. It therefore appears likely that (however weak) the apparent π-arene···Sn interactions in **2** do contribute to the association of the cubanes.

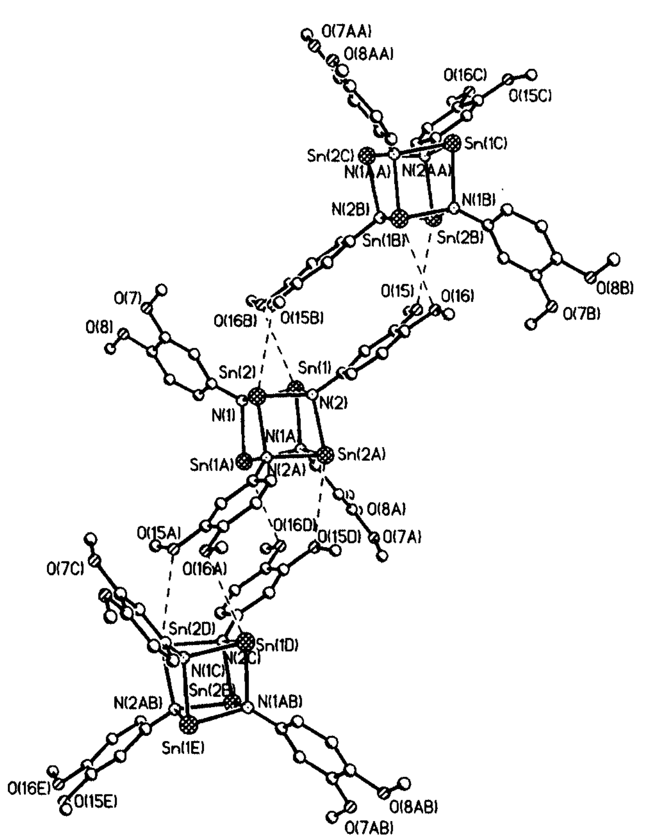


Fig. 5 Association of compound **5** in the crystal lattice into polymers *via* bidentate O···Sn interactions between neighbouring, centrosymmetrically related molecules, each of C_2 symmetry.

Table 5 Selected bond lengths (Å) and angles (°) for $[SnN\{3,4\text{-}(MeO)_2C_6H_3\}]_4$·$2C_6H_5Me$ **5**·$2C_6H_5Me$

Sn(1)–N(1)	2.213(4)	Sn(2)–N(2A)	2.229(4)
Sn(1)–N(2)	2.186(4)	Sn(2)···O(15A)	3.391(6)
Sn(1)–N(1A)	2.239(4)	Sn(2)···O(16A)	3.303(6)
Sn(2)–N(1)	2.193(4)		
Sn(2)–N(2)	2.190(5)		
N–Sn–N	80.2(2)–81.6(2)	Sn–N–Sn	97.7(2)–99.5(2)

The structures of $[SnN\{2\text{-MeO-6-Me}C_6H_3\}]_4$ **3** (Fig. 3) and $[SnN\{N(CH_2CH_2)_2O\}]_4$ in **4**·thf (Fig. 4) make an interesting comparison with those of compounds **1** and **2**. In **3** (whose cubane units are isomeric with **2**) the presence of intramolecular μ-O co-ordination of four of the Sn_2N_2 faces by the 6-MeO donors, and the resulting disposition of the 2-Me groups (which shield the remaining two faces of the cubane), precludes any intermolecular association whatsoever. In **4** intermolecular association involves both Sn···Sn and Sn···N(morpholine) interactions (Fig. 4). The Sn···Sn interactions in this complex are far more significant than those in **2** [Sn(1)···Sn(2B) 3.677(5), Sn(1)···Sn(3B) 3.655(5) Å; *cf. ca.* 3.88 Å in **2**]. However, the overall patterns of intermolecular association (*via* Sn···Sn/donor N···Sn in **4** *versus* Sn···Sn/π-aryl···Sn in **2**) are comparable in their overall nature and connectivity. Somewhat surprisingly, although very similar association *via* two Sn···Sn interactions was observed in $[SnNNMe_2]_4$, the presence of additional intermolecular

