Self-assembly of diphenyltin(IV) and tris-dithiocarbamate ligands to racemic trinuclear cavitands and capsules[†]

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Racemic trinuclear diphenyltin(IV) cavitands and capsules have been assembled from diphenyltin(IV) and tris-dithiocarbamate ligands.

1 Introduction

Currently, it is one of the major objectives of supramolecular chemistry to establish synthetic strategies that allow for the generation of assemblies capable to encapsulate guest molecules in a selective manner.¹ Dithiocarbamate (dtc) ligands can be useful tectons for this purpose, since complex supramolecular architectures such as macrocycles, cages, catenanes and nanodimensional assemblies can be generated from a variety of oligofunctional constructs in combination with metal ions.² Moreover, it has been shown that macrocycles derived from di- and tripodal-dtc ligands have the potential to bind, sense and react together with guest substrates. Additionally, they can have unique redox, magnetic and photochemical properties, thus making them interesting objects of study.³ Previously, the synthesis of neutral trinuclear metallocryptands has been achieved via the combination of tris-(pyrrole-functionalized)-dtc frameworks with metal centers having a square-planar coordination preference [zinc(II), nickel(II) or copper(II) salts].^{4a} When bis-dithiocarbamate salts were combined with octahedral centers such as Fe(III) and Co(III), bimetallic capsules were obtained.4b

So far, little is known about supramolecular assemblies derived from organometallic building blocks. In reality, there are only few useful candidates and among these organotin systems have shown to be particularly interesting.⁵ However, so far the vast majority of metallosupramolecular tin assemblies have been constructed from ligands having nitrogen or oxygen as metal-coordinating donors, and systems with other donor atoms such as sulfur and phosphorus are almost unexplored.⁶

Recently, we reported the synthesis of two new dinuclear tin macrocycles based on dtc ligands.⁷ In this contribution we present now the synthesis of a series of chiral trinuclear diphenyltin(IV) cavitands, 1–3, and capsules, 4–5, which were derived from tris[2-(*N*-alkyldithiocarbamate)ethyl]amine ligands (Scheme 1). The synthesis of chiral molecular capsules *via* coordination-bonds is important, because they should show more interesting recognition properties from the viewpoints of potential applications.⁸



2 Results and discussion

2.1 Syntheses and spectroscopy characterization

The tripodal tris-dithiocarbamate ligands required for the preparation of compounds 1–5 were obtained from the combination of three different trisamines: tris[2-(methylamino)ethyl]amine, tris[2-(isopropylamino)ethyl]amine and tris[2-(benzylamino)ethyl]-amine, with carbon disulfide and potassium hydroxide as base. Subsequent reaction with diphenyltin dichloride, Ph_2SnCl_2 , in 1 : 3 and 2 : 3 ligand-to-diphenyltin(IV) ratios formed the trinuclear vase-shaped cavitands 1–3 and capsules 4–5 in yields ranging from 45 to 69%. The inherently chiral cavitands 1–3 and capsules 4–5 are formed as racemates because nonchiral ligands and solvents were used.⁹

The composition of the resulting products was established as far as possible by elemental analysis, mass spectrometry, IR and NMR (¹H, ¹³C, ¹¹⁹Sn) spectroscopy, and X-ray crystallography (1, 4 and 5). The formation of the dtc functions could be evidenced straightforward from the IR, ¹³C and ¹¹⁹Sn NMR spectra. The IR spectra showed bands in the range from 1451 to 1518 cm⁻¹ and 954 to 996 cm⁻¹ that are typical for the vibrations of the C–N_{dtc} bonds and CS₂ groups, respectively.¹⁰ The ¹³C NMR signals of the dtc carbon atoms (N¹³CSS) are found in the range of δ_C 196.32 to 198.72 ppm for compounds 1–3, and δ_C 200.31 to 202.13 ppm for compounds 4–5, and agree well with previously reported data on metal dtc complexes.⁶ The ¹¹⁹Sn NMR chemical shift values for compounds 1–3 and 4–5 were found in the ranges of –311 to –319 ppm and $\delta = -512$ to –514 ppm, respectively, indicating that

