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FULL PAPER

Effects of *meta*-substitution on aggregation in the cubanes $[SnNR]_4$ {R = $[2\text{-Me-5-MeOC}_6H_3]$, $[2,5\text{-(MeO)}_2C_6H_3]$ and $[3,5\text{-(MeO)}_2C_6H_3]$}

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An investigation of the solid-state X-ray structures of the cubanes $[SnN\{2\text{-Me-5-MeOC}_6H_3\}]_4$, (**1**), $[SnN\{2,5\text{-(MeO)}_2C_6H_3\}]_4$, (**2**), and $[SnN\{3,5\text{-(MeO)}_2C_6H_3\}]_4$, (**3**), containing *meta*-MeO substituents on their aromatic groups, shows that unprecedented modes of intra- and intermolecular association occur. In **1**, novel co-ordination of two of the cubane Sn_2N_2 faces by thf ligands is found, the first observation of Lewis base solvation by a separate donor ligand in this class of complexes. In **2**, dimerisation of cubane units occurs *via* a combination of Sn ··· Sn, Sn ··· O and arene ··· Sn interactions, whereas in **3**, an unusual 'sinusoidal' pattern of aggregation is seen.

Introduction

Tin(II) imido cubanes of general formula $[SnNR]_4$ are the prototypical imidotin(II) compounds. They were first reported by Veith and co-workers[1] in the early 1980s, isolated from the acid/base reactions of $\{Me_2Si(NMe_2)_2\}Sn$ with primary amines (RNH_2) and hydrazines (H_2NNR). Subsequently, a number of synthetic strategies for their preparation have been employed. These include nucleophilic substitution of $SnCl_2$ with RN^{2-},[2] the reactions of $Sn\{N(SiMe_3)_2\}_2$ with primary amines and borylamines (R_2BNH_2),[3] nucleophilic substitution of $SnCp_2$[4] (Cp = η^5-C_5H_5) with RNH^- and the acid/base reactions of $Sn(NMe_2)_2$ with a variety of primary amines.[5] We have been particularly interested in the reactions of $Sn(NMe_2)_2$ with primary amines (RNH_2), which have the advantage of giving clean formation of the cubanes for a broad range of amines at low temperatures.[4] This is of particular importance where the imidotin(II) complexes are thermally unstable, such as the cubane $[SnNCH_2(C_5H_4N\text{-}2)]_4$.[5] Isolation of intermediates of the type $[\{Sn(NR)_2\}Sn(NMe_2)_2]$ from the reactions of $Sn(NMe_2)_2$ with sterically demanding amines such as $DippNH_2$ (Dipp = $2,6\text{-}^iPr_2C_6H_3$)[6] indicate that cubane formation occurs by a common stepwise process, rather than through the aggregation of discrete :SnNR monomers.

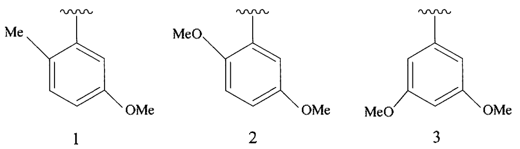
Recently, we carried out a study into the effects of donor functionality on the $[SnNR]_4$ cubane. We wished to investigate how O and N donor functionality in the organic substituent (R) would affect the stability of the Sn_4N_4 core to intramolecular solvation and to explore the factors affecting and controlling intermolecular association. The latter objective may lead to the application of these species as novel, three-dimensional Lewis bases for the assembly of a range of heterometallic arrangements. Investigation of the effect of O donor functionality was carried out by reacting $Sn(NMe_2)_2$ with a selection of methoxy-substituted anilines.[7] The results showed a range of features, from steric shielding of the Sn_4N_4 core to the effects of intra- and intermolecular O donation on association in the crystal lattice. For example, in $[SnN\{4\text{-MeOC}_6H_4\}]_4$, extensive aggregation of the cubane units occurs.[7] However, modification of the amine by methyl substitution in the *ortho* position in $[SnN\{2\text{-Me-4-MeOC}_6H_3\}]_4$,[7] results in steric shielding of the Sn_2N_2 faces, thus preventing association *via* the *para*-MeO groups. Cubanes aggregate by forming loosely-linked polymer strands *via* two Sn ··· Sn interactions.