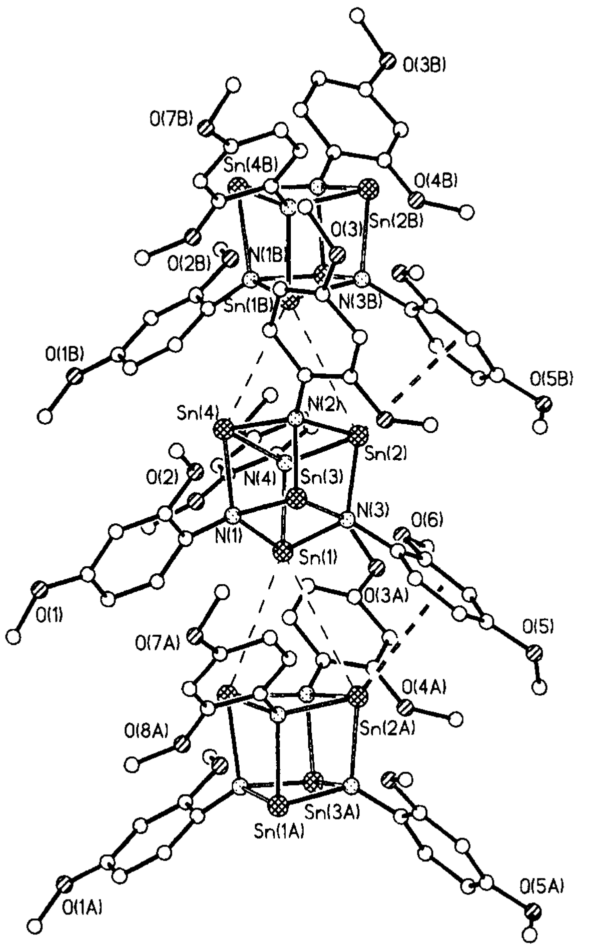


Fig. 6 Association of compound **6** in the crystal lattice into long chain polymers *via* Sn $\cdots$ Sn and Sn $\cdots$ η^6-aryl interactions between neighbouring molecules related by *c*-glide symmetry.

Table 6 Selected bond lengths (Å) and angles (°) for [SnN{2,4-(MeO)$_2$C$_6$H$_3$}]$_4$ **6**

Sn(1)–N(1)	2.18(1)	Sn(4)–N(1)	2.25(2)
Sn(1)–N(3)	2.22(1)	Sn(4)–N(2)	2.18(2)
Sn(1)–N(4)	2.21(1)	Sn(4)–N(4)	2.21(1)
Sn(2)–N(2)	2.22(1)	O(6) $\cdots$ Sn(1,2)	3.10(1), 3.00(1)
Sn(2)–N(3)	2.22(1)	O(8) $\cdots$ Sn(1,4)	2.97(1), 3.08(1)
Sn(2)–N(4)	2.18(2)	Sn(1) $\cdots$ Sn(2A)	3.99(2)
Sn(3)–N(1)	2.22(2)	Sn(1) $\cdots$ Sn(4A)	3.91(2)
Sn(3)–N(2)	2.23(2)	aryl$_{\text{centroid}}$ $\cdots$ Sn(2)	3.72
Sn(3)–N(3)	2.20(1)		
N–Sn–N	79.0(5)–80.9(5)	Sn–N–Sn	98.1(6)–100.1(5)

Sn $\cdots$ N(Me$_2$) interactions in this complex was not noted by the authors.[4c] However, closer inspection of the original crystallographic study reveals that a single short Sn $\cdots$ N interaction is indeed present [*ca.* 3.06 Å; *cf.* N(11) $\cdots$ Sn(1A) 3.426(5) Å in **4**] and that the method of association is in fact identical to that observed in **4**.

