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Tin complexes of tetramethyltetraazadibenzo[14]annulene: organometallic derivatives

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The oxidative addition of alkyl iodides to the tin(II) complex of the 6,8,15,17-tetramethyl-5,9,14,18-tetraazadibenzo-[14]annulene dianion, Sn(tmtaa), in THF produced cationic, five-co-ordinate complexes [Sn(tmtaa)(R)]I, where R = Me, Et, n-Pr or n-Bu. Diiodomethane added to two equivalents of Sn(tmtaa) to give the CH_2 bridged dication [{Sn(tmtaa)}$_2$(μ-CH_2)]I_2. The new alkyl complexes are all air stable in solution and the solid state. Two of the complexes, [Sn(tmtaa)Me]I·2$CHCl_3$ and [{Sn(tmtaa)}$_2$(μ-CH_2)]I_2·2$CHCl_3$·LiI·3H_2O, have been characterised by single crystal X-ray diffraction studies, which confirms the five-co-ordinate geometry of the cations.

Introduction

Complexes containing the 6,8,15,17-tetramethyl-5,9,14,18-dibenzotetraaza[14]annulene dianion (tmtaa^{2-}) and its more highly substituted analogue (Me$_8$taa^{2-}) have attracted considerable renewed attention over the last decade.[1,2] Initially, this was sparked by the features shared by the dibenzotetraaza[14]annulene macrocycles and their much more ubiquitous porphyrin cousins, namely the dianionic charge delocalised over four nitrogen donor atoms disposed in a square planar arrangement. However, the enforced non-planar geometry of the tmtaa and Me$_8$taa ligand frameworks is a key difference and has led to suggestions that unusual co-ordination geometries could be stabilised by these macrocycles. Indeed, as the field has expanded and matured, much novel structural and reaction chemistry has been revealed.[1,2]

The diversity of this chemistry is illustrated well by complexes of the Group 14 elements containing the tmtaa and Me$_8$taa ligands. These span all four of the heavier elements (Si, Ge, Sn and Pb), the two commonly encountered oxidation states (+2 and +4), and co-ordination numbers four, five and six, the last of these with the two additional donors in both *cis* and *trans* geometries. Among the important results has been the finding that *trans* geometry for six-co-ordinate tmtaa and Me$_8$taa complexes is accessible, as evidenced by the crystal structures of Sn(tmtaa)Cl_2, Sn(tmtaa)$(NO_3)_2$ and Sn(Me$_8$taa)I_2.[3,4] Earlier workers in the area had assumed that one of the hallmarks of tmtaa chemistry was a preference for *cis* geometry in six-co-ordinate complexes.[1] Stabilisation of terminal sulfido, selenido and tellurido ligands on tin and germanium, and a variety of new compounds derived from these, has been demonstrated for their Me$_8$taa complexes.[5–7]

Entry into the Group 14 tmtaa and Me$_8$taa chemistry is either through the +2 oxidation state, forming M(L) by reaction of Li_2L with MCl_2 (L = tmtaa or Me$_8$taa; M = Ge, Sn or Pb),[5,8–10] or through the +4 oxidation state, using MX_4 with H_2tmtaa (M = Ge or Sn; X = halide), or $SiCl_4$ with Li_2(tmtaa).[3] For tin the two oxidation states have been linked by oxidative addition of $PhICl_2$ to Sn(tmtaa) and I_2 to Sn(Me$_8$taa), yielding Sn(tmtaa)Cl_2 and Sn(Me$_8$taa)I_2, respectively.[3,4] Addition of methyl iodide to M(tmtaa) (M = Ge or Sn) was also reported, with the products being identified on the basis of elemental analysis, mass spectrometry and NMR data as the six-co-ordinate complexes M(tmtaa)(Me)I. The complexes were assumed to have *cis* geometry in the solid state, although for the germanium complex in solution this structure in equilibrium with a five-co-ordinate cation was postulated.[11]