This previous study, however, was limited to *ortho*- and *para*-methoxy-substituted anilines and one implication is that incorporation of O donor functionality in the *meta* position may lead to novel patterns of association. In particular, the positioning of the MeO groups *meta* to the imido centre should allow the cubanes to aggregate in a "non-linear" manner, potentially forming separate molecular groupings or cyclical or helical supramolecular structures. In this paper, we examine the structures of the *meta*-substituted cubane derivatives $[SnN\{2\text{-Me-5-MeOC}_6H_3\}]_4$, (**1**), $[SnN\{2,5\text{-(MeO)}_2C_6H_3\}]_4$, (**2**), and $[SnN\{3,5\text{-(MeO)}_2C_6H_3\}]_4\cdot 2thf$, (**3**), and their resulting patterns of association in the crystal lattice.

Results and discussion

The compounds $[SnN\{2\text{-Me-5-MeOC}_6H_3\}]_4$, (**1**), $[SnN\{2,5\text{-(MeO)}_2C_6H_3\}]_4$, (**2**), and $[SnN\{3,5\text{-(MeO)}_2C_6H_3\}]_4$, (**3**), were formed by the 1 : 1 reactions of $Sn(NMe_2)_2$ with 2-Me-5-$MeOC_6H_3NH_2$, $2,5\text{-(MeO)}_2C_6H_3NH_2$ and $3,5\text{-(MeO)}_2C_6H_3NH_2$, respectively, as represented in Scheme 1. The compounds were isolated in crystalline form and preliminary elemental analysis and ^{1}H NMR spectroscopy confirmed that **1**–**3** had the expected $[SnNR]_n$ composition. The ^{1}H NMR spectra show that, in each case, the chemical shifts of the aromatic, Me and MeO protons are slightly increased from the values obtained for the free amines. This is due to the developing negative charge on

$$4[Sn(NMe_2)_2] + 4RNH_2 \longrightarrow [SnNR]_4 + 8Me_2NH$$



Scheme 1

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Table 1 Crystal data and refinements for [SnN{2-Me-5MeOC$_6$H$_3$}]$_4$·2thf (**1**·2thf), [SnN{2,5-(MeO)$_2$C$_6$H$_3$}]$_4$·0.5C$_6$H$_5$Me (**2**·0.5C$_6$H$_5$Me) and [SnN{3,5-(MeO)$_2$C$_6$H$_3$}]$_4$·2thf (**3**·2thf)

	1·2thf	**2**	**3**·2thf
Formula	$C_{40}H_{52}N_4O_6Sn_4$	$C_{32}H_{36}N_4O_8Sn_4\cdot 0.5(C_7H_8)$	$C_{40}H_{52}N_4O_{10}Sn_4$
Formula weight	1159.62	1125.48	1223.62
T/K	223(2)	180(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$C2/c$
a/Å	26.134(7)	14.3357(2)	25.532(4)
b/Å	13.7154(18)	33.6746(5)	10.6914(15)
c/Å	265.706(4)	16.5167(2)	16.236(5)
β/°	117.453	95.172(9)	92.325(19)
U/Å^3	8494(3)	7941.0(2)	4428.4(16)
Z	8	8	4
Density/Mg m^{-3}	1.814	1.883	1.835
μ(Mo-Kα)/mm^{-1}	2.374	2.540	2.288
Reflections collected	6914	51195	3763
Independent reflections	5843	18135	3090
R_{int}	0.0727	0.0664	0.0264
$R1,wR2$ [$I > 2\sigma(I)$]	0.0569, 2.1370	0.0450, 0.0976	0.0351, 0.0803
$R1,wR2$ (all data)	0.1061, 0.1699	0.0887, 0.1555	0.0496, 0.0924

Table 2 Selected bond lengths (Å) and angles (°) for [SnN{2-Me-5MeOC$_6$H$_3$}]$_4$·2thf (**1**·2thf)

Sn(1)–N(1)	2.229(10)	Axial faces	
Sn(2)–N(2)	2.205(10)	Sn–N–Sn range	95.5(4)–97.3(4)
Sn(3)–N(3)	2.217(11)	N–Sn–N range	81.7(4)–83.1(4)
Sn(4)–N(4)	2.217(9)		
Sn(1)–N(2)	2.213(10)	Equatorial faces	
Sn(2)–N(1)	2.209(10)	Sn–N–Sn range	98.0(4)–101.0(4)
Sn(3)–N(4)	2.169(9)	Sn–N–Sn average	98.2
Sn(4)–N(3)	2.231(11)	N–Sn–N range	78.6(3)–81.4(4)
Sn(1)–N(4)	2.252(10)	N–Sn–N average	81.9
Sn(2)–N(3)	2.246(10)		
Sn(3)–N(1)	2.239(10)		
Sn(4)–N(2)	2.268(10)		