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in solution the tin atoms are penta-coordinated in the first case, and hexa-coordinated in the second case.⁶

Interestingly, in the ¹H NMR spectra of compounds **4** and **5** the aliphatic protons of the *i*-propyl and benzyl groups gave signals for diastereotopic hydrogen atoms, indicating that the tin atoms are stereogenic centers. For compound **4** two doublets were observed for the methyl groups at $\delta_{\rm H}$ 1.15 and 1.26 ppm, while the hydrogen atoms in the methylene group of compound **5** gave an AB system ($\delta_{\rm H}$ 4.75 and 5.34 ppm with $J_{\rm gem}$ 15.2 Hz). In comparison, for the analogous semi-capsules **2** and **3** the ¹H NMR spectra gave only one doublet for the methyl groups ($\delta_{\rm H}$ 1.27 ppm, ³J 6.8 Hz) and a single signal for the methylene group ($\delta_{\rm H}$ 4.83 ppm), respectively.

The mass spectra (FAB⁺) of compounds 1–5 support the assumption that trinuclear diorganotin(IV) dithiocarbamate cavitands and capsules had been obtained. In all cases the molecular ions could not be detected, but it was possible to detect peaks corresponding to the $[M - Cl]^+$ (compounds 1–3) and $[M - C_6H_5]^+$ (compounds 4–5) fragments: m/z 1303 for 1, 1387 for 2, 1531 for 3, 1737 for 4 and 2025 for 5.

2.2 X-Ray crystal structures

Single crystals of 1, 4 and 5 were grown at room temperature by slow evaporation of chloroform–ethanol (1:1, 1), bromoform– methanol (1:2, 4) and chloroform–benzene (3:2, 5) solutions.‡ The molecular structure of complex 1 is given in Fig. 1 (top view), showing that this compound possesses a trinuclear vaseshaped cavitand structure. A careful inspection of the molecular



Fig. 1 Perspective view of the molecular structure of compound $1,\ddagger$ showing 50% probability displacement ellipsoids. For clarity, hydrogen atoms are omitted.

‡ Crystal data for **1**, **4** and **5**: C₄₈H₅₁Cl₃N₄S₆Sn₃ **1**, M = 1338.71, triclinic, space group *P*-1, a = 10.0012(6), b = 17.2313(10), c = 18.2621(10) Å, $\alpha = 115.029(1)^\circ$, $\beta = 103.792(1)^\circ$, $\gamma = 90.019$ (1)°, V = 2751.0 (3) Å³, T = 293 K, Z = 2. 26606 reflections measured, 9651 unique ($R_{int} = 0.0580$) and 7263 with $I > 2 \sigma(I)$. The final *R* values were $R_1 = 0.0931$ and wR_2 (all data) = 0.1827. CCDC 666754. C₇₂H₉₆N₈S₁₂Sn₃·2CHBr₃ **4**, M = 2319.85, trigonal, space group *R*-3*c*, a = 16.423(5), c = 59.95(3) Å, V = 14005 (9) Å³, T = 293 K, Z = 6. 21255 reflections measured, 2757 unique ($R_{int} = 0.0460$), 2278 with $I > 2 \sigma(I)$. The final *R* values were $R_1 = 0.0431$ and wR_2 (all data) = 0.1122. CCDC 691815. C₉₆H₉₆N₈S₁₂Sn₃·2(CHCl₃)·3(C₆H₆) **5**, M = 2575.66, trigonal, space group *P*-3, a = 22.2740(12), c = 13.8830(11) Å, V = 5965.0 (7) Å³, T = 100 K, Z = 2, 43833 reflections measured, 7027 unique ($R_{int} = 0.0698$), 5787 with $I > 2 \sigma(I)$. The final *R* values were $R_1 = 0.0531$ and wR_2 (all data) = 0.1316. CCDC 691697.

structure shows that both the *N*-methyl and $Ph_2(Cl)Sn$ groups oriented to the outer-sphere of the cavitand are arranged in form of a propeller, thus giving a chiral assembly. However, within the crystal lattice, both enantiomers are present (space group *P*-1), whereas in solution the chirality is vanished due to the unhindered rotational movement of the tripodal arms (*vide supra*).