The focus of the work reported in this paper is a re-examination and extension of the oxidative addition of alkyl halides to Sn(tmtaa). This study was undertaken for several reasons. First, the original report of this chemistry occurred prior to the publication demonstrating *trans* geometry for the six-co-ordinate complexes Sn(tmtaa)Cl_2 and Sn(tmtaa)$(NO_3)_2$.[3] Assignment of *cis* stereochemistry for Sn(tmtaa)(Me)I was made in part on the basis of a historical assumption, and was supported for the tin example by the apparent observation of lower symmetry for the tmtaa ligand (two tmtaa methyl peaks) in the ^1H NMR spectrum. Structural characterisation of this complex was of interest in the light of the uncertain nature of its geometry. In addition, this report represented the first organometallic derivatives of the Group 14 tmtaa or Me$_8$taa complexes, and presented the possibility of pursuing and extending this chemistry. One other report of organometallic Group 14 tmtaa complexes does exist, prepared by reaction of $M(Me)_2Cl_2$ with Li_2(tmtaa) (M = Si or Sn).[12] Analytical and spectroscopic data were presented, but the ^1H and ^{13}C NMR data given correspond exactly to the free macrocycle H_2tmtaa, casting the identity of the proposed products into doubt.[3] Surprisingly, organometallic derivatives of tin porphyrins are remarkably few, with only three structurally characterised examples reported to date, *cis*- and *trans*-Sn(Por)Ph_2 and *trans*-Sn(Por)$(C{\equiv}CPh)_2$ (Por = meso-tetraarylporphyrin).[13]

Experimental

Reagents and general procedures

All preparations were carried out under nitrogen using Schlenk techniques and dried, distilled and degassed solvents. The compound Sn(tmtaa) was prepared as described in the literature.[8] The ^1H and ^{13}C NMR spectra were recorded on either Bruker AM 400 or AM 200 spectrometers using $CDCl_3$ as solvent, mass spectra on a VG 70-SE spectrometer using the Fast Atom Bombardment (FAB) technique.

Preparations

[Sn(tmtaa)(Me)]I. Methyl iodide (1 mL, 16.1 mmol) was added to a solution of Sn(tmtaa) (0.100 g, 0.22 mmol) in THF (10 mL) and the mixture stirred under a nitrogen atmosphere for 30 min. During this period the solution paled in colour and a bright orange precipitate formed. This was collected by filtration in air and recrystallised from CH_2Cl_2–hexane (0.121 g, 93%). Found: C, 45.46; H, 3.91; N, 9.49. $C_{23}H_{25}IN_4Sn$ requires C, 45.79; H, 4.18; N, 9.29%. ^1H NMR: δ 7.34 (m, 4 H, H_m), 7.28 (m, 4 H, H_o), 5.44 (s, 2 H, CH), 2.47 (s, 12 H, CH_3) and 0.58 (s, 3 H, $SnCH_3$, $^2J(^{117}SnH) = 86.1$, $^2J(^{119}SnH) = 89.8$ Hz). $^{13}C-\{^1H\}$ NMR: δ 166.59 (NC_{Ar}), 135.28 ($N\mathit{C}CH_3$), 126.58 (CH_m), 124.61 (CH_o), 101.67 (CH), 24.56 (CH_3) and 11.47 ($SnCH_3$).

[Sn(tmtaa)Et]I. Prepared as described for [Sn(tmtaa)Me]I using EtI (0.21 mL, 2.61 mmol), Sn(tmtaa) (0.136 g, 0.295 mmol) in THF (5 mL), and stirring for 17 h. The bright orange solid was collected and washed twice with THF (2 × 1 mL) (0.066 g, 36%). FAB$^+$ MS: *m/z* 491 (M^+) and 462 ($M^+ - C_2H_5$). ^1H NMR: δ 7.34 (m, 4 H, H_m), 7.20 (m, 4 H, H_o), 5.43 (s, 2 H, CH), 2.47 (s, 12 H, CH_3), 1.32 (q, 2 H, $^3J_{HH} = 7.8$, $SnC\mathit{H}_2CH_3$) and 0.83 (t, 3 H, $^3J_{HH} = 7.8$ Hz, $SnCH_2C\mathit{H}_3$). $^{13}C-\{^1H\}$ NMR: δ 166.55 (NC_{Ar}), 135.68 ($N\mathit{C}CH_3$), 126.63 (CH_m), 124.54 (CH_o), 101.53 (CH), 24.52 (CH_3), 9.14 ($Sn\mathit{C}H_2CH_3$) and 8.85 ($SnCH_2\mathit{C}H_3$).

