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Synthesis and structure of $[Sn_9(Ndmp)_7(HNdmp)_2O_2]$, containing a bidentate double-cubane oxo fragment (H_2Ndmp = 2-amino-4,6-dimethoxypyrimidine

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The reaction of $Sn(NMe_2)_2$ with H_2Ndmp (H_2Ndmp = 2-amino-4,6-dimethoxypyrimidine) and H_2O (*ca.* 4 : 4 : 1 equivalents, respectively) gives the cage complex $[Sn_9(Ndmp)_7(HNdmp)_2O_2]$ 1, containing an oxo double-cubane fragment $[Sn_7(Ndmp)_6O_2]$ coordinated to a neutral $(HNdmpSn)_2(\mu\text{-}Ndmp)$ unit; 1 is the largest imido Sn(II) complex so far characterised.

The reactions of $Sn(NMe_2)_2$ with aliphatic primary amines (RNH_2) provide an efficient low-temperature route to imido Sn(II) cubanes of the type $[SnNR]_4$.[1] However, we showed recently that the analogous reactions of 2-amino-pyridines and 2-amino-pyrimidines produce mixed-oxidation state complexes of formulae $[Sn_7(NR)_8]$, in which two cubane units are fused *via* a central Sn(IV) atom into double-cubane structures.[2] By illustrating that larger oligomers can be obtained, depending on the nature of the organic substituents present, this discovery provides a new direction in the chemistry of imido Sn(II) compounds (which has previously been dominated by the simple imido cubanes[3–5]). Previous studies by Veith and Lange illustrated that the imido–oxo cubane $[Sn_4(NBu^t)_3O]$,[6] in which formal replacement of Bu^tN group in the cubane $[Sn(NBu^t)]_4$ by isoelectronic O^{2-} has occurred, can be used as an 'ether-like' ligand in the donor–acceptor adduct $[Sn_4(NBu^t)_3O\cdot AlMe_3]$.[7] Our interest in this ligand stems from the very high development of negative charge on the O centre, making it a highly effective, sterically demanding donor for high oxidation state metal ions.[8] We show here that the double-cubane framework $[Sn_7(NR)_8]$ provides access to a bidentate homologue of this ligand system, $[Sn_7(NR)_6O_2]$, present within the structure of the cage $[Sn_9(Ndmp)_7(HNdmp)_2O_2]$ (H_2Ndmp = 2-amino-4,6-dimethoxypyrimidine).

Complex **1** was originally obtained fortuitously from the 1 : 1 reaction of H_2Ndmp with $Sn(NMe_2)_2$ in toluene, in low (15%) yield. Subsequently, it was shown that the 1 : 1 reaction of rigorously dried H_2Ndmp with $Sn(NMe_2)_2$ gives the expected double-cubane $[Sn_7(Ndmp)_8]$.[2b] These observations suggest that the initial formation of **1** was due to water of crystallisation present in the H_2Ndmp. Complex **1** can be isolated using a variety of stoichiometric ratios of $H_2Ndmp : Sn(NMe_2)_2 : H_2O$ (*ca.* 4 : 4 : 1, respectively[8]), the cleanest reaction being obtained using the apparently correct mixture of H_2Ndmp (9 equiv.) and H_2O (2 equiv.) with $Sn(NMe_2)_2$ (10 equiv.) (Scheme 1).† Like the formation of the double-cubanes $[Sn_7(NR)_8]$, the production of **1** formally involves disproportionation into Sn(0) and Sn(IV). However, there was no obvious indication of the presence of Sn metal here, so that the exact course of the reaction remains unclear at this stage. Although the ^{119}Sn NMR spectrum of **1** in DMSO at room temperature shows the presence of Sn(II) (a broad resonance at δ −284.8, width *ca.* 210 Hz) and Sn(IV) (at δ +75.4), the low solubility of the complex in other organic solvents (once isolated) precluded variable-temperature studies which may have resolved the two Sn(II) environments.