Table 3 Selected bond lengths (Å) and angles (°) for [SnN{2,5-(MeO)$_2$C$_6$H$_3$}]$_4$·0.5C$_6$H$_5$Me (**2**·0.5C$_6$H$_5$Me)

Sn(1A)–N(1A)	2.192(4)	O(11B) ··· Sn(2A)	2.836
Sn(1A)–N(3A)	2.256(5)	O(11B) ··· Sn(4A)	3.185
Sn(2A)–N(1A)	2.217(5)	O(21A) ··· Sn(1A)	2.822
Sn(3A)–N(3A)	2.209(5)	O(21A) ··· Sn(2A)	3.95
Sn(3A)–N(4A)	2.226(4)	O(31A) ··· Sn(1A)	3.017
Sn(4A)–N(1A)	2.225(5)	O(31A) ··· Sn(4A)	3.002
Sn(1B)–N(1B)	2.211(5)	O(41A) ··· Sn(3A)	2.806
Sn(1B)–N(2B)	2.236(4)	O(41A) ··· Sn(4A)	3.164
Sn(2B)–N(4B)	2.215(5)	O(11B) ··· Sn(2B)	3.219
Sn(3B)–N(2B)	2.188(5)	O(11B) ··· Sn(4B)	2.900
Sn(3B)–N(4B)	2.269(5)	O(21B) ··· Sn(1B)	2.948
Sn(4B)–N(1B)	2.211(5)	O(21B) ··· Sn(2B)	2.960
Sn(1A)–N(2A)	2.224(5)	O(31B) ··· Sn(1B)	2.847
Sn(2A)–N(4A)	2.212(4)	O(31B) ··· Sn(4B)	2.989
Sn(2A)–N(2A)	2.240(5)	O(41B) ··· Sn(2B)	3.035
Sn(3A)–N(2A)	2.212(5)	O(41B) ··· Sn(4B)	3.079
Sn(4A)–N(3A)	2.199(5)		
Sn(4A)–N(4A)	2.233(5)	Sn–N–Sn range	97.0(2)–101.6(2)
Sn(1B)–N(3B)	2.224(5)	Sn–N–Sn average	99.2
Sn(2B)–N(2B)	2.208(5)	N–Sn–N range	77.5(2)–82.3(2)
Sn(2B)–N(1B)	2.226(5)	N–Sn–N average	80.0
Sn(3B)–N(3B)	2.206(4)		
Sn(4B)–N(4B)	2.181(5)	aryl$_{centroid}$ ··· Sn(3B)	3.923(5)
Sn(4B)–N(3B)	2.221(5)		

the aromatic ring in the imidotin(II) complexes. Solvent peaks due to thf (in compounds **1** and **3**) and toluene (in compound **2**) are also observed in the ^{1}H NMR spectra. Although the role of thf in **1** and **3** is markedly different (it transpires from later structural investigations), no noticeable variation in the thf chemical shifts was observed (the role of thf in compound **1** will be discussed later). The structures of **1**–**3** were later elucidated by low temperature X-ray crystallography, the experimental details of which are listed in Table 1. Tables 2–4 list key bond lengths and angles for **1**–**3** respectively.

Table 4 Selected bond lengths (Å) and angles (°) for [SnN{3,5-(MeO)$_2$C$_6$H$_3$}]$_4$·2thf (**3**·2thf)

Sn(1)–N(1)	2.191(6)	Sn–N–Sn range	97.4(2)–100.3(2)
Sn(1)–N(2)#1	2.211(6)	Sn–N–Sn average	98.6
Sn(1)–N(2)	2.211(6)	N–Sn–N range	79.9(2)–81.1(2)
Sn(2)–N(1)#1	2.213(6)	N–Sn–N average	80.6
Sn(2)–N(2)	2.216(5)		
Sn(2)–N(1)	2.242(6)	Sn(2) ··· O(13A)	3.42(5)