[Sn(tmtaa)Pr]I. Prepared as described for [Sn(tmtaa)Et]I using n-PrI (0.10 mL, 1.03 mmol), Sn(tmtaa) (0.136 g, 0.295 mmol) in THF (5 mL) to give a yellow solid (0.032 g, 17%). A sample for elemental analysis was recrystallised from $CHCl_3$–hexane. Found: C, 42.93; H, 4.65; N, 7.50. $C_{25}H_{29}IN_4Sn\cdot CHCl_3$ requires C, 41.61; H, 4.03; N, 7.46%. FAB$^+$ MS: *m/z* 505 (M^+) and 462 ($M^+ - C_3H_7$). ^1H NMR: δ 7.31 (m, 8 H, H_m, H_o), 5.42 (s, 2 H, CH), 2.46 (s, 12 H, CH_3), 1.29 (t, 2 H, $SnC\mathit{H}_2CH_2CH_3$), 1.25 (m, 2 H, $SnCH_2C\mathit{H}_2CH_3$) and 0.68 (t, 3 H, $^3J_{HH} = 6.7$ Hz, $SnCH_2CH_2C\mathit{H}_3$). $^{13}C-\{^1H\}$ NMR: δ 166.44 (NC_{Ar}), 135.65 ($N\mathit{C}CH_3$), 126.67 (CH_m), 124.55 (CH_o), 101.48 (CH), 24.51 (CH_3), 18.49, 18.22, 16.95 ($SnCH_2CH_2CH_3$).

[Sn(tmtaa)Bu]I. Prepared as described for [Sn(tmtaa)Et]I using n-BuI (0.16 mL, 1.40 mmol), Sn(tmtaa) (0.136 g, 0.295 mmol) in THF (5 mL), and stirring for 20 h to give a yellow solid (0.033 g, 17%). FAB$^+$ MS: *m/z* 519 (M^+) and 462 ($M^+ - C_4H_9$). ^1H NMR: δ 7.35 (m, 4 H, H_m), 7.28 (m, 4 H, H_o), 5.44 (s, 2 H, CH), 2.47 (s, 12 H, CH_3), 1.31 (t, 2 H, $^3J_{HH} = 7.7$, $SnC\mathit{H}_2CH_2CH_2CH_3$), 1.11 (m, 2 H, $SnCH_2C\mathit{H}_2CH_2CH_3$), 1.00 (m, 2 H, $SnCH_2CH_2C\mathit{H}_2CH_3$) and 0.62 (t, 3 H, $^3J_{HH} = 7.2$ Hz, $SnCH_2CH_2CH_2C\mathit{H}_3$). $^{13}C-\{^1H\}$ NMR: δ 166.45 (NC_{Ar}), 135.66 ($N\mathit{C}CH_3$), 126.62 (CH_m), 124.54 (CH_o), 101.50 (CH), 24.51 (CH_3), 26.37, 25.35, 15.99, 13.15 ($SnCH_2CH_2CH_2CH_3$).