The 2:3 reaction products **4** and **5** gave spherical capsules (Fig. 2–3) that crystallized in the D_{3d} and C_{3i} crystallographic point groups, respectively, indicating that they are racemic compounds, too. In capsules **4** and **5** the tin and amine nitrogen atoms are forming a trigonal-bipyramidal polyhedron with average Sn \cdots Sn, Sn \cdots N and N \cdots N distances of 10.73, 6.79 and 5.19 Å, respectively.



Fig. 2 Perspective view of the molecular structure of compound **4**,‡ showing 50% probability displacement ellipsoids. For clarity, hydrogen atoms and solvent molecules are omitted.



Fig. 3 Perspective view of the molecular structure of compound 5,‡ showing 50% probability displacement ellipsoids. For clarity, hydrogen atoms and solvent molecules are omitted.

In all cases, the dtc moieties are coordinated to the tin atoms in the anisobidentate manner. The covalent Sn–S bonds are in the range [2.437(3)–2.5813(13) Å], and the secondary interactions are in the range [2.667(2)–2.7081(13) Å]. While the tin atoms in 1 are penta-coordinated, showing a distorted trigonal-bipyramidal polyhedron, in which the equatorial angles vary from 111.9(3) to 124.7(3)° and the axial angles from 153.35(10) to 157.33(9)°, the tin atoms in compounds 4 and 5 are hexa-coordinated with distorted octahedral polyhedron geometries (twist distortion).

3 Conclusions

In conclusion, this contribution has shown that the self-assembly process of dtc ligands with diorganotin centers allows to construct racemic cavitands and capsules, in which in the latter case the tin atoms are the stereogenic centers. This makes these capsules interesting candidates for the molecular recognition of chiral Lewis basic substrates.

4 Experimental

4.1 General details

Instrumental: NMR studies were carried out with Varian Gemini 200 and Varian Inova 400 instruments. Chemical shifts ($\delta_{\rm H}$, $\delta_{\rm C}$ and $\delta_{\rm Sn}$) and J values are given in ppm and Hz, respectively. Standard references were used: TMS ($\delta_{\rm H} = 0$ and $\delta_{\rm C} = 0$) and SnMe₄ (δ^{119} Sn = 0). The $\delta_{\rm H}$ and $\delta_{\rm C}$ values for the racemic capsules 4–5 were assigned by 2D NMR experiments. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on a Jeol JMS 700 equipment. Elemental analyses have been carried out on an Elementar Vario ELIII instrument, using samples that have been dried previously at 65 °C for 2 h in an Abderhalden equipment.