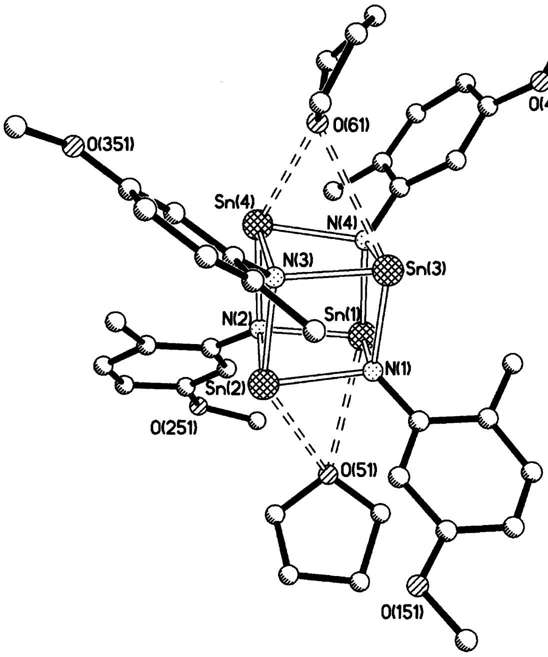

Fig. 1 X-Ray crystal structure of [SnN{2-Me-5MeOC$_6$H$_3$}]$_4$·2thf (**1**·2thf). H-atoms have been omitted for clarity.

The low temperature X-ray crystal structure of [SnN{2-Me-5MeOC$_6$H$_3$}]$_4$·2thf (**1**·2thf) (Fig. 1) reveals isolated cubane units in the crystal lattice. Contrary to our predictions, there is no aggregation *via* the *meta*-methoxy groups. Although the bond lengths and internal angles of the Sn$_4$N$_4$ core fall over large ranges [Sn–N: 2.205(10)–2.268(10) Å; Sn–N–Sn: 95.5(4)–101.0(4); N–Sn–N: 78.6(3)–81.4(4)°], they are within the reported ranges for previously characterised cubanes [Sn–N: 2.15(1)–2.34(2) Å; Sn–N–Sn: 96.0(3)–102.4(2); N–Sn–N 77.1(2)–83.3(4)°].[1–5,7] However, closer examination reveals a clear distinction between two of the Sn$_2$N$_2$ faces, which we refer to as *axial*, and the remaining four Sn$_2$N$_2$ faces, which we refer

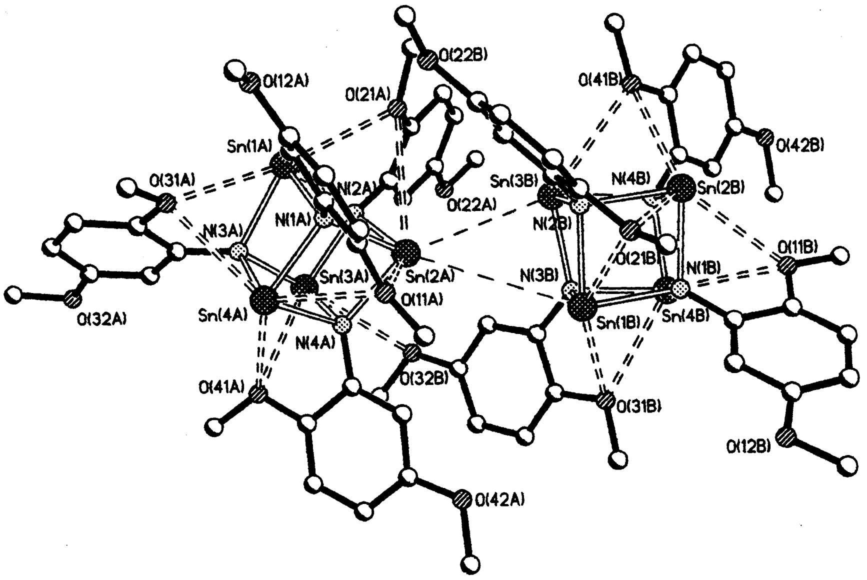

Fig. 2 X-Ray crystal structure of $[SnN\{2,5\text{-}(MeO)_2C_6H_3\}]_4 \cdot 0.5C_6H_5Me$ (**2**$\cdot 0.5C_6H_5Me$), showing the two independent molecules, A and B, within the asymmetric unit of the crystal lattice. H-atoms and lattice-bound toluene molecules have been omitted for clarity.