[{Sn(tmtaa)}$_2$(μ-CH_2)]I_2. Prepared as described for [Sn(tmtaa)Et]I using CH_2I_2 (0.07 mL, 0.87 mmol), Sn(tmtaa) (0.136 g, 0.295 mmol) in THF (5 mL), and stirring for 2 h to give a yellow solid (0.060 g, 34%). A sample for elemental analysis was recrystallised from CH_2Cl_2–hexane. Found: C, 42.26; H, 4.22; N, 8.84. $C_{45}H_{46}I_2N_8Sn_2\cdot 1.5CH_2Cl_2$ requires C, 42.39; H, 3.75; N, 8.50%. FAB$^+$ MS: *m/z* 1063 ([{Sn(tmtaa)}$_2$(μ-CH_2)]I^+). ^1H NMR: δ 7.31 (m, 8 H, H_m), 7.15 (m, 8 H, H_o), 5.57 (s, 4 H, CH), 2.43 (s, 24 H, CH_3) and 0.58 (s, 2 H, $^2J(^{117/119}SnH) = 93$ Hz, $SnCH_2Sn$). $^{13}C-\{^1H\}$ NMR: δ 167.17 (NC_{Ar}), 134.41 ($N\mathit{C}CH_3$), 126.52 (CH_m), 124.58 (CH_o), 102.80 (CH), 25.26 (CH_3) and 14.06 ($SnCH_2Sn$).

X-Ray crystallography

Accurate intensity data were collected on a Siemens SMART CCD diffractometer using graphite monochromated Mo-Kα radiation. Unit cell parameters were determined by automated matrix determination. Data were collected over a hemisphere of reciprocal space and corrected for Lorentz-polarisation effects by empirical absorption correction.[14]

Table 1 Crystal data and structure refinement for [Sn(tmtaa)Me]I·2$CHCl_3$ and [{Sn(tmtaa)}$_2$(μ-CH_2)]I_2·2$CHCl_3$·LiI·3H_2O

Chemical formula	$C_{25}H_{20}Cl_6IN_4Sn$	$C_{47}H_{48}Cl_6I_3LiN_8O_3Sn_2$
M	834.74 g mol^{-1}	1610.65 g mol^{-1}
T/K	203(2)	203(2)
λ/Å	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/n$
a/Å	10.4459(3)	14.451(1)
b/Å	10.6470(2)	16.7506(2)
c/Å	28.3609(7)	24.8794(4)
β/°		104.176(1)
V/Å^3	3154.23(13)	5838.99(12)
Z	4	4
D_c/g cm^{-3}	1.758	1.832
μ/mm^{-1}	2.319	2.761
F(000)	1612	3096
Reflections collected	18687	33860
Reflections observed [$I > 2\sigma(I)$]	3167	8591
Independent reflections	3734 [$R_{int} = 0.0272$]	11899 [$R_{int} = 0.0403$]
Final $R1$ [$I > 2\sigma(I)$]	0.0345	0.0561
$wR2$ (all data)	0.0919	0.1372

The structure of [Sn(tmtaa)Me]I·2$CHCl_3$ was determined by direct and that of [{Sn(tmtaa)}$_2$(μ-CH_2)]I_2·2$CHCl_3$·LiI·3H_2O by Patterson and Fourier methods.[15] The structures were refined by full-matrix least-squares analysis[16] against F^2. All non-hydrogen atoms were allowed to refine anisotropically and hydrogen atoms included in calculated positions and refined with a riding model with thermal parameter 1.2 times U_{iso} of the carrier atom (1.5 times for methyl groups, the hydrogen atoms being located from a circular Fourier). Data for the cell parameters, intensity data collection and final least-squares refinement are in Table 1.

CCDC reference number 186/1530.

See http://www.rsc.org/suppdata/dt/1999/2833/ for crystallographic files in .cif format.

Results and discussion

Syntheses

When an excess of methyl iodide was added to a deep red solution of Sn(tmtaa) in THF at RT a bright orange precipitate of the product formed over the course of 30 min. Proton and $^{13}C-\{^1H\}$ NMR spectroscopy of the product revealed that the tmtaa ligand retains its C_{2v} symmetry, with a singlet for the four methyl groups, a singlet for the two methine groups and two multiplets for the aromatic protons observed in the ^1H NMR spectrum. An additional singlet (with ^{117}Sn and ^{119}Sn satellites) observed at δ 0.58 integrating for 3 protons was assigned to the methyl group bonded to tin. A spectrum with additional peaks corresponding to a product of apparently lower symmetry was originally reported for this reaction, and on this basis the product had been assigned as *cis*-Sn(tmtaa)(Me)I.[11] However, on re-examination, the reported data can be accounted for by a mixture of the same product we observed together with free base H_2tmtaa. Our data, in which the complex has retained its axial symmetry, is consistent with either *trans*-Sn(tmtaa)(Me)I or a five-co-ordinate cation, [Sn(tmtaa)Me]I. X-Ray crystallography of the complex confirmed that the latter formulation is indeed observed in the solid state (Fig. 1).