The presence of *exo*-directed MeO groups in the cubane constituents of [SnN{3,4-(MeO)$_2$C$_6$H$_3$}]$_4$ in **5**·2C$_6$H$_5$Me, like those of **1**, leads to extensive intermolecular association (Fig. 5). Here the cubanes are arranged into a polymer structure propagated by the chelation of the opposite, symmetry-related Sn$_2$N$_2$ faces of each cubane by both of the MeO groups of a 3,4-(MeO)$_2$C$_6$H$_3$ substituent of a centrosymmetrically related neighbouring molecule [Sn(2) $\cdots$ O(15A) 3.391(6) and Sn(2) $\cdots$ O(16A) 3.303(6) Å]. The remaining two 3,4-(MeO)$_2$C$_6$H$_3$ groups and four of the Sn$_2$N$_2$ faces of each cubane are not involved in intermolecular association. As in the case of the 4-MeOC$_6$H$_4$ rings of **1**, since the 3,4-(MeO)$_2$C$_6$H$_3$ substituents involved in the intermolecular association of **5** are not aligned appropriately the presence of any graphitic interactions can be ruled out.

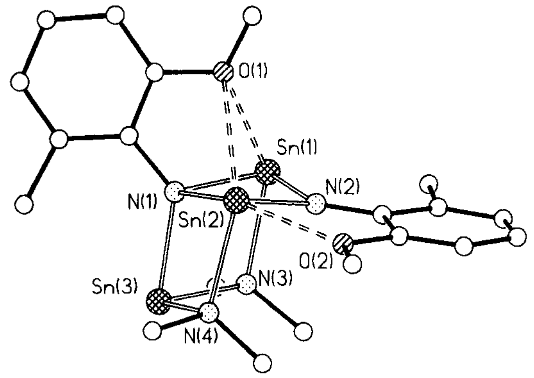


Fig. 7 The *nido*-cubane structure of [{SnN(2-MeO-6-MeC$_6$H$_3$)}$_2$-Sn(NMe$_2$)$_2$] **7**.

Table 7 Selected bond lengths and angles for [{SnN(2-MeO-6-MeC$_6$H$_3$)}$_2$Sn(NMe$_2$)$_2$] **7**

Sn(1)–N(1)	2.232(2)	Sn(3)–N(3)	2.224(3)
Sn(1)–N(2)	2.106(2)	Sn(3)–N(4)	2.223(3)
Sn(1)–N(3)	2.269(2)	Sn(2)–O(2)	2.515(2)
Sn(2)–N(1)	2.346(2)	Sn(2)–O(1)	2.862(3)
Sn(2)–N(2)	2.120(2)	Sn(1)–O(1)	2.856(3)
Sn(2)–N(4)	2.274(3)	Sn(2) $\cdots$ Sn(2A)	4.28
Sn(3)–N(1)	2.182(2)		
N(1)–Sn(1)–N(2)	82.89(9)	N(1)–Sn(3)–N(4)	82.76(9)
N(1)–Sn(1)–N(3)	78.84(9)	N(3)–Sn(3)–N(4)	101.7(1)
N(2)–Sn(1)–N(3)	90.03(9)	Sn–N(1)–Sn	91.95(9)–101.2(1)
N(1)–Sn(2)–N(2)	79.91(9)	Sn(1)–N(2)–Sn(2)	102.4(1)
N(1)–Sn(2)–N(4)	78.14(9)	Sn–N(3,4)–Sn	mean 99.3
N(2)–Sn(2)–N(4)	92.2(2)	Sn(1)–O(1)–Sn(2)	70.3(9)
N(1)–Sn(3)–N(3)	80.90(9)		