4.2 Syntheses

Tris[2-(N-methyldithiocarbamate)ethyl]amine diphenyltin(IV) chloride 1. To a solution of tris[2-(methylamino)ethyl]amine (0.100 g, 0.53 mmol) and potassium hydroxide (0.089 g, 1.59 mmol) in methanol (5 ml) carbon disulfide was added (0.2 ml, 3.3 mmol), and the solution was stirred at 20 °C for 1 hour. A solution of Ph₂SnCl₂ (0.547 g, 1.59 mmol) in methanol (5 ml) was added. The white precipitate was collected by filtration (yield 0.49 g, 69%). Mp 183-185 °C (from MeOH). Crystals suitable for X-ray crystallography were grown from a solution of 1 in chloroform-ethanol (1:1). Elemental analysis (Found: C, 42.5; H, 3.7; N, 4.0. Calc. for C48H51Cl3N4S6Sn3: C, 43.1; H, 3.8; N, 4.2). IR (KBr) $v_{\text{max}}/\text{cm}^{-1}$ 982 (CS₂), 1518 (N-CS₂). δ_{H} (200 MHz; CDCl₃; Me₄Si) 2.83 (6H, t, ${}^{3}J = 6.2$, N(1)CH₂), 3.21 (9H, s, NCH₃), 3.67 (6H, t, ${}^{3}J = 6.2$, CH₂NCS₂), 7.38–7.50 (18H, m, CH*m*,*p* of Sn*Ph*₂), 8.03 (12H, d, J = 6.4, CH*o* of Sn*Ph*₂), ${}^{3}J({}^{119}Sn$, ¹H) 83.0. $\delta_{\rm C}$ (200 MHz; CDCl₃; Me₄Si) 44.76 (NCH₃), 50.85 (NCH_2) , 56.65 (CH_2NCS_2) , 129.01 (C_m) , 130.46 (C_p) , 135.68 (C_o) , 141.56 (C_i) , 197.17 (CS_2) ; ² $J(^{119}Sn, ^{13}C)$ 61.0, ³ $J(^{119}Sn, ^{13}C)$ 85.4. δ_{sn} (400 MHz; CDCl₃; Me₄Sn) 319. m/z (FAB⁺) 1303 (M⁺ – Cl, 12%).

Tris[2-(*N*-isopropyldithiocarbamate)ethyl]amine diphenyltin(IV) chloride 2. To a solution of tris[2-(isopropylamino)ethyl]amine

(0.100 g, 0.37 mmol) and potassium hydroxide (0.061 g, 1.10 mmol) in methanol (5 ml) carbon disulfide (0.2 ml, 3.3 mmol) was added, and the solution was stirred at 20 °C for 1 hour. A solution of Ph₂SnCl₂ (0.378 g, 1.10 mmol) in methanol (5 ml) was added. The white precipitate was collected by filtration (yield 0.25 g, 48%). Mp 164–165 °C (from MeOH). Elemental analysis (Found: C, 44.8; H, 4.5; N, 4.6; Calc. for C₅₄H₆₃Cl₃N₄S₆Sn₃, C, 45.6; H, 4.5; N, 3.9). IR (KBr) $v_{\text{max}}/\text{cm}^{-1}$ 967 (CS₂), 1480 (N-CS₂). $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 1.27 (18H, d, ³J = 6.8, CH₃), 3.01 (6H, t, ${}^{3}J = 7.6$, N(1)*CH*₂), 3.66 (6H, t, ${}^{3}J = 7.6$, *CH*₂NCS₂), 4.89 (3H, h, ${}^{3}J = 6.8$, NCH), 7.41–7.49 (18H, m, CHm,p of Sn*Ph*₂), 8.00–8.04 (12H, m, CH*o* of Sn*Ph*₂); ${}^{3}J({}^{119}Sn, {}^{1}H)$ 85.9. δ_{C} (200 MHz; CDCl₃; Me₄Si) 20.58 (CH₃), 52.35 (N(1)CH₂), 48.60 (CH₂NCS₂), 58.70 (NCH), 129.00 (C_m), 130.43 (C_p), 135.79 (C_p), 141.86 (C_i), 196.32 (CS_2); ${}^{2}J({}^{119}Sn, {}^{13}C)$ 64.0, ${}^{3}J({}^{119}Sn, {}^{13}C)$ 86.9. δ_{Sn} (400 MHz; CDCl₃; Me₄Sn) 311. m/z (FAB⁺) 1387 (M⁺ - Cl, 21%).