This reaction is general, and can be extended to form the corresponding ethyl, *n*-propyl and *n*-butyl derivatives, [Sn(tmtaa)R]I (R = Et, n-Pr or n-Bu) by reaction of Sn(tmtaa) with EtI, n-PrI and n-BuI, respectively. In each case the reaction proceeds in THF at RT, although the rate slows with increasing length of the alkyl chain, as evidenced by the time required for the change from the deep red Sn(tmtaa) to the orange or yellow product. The new alkyl complexes were

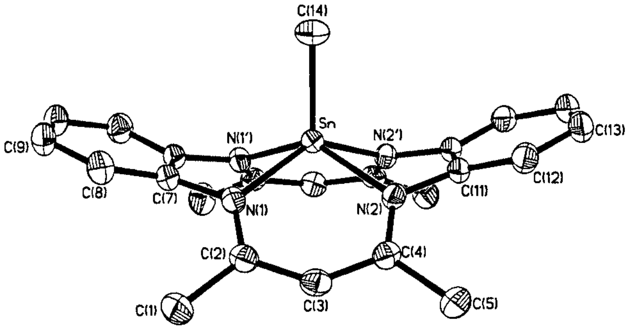

Fig. 1 Molecular structure of the [Sn(tmtaa)Me]$^+$ cation. Important bond lengths (Å): Sn–C(14), 2.118(5); Sn–N(1), 2.114(3); Sn–N(2), 2.114(3).

characterised by ^{1}H and ^{13}C NMR spectroscopy, and by elemental analysis and/or high resolution FAB$^+$ mass spectrometry. In the ^{1}H NMR spectrum of each the tmtaa ligand retains its C_{2v} symmetry, and peaks corresponding to the alkyl fragment are clearly resolved, with the CH$_2$ group attached to the tin atom shifted the furthest downfield. FAB$^+$ Mass spectra show [Sn(tmtaa)R]$^+$ as the highest mass peak, consistent with the cationic formulation of the new alkyl complexes. Although the Sn(tmtaa) starting material is air-sensitive, and the reactions are carried out under nitrogen, the cationic alkyltin products can be handled in air in both solution and the solid state.

Secondary alkyl iodides (i-PrI) or primary alkyl bromides were not successful as reagents for the oxidative addition reaction to Sn(tmtaa), with no tractable products being observed even after reaction times of up to one week. However, diiodomethane did react with two equivalents of Sn(tmtaa) to give a dinuclear dication containing two Sn(tmtaa) units linked by a bridging methylene group. The protons of the bridging methylene group are observed at δ 0.58, the same chemical shift as observed for the mononuclear methyl complex, but integrating for one CH$_2$ group per two Sn(tmtaa) units. The two tmtaa ligands in the dinuclear complex appear equivalent in the ^{1}H and ^{13}C-{^{1}H} NMR spectra. The molecular structure of this compound, [{Sn(tmtaa)}$_2$(μ-CH$_2$)]I$_2$, was also confirmed by X-ray crystallography (Fig.2). The reaction of 1,2-diiodoethane with Sn(tmtaa) did not give an organometallic product, but rather a complex identified as the known Sn(tmtaa)I$_2$.[3] This is a similar result to the reaction of Sn(Me$_8$taa)E (E = S or Se) with 1,2-diiodoethane which also resulted in the diiodo complex Sn(Me$_8$taa)I$_2$.[7]