As noted earlier, the cubane units of [SnN{2,4-(MeO)$_2$-C$_6$H$_3$}]$_4$ **6** (isomeric with **5**) contain μ-O face-bridging interactions (Fig. 6). In effect, these shield the Sn$_2$N$_2$ faces from involvement in intermolecular interactions. This situation is very similar to the steric shielding of the equatorial Sn$_2$N$_2$ faces in cubane units of **2**, and an extemely similar pattern of intermolecular association therefore results in **6** (Fig. 6). Again, association takes place through a combination of two Sn $\cdots$ Sn interactions [Sn(1) $\cdots$ Sn(2A) 3.99(2), Sn(1) $\cdots$ Sn(4A) 3.91(2) Å] and a π-aryl $\cdots$ Sn interaction [aryl$_{\text{centroid}}$ $\cdots$ Sn(2) 3.72 Å]. The presence of longer Sn $\cdots$ Sn interactions compared to those in **2** is a direct consquence of the crowding of the Sn$_4$N$_4$ core in **6**, resulting from the intramolecular μ-O bridges.

The complex [Sn{N(2-MeO-6-MeC$_6$H$_3$)}$_2$Sn(NMe$_2$)$_2$] **7** has an unusual '*nido*-cubane' cage structure in the solid state, composed of a [Sn(NR)]$_2$ dimer unit co-ordinated by an unchanged Sn(NMe$_2$)$_2$ monomer (Fig. 7). The composition of this cage is exactly the same as that of [{Sn(NR)}$_2$Sn(NMe$_2$)$_2$] (R = Dipp or Mes), which are obtained from the incomplete 1 : 1 reactions of RNH$_2$ with Sn(NMe$_2$)$_2$.[9] However, the latter adopt a completely different 'basket-like' cage arrangement (like structure **II**, illustrated in Scheme 1). The formation of an isomeric, alternative structure for **7** is no doubt due to the presence of less sterically encumbered 2-MeO-6-MeC$_6$H$_3$ groups and to the intramolecular Sn $\cdots$ O interactions occurring in the complex. Two other complexes related to **7** are [{Sn(μ-N^{t}Bu)}$_2$Sn(O^{t}Bu)$_2$], composed of a [Sn(μ-N^{t}Bu)]$_2$ dimer 'trapped' by its co-ordination to a Sn(O^{t}Bu)$_2$ monomer,[15] and [Sn$_3$(N^{t}Bu)$_4$H$_2$], having a *nido*-cubane structure similar to that of **7**.[16] The latter can be regarded as being constructed from the co-ordination of a [Sn(μ-N^{t}Bu)]$_2$ imido dimer by a [Sn(NH^{t}Bu)$_2$] amido monomer (Scheme 1, complex **III**) and is the closest structural relative to **7**.

An interesting feature in the structure of compound **7** is the adoption of different O-bonding modes for the two 2-MeO-6-MeC_6H_3 ligands, which results in distinct environments for the two tin centres of the $[Sn\{N(2\text{-}MeO\text{-}6\text{-}MeC_6H_3)\}]_2$ dimer unit [four-co-ordinate Sn(1) and five-co-ordinate Sn(2)]. The bridging Sn···O interactions [Sn(2,1)–O(1) mean 2.86 Å] are similar to those found in **3** and **6**. However, the terminal Sn···O bond length [Sn(2)–O(2) 2.515(4) Å] can be compared to those found between neutral O-donor ligands and Sn(II), *e.g.* in polymeric $SnBr_2\cdot 1,4\text{-}C_4H_8O_2$ [2.527(5)–2.549(9) Å],[11] and is consistent with a significant donor interaction. The shortest imido N–Sn bonds in **7** occur with the two-co-ordinate imido centre N(2). The greater co-ordination number of Sn(2) compared to that of Sn(1) results in a longer Sn(2)–N(2) bond [2.120(2) Å] than Sn(1)–N(2) [2.106(2) Å]. Both of these bonds are appreciably longer than those between the two-co-ordinate tin(II) and two-co-ordinate nitrogen centres in the N–Sn–N bridge of $[\{Sn(NR)\}_2Sn(NMe_2)_2]$ (R = Dipp or Mes) [2.06(1)–2.072(9) Å].[9] Longer imido N–Sn bonds, which are comparable with those found in $[SnNR]_4$ cubanes,[4–8] occur at the three-co-ordinate imido centre N(1) [Sn–N(1) range 2.182(2)–2.346(2) Å; the longest of these being made with Sn(2)]. The amido N–Sn bond lengths in the $Sn(NMe_2)_2$ monomer unit of **7** are identical within the crystallographic errors [Sn(3)–N(3,4) mean 2.22 Å], and are similar to those observed in the Sn(μ-N)Sn bridge of dimeric $[Sn(NMe_2)_2]_2$ [mean 2.27 Å].[17] Molecules of **7** are loosely associated into dimers by Sn···Sn interactions [Sn(2)···Sn(2A) *ca.* 4.28 Å; *cf. ca.* 4.40 Å estimated for a van der Waals interaction].