to as *equatorial*. The origin of this effect is the surprising co-ordination of the two axial faces of the cubane core by thf, *via* O μ-bridging of two Sn centres of the two faces [Sn(1) ··· O(51) 2.986(5), Sn(2) ··· O(51) 3.385(5) Å] and [Sn(3) ··· O(61) 3.178(5), Sn(4) ··· O(61) 2.947(5) Å]. The associated bond distances are far lower than the estimated sum of the van der Waal's radii [estimated Sn ··· O distance 3.70 Å][8] and are noticeably shorter than previously reported Sn ··· O bridges in cubanes of this type {*e.g.*, the cubane $[SnN\{4\text{-}MeOC_6H_4\}]_4$, which associates in the crystal lattice *via* 'face' Sn ··· (μ-O) ··· Sn interactions: Sn ··· O range 3.441(5)–3.366(5) Å}.[7] This co-ordination of thf in **1** results in a slight shortening of the Sn–N bonds in the axial faces [$Sn\text{–}N_{ax}$: 2.205(10)–2.229(10) (mean 2.21); $Sn\text{–}N_{eqt}$: 2.239(10)–2.268(10) Å (mean 2.25 Å)], an associated expansion of the N–Sn–N angles [$N\text{–}Sn\text{–}N_{ax}$: 81.7(4)–83.1(4); $N\text{–}Sn\text{–}N_{eqt}$: 78.6(3)–81.4(4)°] and a compression of the Sn–N–Sn angles [$Sn\text{–}N\text{–}Sn_{ax}$: 95.5(4)–97.3(4); $Sn\text{–}N\text{–}Sn_{eqt}$: 98.0(4)–101.0(4)°]. Visually, this results in a slight folding of the two Sn_2N_2 rings into a butterfly shape, which enables the Sn centres to further 'engage' the donor O centres.

The 2-Me groups of the arene rings in **1** mask each of the equatorial faces of the cubane core, preventing further solvation or association of the cubane units. Thus in **1**, aggregation in the crystal lattice is prevented by thf solvation and by steric hindrance. The co-ordination of electropositive metal centres by solvent molecules is well known in early main group metal aggregates, such as organolithiums and imidolithiums, where dissociation normally occurs upon Lewis base co-ordination.[9] However, the solvation of a tin(II) imido cubane by a separate Lewis base ligand is unknown. Clearly, this interaction is largely electrostatic and owes much to the developing positive charge on Sn(II), resulting from the bonding to three electronegative N centres within the cubane framework. Donor–acceptor type bonding can be ruled out, as there are no accessible vacant low-lying metal orbitals.

Comparison of the low temperature X-ray crystal structure of **1** with $[SnN\{2,5\text{-}(MeO)_2C_6H_3\}]_4 \cdot 0.5C_6H_5Me$ (**2**$\cdot 0.5C_6H_5Me$), where the 2-Me group is replaced by a 2-methoxy group, shows how simple modification of the imido R group can lead to different patterns of association in the crystal lattice. The asymmetric unit in the crystal structure of **2** consists of two crystallographically independent cubanes and a molecule of toluene (Fig. 2). The Sn–N bond lengths and angles are again within the ranges for previously reported structures [Sn–N: 2.181(5)–2.269(5) Å; Sn–N–Sn: 97.0(2)–100.3(2); N–Sn–N: 77.5(2)–82.3(2)°].

Within each independent Sn_4N_4 unit, each $2,5\text{-}(MeO)_2C_6H_3$ group pivots towards four of the Sn_2N_2 faces of the cubane core, thus allowing the 2-MeO groups to μ-bridge the tin centres within these faces [Sn ··· O range 2.836(5)–3.219(5) Å], leaving two Sn_2N_2 faces unbridged. Although these Sn ··· O interactions fall over a large range, they are well within the distance estimated for van der Waal's interactions (*ca.* 3.70 Å)[8] and a similar pattern of intramolecular Sn ··· O bonding was previously observed in the complexes $[SnN\{2\text{-}MeO\text{-}6\text{-}MeC_6H_3\}]_4$ and $[SnN\{2,4\text{-}(MeO)_2C_6H_3\}]_4$.[7] However, in these complexes, the four equatorial faces were bridged by the MeO groups, leaving the two axial faces unmasked. In compound **2**, however, a different pattern of μ-O bridging is present, which leaves two *adjacent* Sn_2N_2 faces uncoordinated and free for intermolecular interactions.