Tris[2-(N-benzyldithiocarbamate)ethyl]aminodiphenyltin (\mathbf{IV}) **chloride 3.** To a solution of tris[2-(benzyl)ethyl]amine (0.100 g, 0.24 mmol) and potassium hydroxide (0.040 g, 0.72 mmol) in methanol (5 ml) carbon disulfide (0.2 ml, 3.3 mmol) was added, and the solution was stirred at 20 °C for 1 hour. A solution of Ph₂SnCl₂ (0.248 g, 0.72 mmol) in methanol (5 ml) was added. The white precipitate was collected by filtration (yield 0.26 g, 69%). Mp 182-186 °C (from MeOH). Elemental composition by HR-FAB-MS, observed m/z 1532.0037 (M⁺ – Cl, 100%) error +19.2 ppm. IR (KBr) v_{max} /cm⁻¹ 996 (CS₂), 1497 (N-CS₂). δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.50 (6H, t, ${}^{3}J$ = 7.4, N(1)CH₂), 3.49 (6H, t, ${}^{3}J$ = 7.4, CH₂NCS₂), 4.83 (6H, s, NCH₂Ph), 7.17–7.28 (15H, m, CH₂Ph), 7.43–7.49 (18H, m, CHm, p of SnPh₂), 8.03–8.06 $(12H, m, CHo \text{ of } SnPh_2); {}^{3}J({}^{119}Sn, {}^{1}H) 87.0. \delta_C (400 \text{ MHz}; CDCl_3;$ Me₄Si), 50.57 (N(1)CH₂), 53.41 (CH₂NCS₂), 60.94 (CH₂Ph), $[129.09(C_m), 130.55(C_p), 135.81(C_o), 141.77(C_i); SnPh_2]; [128.10$ (C_m) , 128.45 (C_p) , 129.39 (C_q) , 133.27 (C_i) , CH₂*Ph*], 198.72 (CS_2) ; $^{2}J(^{119}\text{Sn},^{13}\text{C})$ 64.0, $^{3}J(^{119}\text{Sn},^{13}\text{C})$ 80.8. δ_{Sn} (400 MHz; CDCl₃; Me₄Sn) 315. *m/z* (FAB⁺) 1531 (M⁺ - Cl, 11%).

Bis-{tris[2-(N-isopropyldithiocarbamate)ethyl]amino} diphenyltin(IV) 4. To a solution of tris[2-(isopropylamino)ethyl]amine (0.100 mL, 0.314 mmol) and potassium hydroxide (0.052 g, 0.944 mmol) in methanol (5 ml) carbon disulfide (0.2 mL, 3.3 mmol) was added and the solution was stirred at 20 °C for 1 hour. A solution of Ph₂SnCl₂ (0.160 g, 0.467 mmol) in methanol (5 ml) was added and the resulting precipitate was collected by filtration. The solid was recrystallized in a mixture of CH₂Cl₂-MeOH (1:2) (yield 0.128 g, 45.2%). Mp 243–245 °C (from CH₂Cl₂/MeOH). Crystals suitable for X-ray crystallography were grown from a solution of 4 in bromoform-methanol (1:2). Elemental analysis (Found: C, 47.1; H, 5.4; N, 6.3; Calc. for C₇₂H₉₆N₈S₁₂Sn₃: C, 47.7; H, 5.3; N, 6.2). IR (KBr) v_{max}/cm^{-1} 970 (CS₂), 1451 (N-CS₂). δ_H (400 MHz; CDCl₃; Me₄Si; COSY) 1.15 (18H, d, ${}^{3}J =$ 6.8, CHCH_{3A}), 1.26 (18H, d, ${}^{3}J = 6.4$, CHCH_{3B}), 2.91 (6H, m, N(1)CH_A), 3.22 (6H, m, CH_BNCS₂), 3.24 (6H, m, N(1)CH_B), 3.85 (6H, m, CH_ANCS₂), 4.91 (6H, m, NCH(CH₃)₂), 7.27-7.32 (18H, m, CHo,p of SnPh₂), 7.69–7.71 (12H, m, CHo of SnPh₂); ³J(¹¹⁹Sn, ¹H) 84. δ_{C} (400 MHz; CDCl₃; Me₄Si; HSQC), 20.56 (CH_{3A}), 21.78 (CH_{3B}) , 48.33 (CH_2NCS_2) , 53.03 $(N(1)CH_2)$, 57.78 $(NCH(CH_3)_2)$, $[128.20 (C_m), 128.4 (C_p), 133.99 (C_o), 153.51 (C_i), SnPh_2], 200.31$ (CS_2) . δ_{Sn} (400 MHz; CDCl₃; Me₄Sn) 514. m/z (FAB⁺) 1737 (M⁺ – C₆H₅, 20%).