In compounds **1**–**6** it can be seen that, although donor substituents disposed correctly for intra- and inter-molecular co-ordination have a marked effect on the pattern of association and some distortional effects on the structures, the cubane structures persist. The question of whether donor functionality can disrupt or modify the formation of cubanes is answered in the structure of **7**. It has been shown previously that reactions of sterically demanding amines with $Sn(NMe_2)_2$ only go as far as the cages $[\{Sn(NR)\}_2Sn(NMe_2)_2]$ (R = Dipp or Mes), even under reflux and employing the 1 : 1 stoichiometry appropriate for the formation of cubanes.[9] In addition, Veith and Frank have shown that trapping of $(SnNR)_2$ dimer units can be achieved during the formation of cubanes, by the addition of $Sn(O^tBu)_2$ (as occurs in $[\{Sn(\mu\text{-}N^tBu)\}_2\cdot Sn(O^tBu)_2]$).[15] The formation of **7** illustrates that, in addition to steric retardation and trapping, the presence of accessible donor functionalities (capable of intramolecular co-ordination of the tin(II) centres) can also facilitate formation and stabilisation of cubane fragments.

Experimental

General

Compounds **1**–**7** are air- and moisture-sensitive.[18] They were handled on a vacuum line using standard inert atmosphere techniques and under dry/oxygen-free argon. Toluene and thf were dried by distillation over sodium–benzophenone prior to the reactions. The products were isolated and characterised with the aid of an argon-filled glove box fitted with a Belle Technology O_2 and H_2O internal recirculation system. $Sn(NMe_2)_2$ was prepared using the literature procedure, from the reaction of $SnCl_2$ with a suspension of $LiNMe_2$ in Et_2O.[17] All the amines were acquired from Aldrich and used as supplied. Melting points were not corrected. 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 AM 400 MHz spectrometer in dry deuteriated DMSO (using the solvent resonances as the internal reference standard).

Syntheses

Compound 1. A solution of $4\text{-}MeOC_6H_4NH_2$ (0.48 g, 4.0 mmol) in toluene (10 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in toluene (20 ml) at −78 °C. After stirring (20 min), the mixture was brought to room temperature and stirred (3 h). A small quantity of precipitate was removed by filtration and the yellow-brown filtrate reduced to *ca.* 10 ml. Storage at room temperature (12 h) gave a crop of light yellow crystalline blocks of compound **1**. Yield 0.10 g (10%). Decomp. to brown solid 100 °C. ^1H NMR (400 MHz, D_6-DMSO, 25 °C): $\delta = 6.86$ [m (apparent dd), 4 H, C–H aryl] and 3.67 (s, 3 H MeO). Found: C, 34.4; H, 2.9; N, 5.6%. Calc. for $[NC_7H_7NOSn]_n$ C 35.0, H 2.9, N 5.8%.