$$9\ H_2Ndmp + 10\ Sn(NMe_2)_2 \xrightarrow[-Sn(0)]{2H_2O} \underset{\mathbf{1}}{[Sn_9(Ndmp)_7(HNdmp)_2O_2]} + 20\ Me_2NH$$

Scheme 1

The low-temperature crystallographic study of **1**‡ shows that it is the cage compound $[Sn_9(Ndmp)_7(HNdmp)_2O_2]$, consisting of a neutral $[Sn_7(Ndmp)_6O_2]$ oxo double-cubane fragment coordinated *via* both O centres to the Sn(II) centres of a $[\{Sn(HNdmp)\}_2(\mu\text{-}Ndmp)]$ fragment (Fig. 1). In addition, there

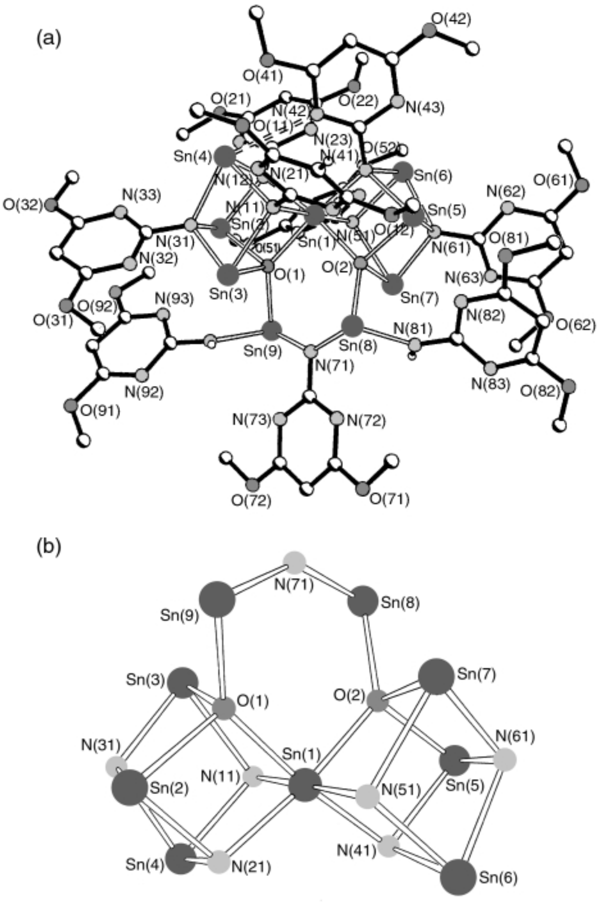

Fig. 1 (a) Molecular structure of **1**. H-atoms and the lattice-solvation by toluene molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(1) 2.129(5), Sn(1)–O(2) 2.139(4), Sn(1)–N range 2.103(4)–2.139(6), Sn(2,3,5,7)–N range 2.162(6)–2.378(6), Sn(2,3,5,7)–O range 2.238(4)–2.268(4); O(1)–Sn(1)–O(2) 90.2(2), N–Sn(1)–O/N within cubanes range 81.6(2)–82.6(2) [between adjacent 97.3(2)–105.7(2), opposite 171.7(2)–179.3(2)], Sn–O(1,2)–Sn within cubanes 99.9(2)–103.1(2), Sn–N–Sn within cubanes range 96.5(2)–105.2(2), N–Sn–N within cubanes range 76.8(2)–81.8(2), O–Sn–N within cubanes 72.9(2)–76.8(2); Sn(8)–O(2) 2.186(4), Sn(8)–N(81) 2.227(6), Sn(8)–N(71) 2.142(6), Sn(9)–O(1) 2.185(5), Sn(9)–N(91) 2.141(6), Sn(9)–N(71) 2.131(6); Sn(1,2)–O(1,2)–Sn(8,9) mean 133.9, O(1,2)–Sn(8,9)–N(71) mean 88.3, Sn(8)–N(71)–Sn(9) 142.4(3), Sn(2,3,5,7)–O(1,2)–Sn(8,9) range 105.8(2)–110.6(2); (b) The $Sn_9N_7O_2$ 'handbag' core of **1**.