The oxidative addition of alkyl halides to Sn(tmtaa) reported here gives five-co-ordinate cationic alkyltin products. This contrasts with the oxidative addition of Cl$_2$ (using the reagent PhICl$_2$) to Sn(tmtaa),[3] and of I$_2$ to Sn(Me$_8$taa),[4] both of which give the *trans*-dihalogeno complexes. The lability of one iodo ligand in the *trans*-diiodo complex was demonstrated by treatment of the product with an excess of iodine which resulted in loss of one iodo ligand and formation of the five-co-ordinate cation [Sn(Me$_8$taa)I][I$_3$].[4] Isolation of the five-co-ordinate cations for the alkyl derivatives may reflect the *trans* influence of the alkyl ligands.

Molecular structures of [Sn(tmtaa)Me]I·2CHCl$_3$ and [{Sn(tmtaa)}$_2$(μ-CH$_2$)]I$_2$·2CHCl$_3$·LiI·3H$_2$O

The crystal of [Sn(tmtaa)Me]I contains two molecules of chloroform, while that of [{Sn(tmtaa)}$_2$(μ-CH$_2$)]I$_2$ contains two chloroform and three water molecules in addition to a lithium iodide. The lithium ion was presumably carried through from the preparation of the precursor Sn(tmtaa) from Li$_2$(tmtaa) and SnCl$_2$. The molecular structures of the [Sn(tmtaa)Me]$^+$ (Fig. 1) and [{Sn(tmtaa)}$_2$(μ-CH$_2$)]$^{2+}$ (Fig. 2) cations each contain five-co-ordinate cationic tin centres, with the tin atoms displaced from the N$_4$ planes of the ligands by 0.78 Å for the former and by 0.61 and 0.69 Å for the latter. These values compare to those observed for the three other reported five-co-ordinate tin Me$_8$taa complexes (0.72–0.87 Å).[6,7] In each case, the tin atom is displaced toward the benzenoid face of the saddle-shaped tmtaa ligand, as is most commonly observed in four- and five-co-ordinate tmtaa or Me$_8$taa complexes.[1,2] The Sn–C distances are 2.118(5) Å for [Sn(tmtaa)Me]I and 2.101(7) and 2.111(7) Å for [{Sn(tmtaa)}$_2$(μ-CH$_2$)]I$_2$, slightly shorter than the sum of the covalent radii, 2.17 Å.[17] The average Sn–N distances are 2.114(3) Å for the mononuclear complex and 2.106(6) and 2.090(6) Å for the dinuclear complex, all comparable to the range observed for other five-co-ordinate tin Me$_8$taa complexes (2.11–2.15 Å).[6,7]