Compound 2. $2\text{-}Me\text{-}4\text{-}MeOC_6H_3NH_2$ (0.4 ml, 0.55 g, 4.0 mmol) was added to a stirred solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in toluene (20 ml) at −78 °C. The reaction mixture was brought to room temperature and stirred for 2 h. A green solution containing a fine precipitate was produced. The precipitate was heated into solution and the solution reduced under vacuum to *ca.* 10 ml. Storage at room temperature (12 h) gave a crop of yellow-green crystalline needles. Elemental analysis and ^1H NMR show that *ca.* one toluene molecule is removed during isolation of the crystals under vacuum (15 min, 10^{-2} atm). The following data refer to this material. Yield 0.15 g (14%). Decomp. 270–280 °C to black solid. ^1H NMR (400 MHz, D_6-DMSO, 25 °C): δ 6.7–6.5 (m, 3 H, aryl C–H), 3.67 (s, 3 H, MeO) and 2.61 (s, 3 H, Me). Found: C, 39.8; H, 4.2; N, 5.5%. Calc. for $[NC_8H_9NOSn]_4\cdot 0.5C_7H_8$ C, 40.2; H, 4.0; N, 5.1%.

Compound 3. $2\text{-}MeO\text{-}6\text{-}MeC_6H_3NH_2$ (0.45 ml, 0.55 g, 4.0 mmol) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in toluene (20 ml) at −78 °C, and stirred (10 min). The reaction mixture was brought to room temperature and stirred (3 h). A golden-brown solution containing a precipitate was produced. The precipitate was heated into solution. Storage at room temperature (12 h) gave a crop of large yellow-green crystalline needles. Yield 0.15 g (15%). Decomp. *ca.* 250 °C to brown solid. ^1H NMR (400 MHz, D_6-DMSO, +25 °C): δ 6.7–6.5 [m, 12 H, C(3,4,5)-H], 3.67 (s, 12 H, MeO) and 2.61 (s, 12 H, Me). Found: C, 37.8; H, 3.5; N, 5.4%. Calc. for $[C_8H_9NOSn]_n$ C, 37.8; H, 3.6; N, 5.5%.

Compound 4. $4\text{-}NH_2N(CH_2CH_2)_2O$ (0.39 ml, 0.41 g, 4.0 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in thf (20 ml) at −78 °C. After stirring (15 min), the reaction was brought to room temperature and stirred (2 h). A yellow solution containing a bright orange precipitate was formed. The precipitate was dissolved by adding thf (10 ml) and heating in an oil bath (70 °C). Slow cooling in the oil bath gave a crop of orange crystalline needles of compound **4**·thf. Elemental analysis and ^1H NMR show that only a trace of the lattice solvation by thf remains after isolation under vacuum (15 min, 10^{-2} atm.). Yield 0.20 g (23%). Decomp. 220 °C to black solid. ^1H NMR (400 MHz, D_6-DMSO, +25 °C); δ 3.69 (s, 16 H, CH_2) and 1.73 (s, 16 H, CH_2). Found: C, 25.1; H, 4.0; N, 12.5% Calc. for $[C_4H_8N_2OS]_n$ C, 25.4; H, 4.3; N, 11.8%.

Compound 5. A solution of $3,4\text{-}(MeO)_2C_6H_3NH_2$ (0.61 g, 4.0 mmol) in toluene (10 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in toluene (20 ml) at −78 °C. After stirring (30 min), the mixture was brought to room temperature and stirred (2 h). A brown solution with a yellow-green precipitate was formed. Addition of toluene (10 ml) and vigorous heating in an oil bath (120 °C) gave a clear brown solution. Slow cooling in the oil bath (12 h) gave a large crop of yellow crystalline needles of compound **5**·$2C_6H_5Me$. ^1H NMR and elemental analysis show that *ca.* one lattice toluene molecule is removed