A Sn vertex of one cubane unit of **2** points towards an 'unmasked' Sn_2N_2 face of the second cubane in the unit cell, forming two Sn ··· Sn interactions between the two cubanes [Sn(2A) ··· Sn(1B) 4.131(5), Sn(2A) ··· Sn(2B) 3.654(5) Å]. Although this type of association is common in imidotin(II) complexes (values in the range 3.41–4.40 Å having been observed previously),[1–5,7] it is interesting to note that in **2**, association is *via* a *long* and a *short* Sn ··· Sn distance, instead of two similar distances, which is the case in the previously characterised cubanes. The reason for this disruption in the normal pattern of Sn ··· Sn interactions is the presence of further O ··· Sn and π–arene intermolecular interactions, which reinforce the association of the two cubane units. A *meta*-methoxy group on one cubane interacts with a Sn centre in the second cubane [Sn(3A) ··· O(32A) 3.31(5) Å, within the 3.70Å estimated for the sum of the van der Waal's radii].[8] Reinforcing this molecular aggregation is a π interaction between Sn(3B) in one cubane and the arene ring of the $2,5\text{-}(MeO)_2C_6H_3$ group attached to N(2A) in the adjacent cubane [$aryl_{centroid}$ ··· Sn(3B) 3.92(5) Å, N(2A)–Sn(3B)–centroid(1A) 74.4°]. This type of interaction has also been observed previously in the cubanes $[SnN\{2\text{-}Me\text{-}4\text{-}MeOC_6H_3\}]_4 \cdot 1.5C_6H_5Me$ [$aryl_{centroid}$ ··· Sn(2) 3.74 Å] and $[SnN\{2,4\text{-}(MeO)_2C_6H_3\}]_4$ [$aryl_{centroid}$ ··· Sn(2) 3.72 Å],[7] although the longer distance involved in **2** implies a weaker interaction here. The observation of pairwise association (rather than the formation of a polymer) in **2** confirms one of our predictions, that *meta* substitution may give rise to molecular (rather than extended) aggregation.

From these two examples, one would expect to observe more extensive aggregation of the cubane units in the crystal lattice when there is no group present in the *ortho* position of the arene ring, which can potentially mask the Sn_2N_2 faces. The low temperature X-ray crystal structure of $[SnN\{3,5\text{-}(MeO)_2C_6H_3\}]_4\cdot 2thf$, (**3**·2thf) (Fig. 3) allows this hypothesis to be tested.

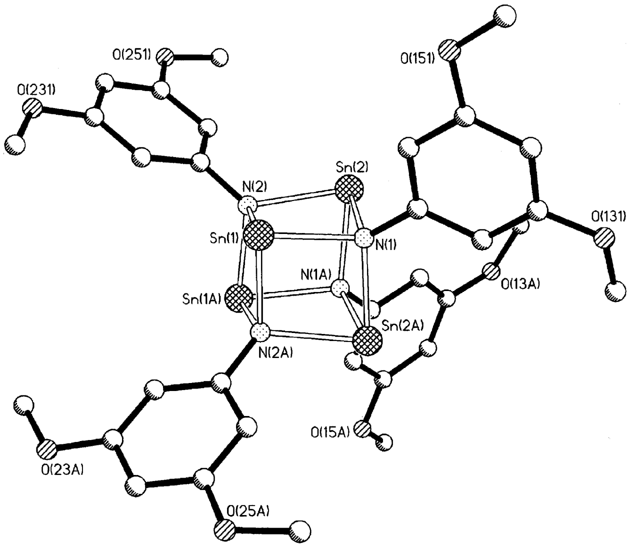

Fig. 3 X-Ray crystal structure of $[SnN\{3,5\text{-}(MeO)_2C_6H_3\}]_4\cdot 2thf$ (**3**·2thf). H-atoms and lattice-bound thf molecules have been omitted for clarity