Bis{tris[2-(N-benzyldithiocarbamate)ethyl]amino} diphenyltin(IV) 5. To a solution of tris[2-(benzyl)ethyl] amine (0.100 g, 0.24 mmol) and potassium hydroxide (0.040 g, 0.72 mmol) in methanol (5 ml) carbon disulfide (0.2 mL, 3.3 mmol) was added, and the solution was stirred at 20 °C for 1 hour. A solution of Ph₂SnCl₂ (0.124 g, 0.36 mmol g) in methanol (5 ml) was added and the resulting precipitate was collected by filtration. The solid was recrystallized in a mixture of chloroform-benzene giving crystals suitable for X-ray crystallography. (Yield 0.070 g, 13.4%). Mp 229-231 °C (from chloroform-benzene). Elemental analysis (Found: C, 54.7; H, 4.8; N, 5.8; Calc. for C₉₆H₉₆N₈S₁₂Sn₃: C, 54.8; H, 4.6; N, 5.3). IR (KBr) $v_{\rm max}/{\rm cm}^{-1}$ 954 and 979 (CS₂), 1477 (N-CS₂). $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si; COSY) 2.85–2.90 (12H, m, CH₂NCS₂), 2.96 (6H, m, N(1)CH_B), 3.91 (6H, m, N(1)CH_A) 4.75 (6H, d, $J_{AB} = 15.2$, NCH_APh), 5.34 (6H, d, $J_{AB} = 15.2$, NCH_BPh), 7.19-7.23 (12H, m, CHo of NCH₂Ph), 7.28-7.32 (18H, m, CHm,p, of CH₂Ph), 7.33-7.39 (18H, m, CHo,p of $SnPh_2$), 7.81–7.85 (12H, m, CHo of $SnPh_2$). δ_c (400 MHz; CDCl₃; Me₄Si, HETCOR), 49.66 (*CH*₂NCS₂), 54.10 (N(1)*CH*₂), 61.49 (NCH₂Ph); [128.35 (C_m), 128.48 (C_p), 133.96 (C_o), 153.24 (C_i) , SnPh₂]; [127.81 (C_m) , 128.87 (C_p) , 129.17 (C_o) , 134.58 (C_i) , CH₂*Ph*], 202.13 (*CS*₂). δ_{sn} (400 MHz; CDCl₃; Me₄Sn) 512. *m/z* (FAB^+) 2025 $(M^+ - C_6H_5, 5\%)$.

4.3 X-Ray crystallography

X-Ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at 293 K for compounds 1 and 4 and 100 K for compound 5 via ω/ϕ -rotation at 10 s per frame (SMART).^{11a} The measured intensities were reduced to F² and corrected for absorption with SADABS (SAINT-NT).^{11b} Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.^{11c,d} Non hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. In compound 4 the central nitrogen N(2) lies on a threefold axis and the unique Sn(1) atom on a twofold axis. In compound 5 the central nitrogens N(2) and N(4) lie on a threefold axis. Solvent molecules are present in the crystal lattices of compounds 4 and 5 (bromoform for 4, benzene and chloroform for 5). All three compounds have elongated ellipsoids on the phenyl groups, suggesting large vibration of the rings and/or disorder. For compound 5 the unit cell contains two capsules (Z = 2), which are localized at crystallographic C₃ axes, six benzene molecules, and four CHCl₃ molecules at two crystallographically independent positions. One of the two crystallographically independent CHCl₃ molecules is disordered (three different orientations with crystallographic C_3 symmetry, occ = 0.25, 0.25 and 0.50). The disorder has been treted using DFIX, DANG, and EADP instructions.

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