Table 8 Crystal data and refinements for $[SnN\{4\text{-}MeOC_6H_4\}]_4$ **1**, $[SnN\{2\text{-}Me\text{-}4\text{-}MeOC_6H_3\}]_4\cdot 1.5C_6H_5Me$ **2**·$1.5C_6H_5Me$, $[SnN\{2\text{-}MeO\text{-}6\text{-}MeC_6H_3\}]_4$ **3**, $[SnN\{N(CH_2CH_2)_2O\}]_4\cdot thf$ **4**·thf, $[SnN\{3,4\text{-}(MeO)_2C_6H_3\}]_4\cdot 2C_6H_5Me$ **5**·$2C_6H_5Me$, $[SnN\{2,4\text{-}(MeO)_2C_6H_3\}]_4$ **6**, $[\{SnN(2\text{-}MeO\text{-}6\text{-}MeC_6H_3)\}_2Sn(NMe_2)_2]$ **7**

	1	**2**·$1.5C_6H_5Me$	**3**	**4**·thf	**5**·$2C_6H_5Me$	**6**	**7**
Formula	$C_{28}H_{28}N_4O_4Sn_4$	$C_{42.5}H_{48}N_4O_4Sn_4$	$C_{32}H_{36}N_4O_4Sn_4$	$C_{20}H_{40}N_8O_5Sn_4$	$C_{46}H_{52}N_4O_8Sn_4$	$C_{32}H_{36}N_4O_8Sn_4$	$C_{20}H_{30}N_4O_2Sn_3$
Formula weight	959.30	1153.61	1015.41	947.36	1263.68	1079.41	714.55
T/K	180(2)	180(2)	223(2)	180(2)	180(2)	180(2)	180(2)
Crystal system	Tetragonal	Monoclinic	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$I\bar{4}$	$P2_1/c$	$P\bar{4}$	$P2_12_12_1$	$C2/c$	$P2_1/c$	$P2_1/c$
a/Å	12.7836(7)	13.7720(17)	9.9679(16)	11.8644(3)	31.6406(15)	14.0750(4)	12.2482(2)
b/Å	12.7836(7)	27.577(3)	—	12.4107(4)	8.9310(3)	24.3080(10)	13.7235(2)
c/Å	9.5220(5)	12.388(4)	8.505(3)	20.7486(5)	18.6514(8)	12.3940(5)	14.4319(3)
a/°	—	—	—	—	—	—	—
β/°	—	111.489(9)	—	—	113.982(2)	102.651(2)	98.9670(10)
γ/°	—	—	—	—	—	—	—
U/Å^3	1556.09(15)	4377.8(14)		3055.14(15)	4815.6(3)	4137.5(3)	2396.18(7)
Z	2	4	1	4	4	4	4
μ(Mo-Kα)/mm^{-1}	3.212	2.300	2.963	3.275	2.105	2.433	3.125
Reflections collected	7211	25437	1270	13472	10524	12426	37964
Independent reflections (R_{int})	1381 (0.069)	7518 (0.053)	1125 (0.041)	6836 (0.063)	4581 (0.046)	7131 (0.046)	5493 (0.063)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.020, 0.042	0.086, 0.201	0.030, 0.073	0.038, 0.078	0.042, 0.114	0.106, 0.261	0.026, 0.053
(all data)	0.028, 0.044	0.096, 0.204	0.033, 0.077	0.048, 0.114	0.061, 0.134	0.134, 0.284	0.038, 0.057

during isolation of the crystals under vacuum (15 min, 10^{-2} atm). Yield 0.80 g (68%). The following data refer to the powder produced. Decomp. *ca.* 187 °C, final melting at 260 °C. ^1H NMR (400 MHz, D_6-DMSO, 25 °C): δ 7.27 (m, 5 H, C_6H_5 toluene), 6.89 [d ($J = 8.5$), 4 H, C(5)-H], 6.71 [d ($J = 2.7$), 4 H, C(2)-H], 6.52 [dd ($J = 2.7$, 8.5), 4 H, C(6)-H], 3.79 (s, 12 H, MeO), 3.73 (s, 12 H, MeO) and 2.34 (s, 3 H, Me toluene). Found: C, 40.7; H, 3.9; N, 4.7%. Calc. for $[C_8H_9NO_2Sn]_4\cdot C_7H_8$ C, 40.0; H, 3.8; N, 4.8%.