Although there are two molecules of thf per cubane unit in the crystal lattice, there is no solvation of the Sn_4N_4 core, as observed in molecules of **1**, and there are no deviations from the expected cubane core geometry found in other cubanes [Sn–N: 2.191(6)–2.242(6) Å; Sn–N–Sn: 97.4(2)–100.3(2); N–Sn–N: 79.9(2)–81.1(2)°]. Within each cubane of **3**, the 3-MeO and 5-MeO groups are directed *exo* to the cubane core. This results in association of cubanes *via* pairwise Sn ··· O interactions [Sn ··· O 3.42(5) Å]. Although these are long-range interactions, they are comparable to similar intermolecular Sn ··· O interactions observed in the cubanes $[SnN\{4\text{-}MeOC_6H_4\}]_4$ [Sn(1) ··· O(1A) 3.366(5), Sn(2) ··· O(1A) 3.441(5) Å] and $[SnN\{3,4\text{-}(MeO)_2C_6H_3\}]_4\cdot 2C_6H_5Me$ [Sn(2) ··· O(15A) 3.391(6), Sn(2) ··· O(16A) 3.303(6) Å].[7] In the latter compound, pairwise interactions are also observed resulting in a linear chain arrangement. Two MeO groups (attached to separate aromatic rings) from each cubane unit of **3** interact with a neighbouring cubane, forming a loosely-linked polymer in the crystal lattice (Fig. 4). The resulting polymer is 'sinusoidal' in nature and these chains aggregate *via* weak O ··· H hydrogen bonds into layers of parallel chains. These O ··· H hydrogen bonds are formed by the interaction of an MeO group on an arene ring of one cubane and the *para* H of an arene ring of a neighbouring cubane in an adjacent chain [O ··· H 2.47 Å, C–O–H 157.7°]. These interactions are observed on the top and bottom surfaces of the layers, which then stack on top of each other in the crystal lattice. There are no interactions between the layers.

In summary, modification of the R groups in the compounds **1**–**3** influences the form and extent of aggregation. The prediction was that MeO substituents *meta* to the imido centre would result in non-linear patterns of association. This rationale is to some extent realised in the structure of **3** which aggregates into a 'sinusoidal' polymer, not a linear chain as was observed in the isomeric compound $[SnN\{3,4\text{-}(MeO)_2C_6H_3\}]_4\cdot 2C_6H_5Me$.[7] An unexpected result occurs in **1**, where thf solvation of the Sn_4N_4 cores prevents aggregation. This type of solvation has never been observed before in a tin(II) imido complex and further investigation of the effects of Lewis base donors on cubanes of this type would be of interest. A unique form of aggregation occurs in **2**, where two cubane units are associated into loosely-linked dimers in the solid state. In addition, **2** is of interest in that the association involves every type of intra- and intermolecular association (*e.g.*, Sn ··· Sn, Sn ··· O, Sn ··· $aryl_{centroid}$) which has been previously observed in the solid state structures of other $[SnNR]_4$ cubanes.[7]

Experimental

General

Compounds **1**–**3** are air- and moisture-sensitive.[10] 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 dried under vacuum, which resulted in some solvent loss from the crystals of **1**–**3** (the extent of this solvent loss could be identified from elemental analysis experiments). The compounds were 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.[11] 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

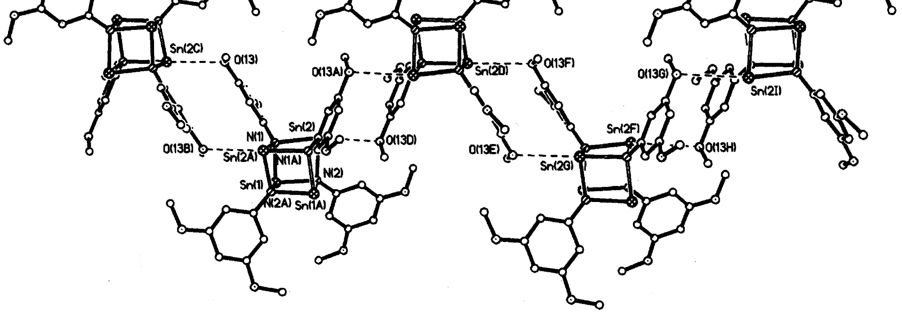

Fig. 4 Packing of molecules of $[SnN\{3,5\text{-}(MeO)_2C_6H_3\}]_4$ (**3**) in the crystal lattice, showing the propagation of the 'sinusoidal' polymer *via* Sn ··· O interactions [Sn(2) ··· O(13A) 3.42(5) Å]. H-atoms and lattice-bound molecules of thf have been omitted for clarity.

DMSO (using the solvent resonances as the internal reference standard).