are three toluene molecules in the lattice. The coordination of the Sn(II) centres by the oxo double-cubane in **1** is similar to the behaviour of [$Sn_4(NBu^t)_3O$] in its complexes with Al,[7] Li and Fe,[8] and of the [$(Me_3Si)(NBu^t)_2Sn_2O$] fragment to $SnCl_2$ in [$(Me_3Si)(NBu^t)_2Sn_2O{\cdot}SnCl_2$].[9] However, apart from [$Sn_4(NBu^t)_3O$] no other oxo–imido Sn(II) complexes of this type have been structurally characterised. In addition, the structure of **1** (containing a total of nine Sn centres) is the largest Sn imido cage to be structurally characterised.

The Sn–O bond lengths to the central Sn(IV) atom [Sn(1)–O mean 2.13 Å] in **1** are similar to the Sn(IV)–N bonds [Sn(1)–N range 2.103(4)–2.139(6) Å] and to the Sn(II)–O bonds in [$Sn_4(NBu^t)_3O$] and its metal complexes (*ca.* 2.10–2.17 Å).[9] The Sn(II)–O bonds in **1** are considerably longer than anticipated [Sn(2,3,5,7)–O range 2.238(4)–2.268(4) Å], and are within the range of values observed for the Sn(II)–N bonds [Sn(2,3,5,7)–N 2.162(6)–2.378(6) Å] in **1**. Thus, despite the substitution of two of the imido groups for O centres, the range of bond lengths and angles found in the [$Sn_7(Ndmp)_6O_2$] oxo double-cubane unit of **1** is broadly similar to that observed in the structurally characterised double-cubanes [$Sn_7(NR)_8$].[2] The internal Sn–O–Sn angles found in the [$Sn_7(Ndmp)_6O_2$] unit of **1** [Sn–O(1,2)–Sn range 99.9(2)–103.1(2)°] are similar to those observed [$Sn_4(NBu^t)_3O$] and its complexes *ca.* 102°].[7,8]

The most obvious difference between the [$Sn_7(NR)_8$] double-cubanes and the oxo double-cubane core of **1** is found in the geometry of the central Sn(IV) atom. Coordination of the O centres to the [$\{Sn(HNdmp)\}_2(\mu\text{-}Ndmp)$] fragment results in the compression of the O(1)–Sn(1)–O(2) angle [90.2(2)°] and in an associated expansion of the N(21)–Sn(1)–N(41) angle [105.7(2)°] [opposite to the Sn(IV)O_2 fragment]. This leads to a departure from the rigid C_2-symmetric geometry found in [$Sn_7(NR)_8$] (with N–Sn–N angles between the [$Sn_4(NR)_4$] cubane subunits of *ca.* 99°)[2] to a more irregular octahedral geometry for the central Sn(IV) atom in **1**. The association of the [$Sn_7(Ndmp)_6O_2$] and [$\{Sn(HNdmp)\}_2(\mu\text{-}Ndmp)$] units [O(1,2)–Sn(8,9) mean 2.186 Å] produces an envelope-shaped, six-membered SnO_2Sn_2N ring, in which the plane of the Sn(IV)O_2 unit is inclined to the plane of the Sn(9)N(71)Sn(8) fragment by 31.5°. Structurally characterised Sn(II) complexes containing two-coordinate imido groups are very rare[10–12] and the presence of a 'captured' [$\{Sn(HNdmp)\}_2(\mu\text{-}Ndmp)$] unit in **1** is unprecedented in this area. The Sn–(μ-N) bond lengths in this unit [Sn(8)–N(71) 2.142(6), Sn(9)–N(71) 2.131(6) Å] are longer than the Sn–N bonds between the Sn(II) centres and two-coordinate imido-N centres in the closest analogue to **1**, the *nido*-cubane [$\{SnN(C_6H_3OMe\text{-}2\text{-}Me\text{-}6)\}_2Sn(NMe_2)_2$] [2.106(2) and 2.120(2) Å] (consisting of a 'trapped' [$SnN(C_6H_3OMe\text{-}2\text{-}Me\text{-}6)]_2$ dimer unit coordinated by a $Sn(NMe_2)_2$ monomer).[12] The expansion of the Sn–(μ-N)–Sn angle in the [$\{Sn(HNdmp)\}_2(\mu\text{-}Ndmp)$] fragment [142.4(3)°] above that in the [$SnN(C_6H_3OMe\text{-}2\text{-}Me\text{-}6)]_2$ dimer units of the latter [102.4(1)°] is presumably a consequence of the greater ring size in **1**.