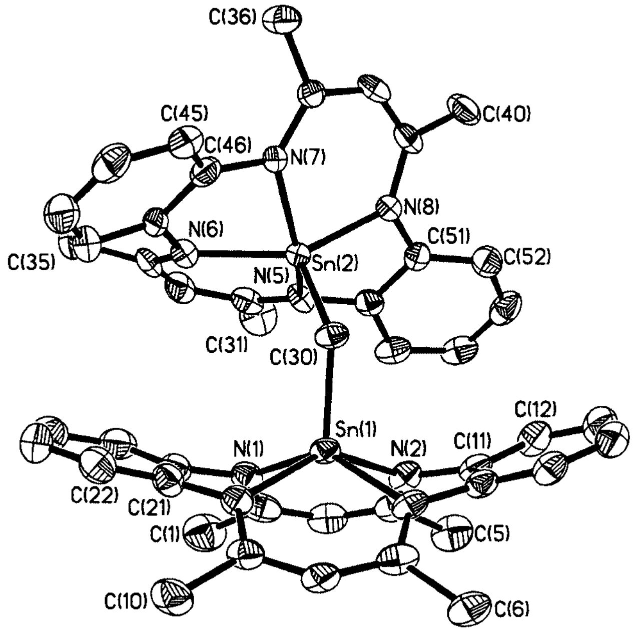

Fig. 2 Molecular structure of the [{Sn(tmtaa)}$_2$(μ-CH$_2$)]$^{2+}$ dication. Important bond lengths (Å) and angles (°): Sn(1)–C(30), 2.101(7); Sn(2)–C(30), 2.111(7); Sn(1)–N(1), 2.101(6); Sn(1)–N(2), 2.100(6); Sn(1)–N(3), 2.122(6); Sn(1)–N(4), 2.101(6); Sn(2)–N(5), 2.097(6); Sn(2)–N(6), 2.098(6); Sn(2)–N(7), 2.095(5) and Sn(2)–N(8), 2.069(6); Sn(1)–C(30)–Sn(2), 122.5(3).

The Sn–C–Sn angle at the bridging CH$_2$ group in the dinuclear complex is 122.5(3)°, considerably wider than the 109° angle expected for tetrahedral carbon, and indicating the steric influence of the bulky Sn(tmtaa) substituents. The two tmtaa ligands in this complex are oriented at an angle of 47° between the two N$_4$ planes, and rotated such that in the region of the closest approach the aromatic ring of one tmtaa ligand, which points in towards the bridging region, is directed towards the diiminato fragment of the second tmtaa group, which is oriented away from the bridging group. The only other example of a dinuclear tin complex containing this ligand type is [{Sn(Me$_8$taa)}$_2$(μ-O)$_2$], which contains two bridging O atoms as part of a rigid Sn$_2$O$_2$ ring, and thus the tmtaa ligands are held in much closer proximity with the two N$_4$ planes approximately parallel.[18]

There are now a sufficient number of structures reported for tin complexes containing the tmtaa or Me$_8$taa ligands (L) to make some general observations regarding geometry. Four-co-ordinate complexes Sn(L) contain tin in the +2 oxidation state, and the large size of this ion is reflected in the large Sn–N$_4$ out-of-plane displacements (1.12, 1.15 Å) and long Sn–N distances (2.26 Å).[6,8] The remaining complexes all contain tin formally in the +4 oxidation state. Of these, the largest Sn–N$_4$ out-of-plane and longest Sn–N$_{av}$ distances occur for the six-co-ordinate complexes with *cis* geometry, Sn(Me$_8$taa)(η^2-SCH$_2$CH$_2$S) (0.99, 2.21 Å)[7] and [{Sn(Me$_8$taa)}$_2$(μ-O)$_2$] (1.00, 2.20 Å).[18] Next are the five-co-ordinate complexes Sn(Me$_8$taa)(=E) (E = S or Se),

$[Sn(Me_8taa)(SeMe)]^+$ and the two new alkyl complexes reported here ($Sn–N_4$ 0.61–0.87, $Sn–N_{av}$ 2.09–2.15 Å).[6,7] Finally the six-co-ordinate complexes with *trans* geometry $Sn(L)X_2$ (L, X = tmtaa, Cl; tmtaa, NO_3; or Me_8taa, I) contain the tin atom lying almost in the N_4 plane ($Sn–N_4$ 0.02–0.06, $Sn–N_{av}$ 2.05–2.06 Å).[3,4] One further example, $[Sn(Me_8taa)(I)(THF)]I$, which contains a normal Sn–I distance (2.708(2) Å) but a very long Sn–O (THF) distance (2.63 Å), is intermediate between five- and *trans* six-co-ordinate geometries, and exhibits intermediate values for $Sn–N_4$ (0.44 Å) and $Sn–N_{av}$ (2.08 Å).[4]

Conclusion

The new complexes reported here represent the first fully characterised examples of organometallic derivatives of Sn(tmtaa), and further broaden the scope of the chemistry of this class of compounds. Two X-ray determinations establish the geometries of the five-co-ordinate tin–methyl cation and the dinuclear dication containing a bridging methylene group. The incomplete characterisation presented in the original report of Sn(tmtaa)(Me)I is now resolved. The new complexes extend the structural trends observed for the four-, five, and six-co-ordinate complexes containing the Sn(tmtaa) moiety.

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