Compound 6. A solution of $2,4\text{-}(MeO)_2C_6H_3NH_2$ (0.61 g, 4.0 mmol) in toluene (10 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4.0 mmol) in toluene (20 ml) at −78 °C. The reaction mixture was stirred (15 min) and then brought to room temperature and stirred (2 h). A dark solution containing some precipitate was formed. The precipitate was removed by filtration and the solution reduced under vacuum to *ca.* 10 ml. Storage at −5 °C (48 h) gave a crop of fine green crystalline needles of compound **6**. Yield 0.40 g (37%). Decomp. *ca.* 210 °C to black solid. ^1H NMR (400 MHz, D_6-DMSO, 25 °C): δ 6.50 [d ($J = 8.4$), 1 H, aryl H(6)], 6.40 [d ($J = 2.7$), 1 H, aryl H(3)], 6.25 [dd ($J = 8.4/2.7$ Hz), 1 H, aryl H(5)], 3.71 (s, 3 H, MeO) and 3.62 (s, 3 H, Me). Found: C, 36.0; H, 3.5; N, 4.5%. Calc. for $[C_8H_9NO_2Sn]_n$ C, 35.6; H, 3.4; N, 5.2%.

Compound 7. $2\text{-}MeO\text{-}6\text{-}MeC_6H_3NH_2$ (0.45 ml, 0.55 g, 4.0 mmol) was added to a solution of $Sn(NMe_2)_2$ (1.24 g, 6.0 mmol) in toluene (10 ml) at −78 °C. The mixture was stirred (10 min) then brought to room temperature and stirred (2 h). A yellow solution containing a small amount of precipitate was formed. The precipitate was removed by filtration and the solvent reduced to *ca.* 5 ml. Storage at −5 °C (12 h) gave colourless crystalline blocks of compound **7**. Yield 0.30 g (21%). Decomp. *ca.* 124 °C, final decomp. at 176 °C to black solid. ^1H NMR (400 MHz, D_6-DMSO, 25 °C): δ 6.77 [d ($J = 8$), 1 H, C(3)-H], 6.68 [d ($J = 7.2$), 1 H, C(5)-H], 6.57 [t ($J = 7.7$ Hz), 1 H, C(4)-H], 3.85 (s, 3 H, MeO), 3.40 (s, 12 H, Me_2N) and 2.16 (s, 3 H, Me). Found: C, 33.6; H, 4.1; N, 8.0%. Calc. for $[C_{20}H_{30}N_4O_2Sn_3]_n$ C, 33.6; H, 4.2; N, 7.8%.

X-Ray crystallographic studies of compounds 1–7

Crystals of compounds **1**–**7** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture.[19] X-Ray intensity data for **1**, **2**, **4**, **5**, **6** and **7** were collected using a Nonius Kappa CCD diffractometer, for **3** on a Siemens P4 four-circle diffractometer. Details of the data collections and structural refinements are given in Table 8. The structures were solved by direct methods and refined by full-matrix least squares on F^2.[20] Two of the $2\text{-}MeO\text{-}4\text{-}MeOC_6H_3$ groups of **6** are disordered over two sites of equal occupancy. In the crystal of **2** 1.5 toluene molecules are present per asymmetric unit, with the half molecules located across an inversion centre so that the methyl group was disordered over two sites of equal occupancy. The thf molecule of **4** shows some conformational disorder and one of the carbon atoms was resolved into two components of 64 : 36 occupancy. In **5**·$2C_6H_5Me$ the asymmetric unit consisted of half the cubane molecule and a toluene solvate. The absolute structure parameters for **1**, **3** and **4** are −0.01(4), 0.00(9) and 0.00(4), respectively.

CCDC reference number 186/2193.

See http://www.rsc.org/suppdata/dt/b0/b005932n/ for crystallographic files in .cif format.

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