In summary, we have illustrated that the double oxo cubane arrangment can be accessed by hydrolysis. This is the next homologue of the monodentate [$Sn_4(NR)_3O$] ligand, and its synthesis provides a key first step in the expansion of the coordination chemistry of this class of ligands. However, still to be achieved is the synthesis of [$Sn_7(NR)_6O_2$] in the absence of coordinated Sn(II) fragments, and the investigation of these species as bidentate ligands to a range of metals. The application of **1** as a source of [$Sn_7(Ndmp)_6O_2$] is under investigation.

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Notes and references

† *Synthesis* of **1**: a mixture of 2-amino-4,6-dimethoxypyrimidine (0.70 g, 4.5 mmol) and H_2O (18 μdm^{-3}, 1.0 mmol) in toluene (10 ml) was added to a solution of $Sn(NMe_2)_2$[13] (1.04 g, 5.0 mmol) in toluene (20 ml) at −78 °C, and the reaction mixture stirred for 30 min. The mixture was allowed to warm to room temperature and stirred (12 h). A faint white precipitate was then filtered off. The solvent was reduced to *ca.* 10 ml and the light yellow powder formed was dissolved by the addition of further toluene (15 ml). Storage at room temperature gave **1** as a light yellow powder. Crystals can be grown by prolonged storage of dilute solutions at room temperature. Elemental analysis and ^{1}H NMR shows that *ca.* two of the three toluene molecules present in the lattice are removed by placing crystalline or powdered samples of **1** under vacuum (10^{-1} atm, 15 min) during isolation. Yield of powder 0.49 g (40%, based on H_2Ndmp consumed and one toluene in lattice); 215 °C melting with decomp. to brown semi-solid. IR (Nujol, NaCl), ν_{max}/cm^{-1} 3396s (N–H str.), 3303s (N–H str.), other bands at 1491m, 1459vs, 1420m, 1246w, 1214s, 1188s, 1160s, 1119s d, 1065s, 1003w, 935w, 795s. ^{1}H NMR (d_6-DMSO, +25 °C, 400.129 MHz), δ 6.55 (s, 9H, aryl rings), 5.31 (s, 2H, N–H), 3.72 (s, 27H, MeO) [toluene at 7.10 (m, Ph), 2.27 (s, Me), *ca.* one per molecule of **1**]. ^{119}Sn NMR (141.21 MHz, d_6-DMSO, +25 °C, rel. sat. $SnCl_2/D_2O$), δ 75.4 (s), −284.8 (br s). Found (typical of several analyses on different reactions) C 28.8, H 2.9, N 15.5; calc. for $\mathbf{1}{\cdot}C_6H_5Me$, C 28.5, H 2.9, N 14.7%.

‡ *Crystal data* for **1**: $C_{75}H_{89}N_{27}O_{20}Sn_9$, M = 2757.13, monoclinic, space group $P2_1/n$, Z = 4, a = 19.9326(3), b = 16.5364(3), c = 29.3746(4), β = 90.965(9) Å, V = 9680.9(3) Å^3, μ(Mo–Kα) = 2.359 mm^{-1}, T = 180(2) K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 53297 reflections collected, 21689 were independent (R_{int} = 0.060). The structure was solved by direct methods and refined by full-matrix least squares on F^2 [with isotropic temperature factors for the light (C,H,O) atoms].[14] Final $R1$ = 0.057 [$I > 2\sigma(I)$] and $wR2$ = 0.159 (all data).

CCDC 159623. See http://www.rsc.org/suppdata/cc/b1/b101247i/ for crystallographic data in .cif or other electronic format.

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