Synthesis of 1

A solution of 2-Me-5-MeO$C_6H_3NH_2$ (0.55 g, 4 mmol) in thf (10 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4 mmol) in thf (20 ml) at −78 °C. After stirring (10 min), the pale yellow solution was brought to room temperature. The solution was reduced under vacuum to *ca.* 5 ml and storage at room temperature (12 h) gave light yellow crystalline blocks of compound **1**. Yield 0.15g (13%). Decomp. to black solid 210 °C. ^{1}H NMR (400 MHz, D_6-DMSO, 25 °C): δ = 6.75 [d (J = 4), 1H, C(4)–H], 6.16 [s, 1H, C(6)–H], 6.01 [d (J = 4), 1H, C(3)–H], 3.59 [s, 3H, thf], 3.28 [s, 3H, MeO], 3.25 [s, 3H, Me] and 1.93 [s, 3H, thf]. Found: C, 38.3; H, 4.41; N, 5.0%. Calc. for $[C_8H_9NOSn]_4$: C, 37.9; H, 3.6; N, 5.5%.

Synthesis of 2

A solution of 2,5-$(MeO)_2C_6H_3NH_2$ (0.613 g, 4 mmol) in toluene (20 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4 mmol) in toluene (10 ml) at −78 °C. After stirring (15 min), a dark green solution containing a pale green precipitate was formed. The mixture was brought to room temperature and the precipitate dissolved, producing a dark green solution and an insoluble precipitate. The precipitate was removed by filtration and the solution reduced under vacuum to *ca.* 3 ml. Storage at room temperature (12 h) gave a crop of fine green crystalline blocks of compound **2**. Yield 0.09 g (8%). Decomp. to black solid 156 °C. ^{1}H NMR (400 MHz, D_6-DMSO, 25 °C): δ = 7.17 [m, 0.67H, C_7H_8], 6.74 [d (J = 4), 1H, C(3)–H], 6.67 [s, 1H, C(6)–H], 6.21 [d (J = 4), 1H, C(4)–H], 3.65 [s, 3H, *ortho*-MeO], 3.57 [s, 3H, *meta*-MeO] and 2.48 [s, 0.4H, C_7H_8]. Found: C, 36.6; H, 3.7; N, 5.1%. Calc. for $[C_8H_9NO_2Sn]_4\cdot 0.25C_7H_8$: C, 36.8; H, 3.5; N, 5.1%.

Synthesis of 3

A solution of 3,5-(MeO)2$C_6H_5NH_2$ (0.613 g, 4 mmol) in thf (10 ml) was added to a solution of $Sn(NMe_2)_2$ (0.83 g, 4 mmol) in thf (10 ml) at −78 °C. After stirring (10 min), the intense yellow solution was brought to room temperature. The solution was reduced under vacuum to *ca.* 8 ml and prolonged storage at −5 °C gave a crop of large yellow crystalline needles of compound **3**. Yield 1.00 g (82%). Decomp. to black solid 170 °C. ^{1}H NMR (400 MHz, D_6-DMSO, 25 °C): δ = 6.06 [s, 2H, C(2,6)–H], 5.94 [s, 1H, C(4)–H], 3.67 [s, 6H, MeO], 3.59 [s, 5H, thf] and 1.74 [m, 5H, thf]. Found: C, 37.6; H, 4.0; N, 5.2%. Calc. for $[C_8H_9NOSn]_4\cdot C_4H_4O$: C, 37.6; H, 3.9; N, 4.9%.

X-Ray crystallographic studies of 1–3

Crystals of **1**–**3** were mounted directly from solution under argon using inert oil, which protects them from atmospheric oxygen and moisture.[12] X-Ray intensity data for **2** was collected using a Nonius Kappa CCD diffractometer, and that for **1** and **3** using a Siemens *P*4 four-circle diffractometer. The structures were solved by direct methods and refined by full-matrix least squares on F^2.[13] In compound **1**, C(53) of the thf molecule is disordered over two 50 : 50 sites and a methoxy group [attached to O(451)] is also disordered over two 50 : 50 sites. In compound **2**, the toluene solvate molecule is poorly resolved; this was refined with bond length restraints and a common, isotropic temperature factor for the carbon atoms. In compound **3**, three carbon atoms [C(33), C(34) and C(35)] of the thf molecule are disordered over two 50 : 50 sites.

CCDC reference numbers 170393–170395.

See http://www.rsc.org/suppdata/dt/b1/b107425c/ for crystallographic data in CIF or other electronic format.

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