Directed derivatization of organotin sulfide compounds: synthesis and self-assembly of an SnS backpack-like cage and a CuSnS ternary cluster

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SUPPORTING INFORMATION
Experimental Syntheses Details

**General:** All manipulations steps were performed under an Ar atmosphere. All solvents were dried and freshly distilled prior to use. Water was degassed by applying dynamic vacuum \((10^{-3} \text{ mbar})\) for several hours. \([\text{CuCl(PPh}_2\text{Me)}_3]\) and \([(\text{R}_1\text{Sn})_4(\mu-S)_6]\) (\(\text{R}_1 = \text{CMe}_2\text{CH}_2\text{COMe}\)) was prepared according to the reported methods.\(^{[1,2]}\) \(\text{Na}_2\text{S}·9\text{H}_2\text{O}\) and carbohydrazide were purchased from Aldrich and used as received. \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR and \(^{31}\text{P}\) NMR measurements were carried out using a Bruker DRX 400 MHz spectrometer at 25°C. In \(^1\text{H}\) and \(^{13}\text{C}\) NMR, the chemical shifts were quoted in ppm relative to the residual protons of deuterated solvents. In \(^{31}\text{P}\) NMR, phosphoric acid was used as internal standard. Infrared (IR) spectra were recorded on a Bruker IFS 88 spectrometer. The crystals of 1 and 3 were ground with KBr and compacted to a transparent pellet. For measurements in the region 100-500 cm\(^{-1}\), the samples were prepared as mulls in Nujol oil and pressed between polyethylene windows.

**Synthesis of** \([(\text{R}_1\text{NSn}_2)_2(\mu-S)_6]·1.1\text{MeOH}·1.9\text{H}_2\text{O}, \ [1·1.1\text{MeOH}·1.9\text{H}_2\text{O}, \ R^N = (\text{CMe}_2\text{CH}_2\text{CMeNNH})_2\text{CO}]:\)

\([(\text{R}_1\text{Sn})_4(\mu-S)_6] (0.05 \text{ g}, 0.047 \text{ mmol})\) and carbohydrazide (0.010 g, 0.111 mmol) were suspended in a mixture of methanol (4 mL) and dichloromethane (4 mL). The mixture was stirred for 1 minute and left undisturbed at room temperature for 24 hours. The clear light yellow solution was layered by n-hexane. Colorless, cubic crystals of 1 were obtained within two days. Yield: 0.046 g (0.0375 mmol, 80%). \(^1\text{H}\) NMR (400 MHZ, CDCl\(_3\), 25°C): \(\delta = 1.36\) (br, 24H; Me\(_2\)C), 2.20 (br, 12H; Me), 2.77 (br, 8H; CH\(_2\)), 6.11 ppm (br, 4H; NH); \(^{13}\text{C}\) NMR (100 MHZ, CDCl\(_3\), 25°C): \(\delta = 25.38\) (Me\(_2\)), 29.81 (Me), 42.17 (CSn), 50.94 (CH\(_2\)), 153.08 (C=N), 155.98 ppm (C=O); FT-IR (KBr, Nujol mull in polyethylene windows): \(\tilde{\nu} = 3505\) (w), 3350 (w), 3314 (w), 3225 (m), 2932 (w), 2845 (s), 1706 (s), 1471 (s), 1365 (s), 1272 (w), 1302 (s), 1220 (s), 1138 (m), 1020 (w), 822 (w), 745 (w), 694 (w), 678 (w), 632 (w), 566 (w), 488 (w), 470 (w), 333 (s), 279 (w), 230 (w), 206 (w), 131 cm\(^{-1}\)(m); Raman: 2957 (w), 2937 (w), 2917 (w), 2886 (w), 2865 (m), 2856 (m), 2762 (w), 2721 (w), 1680 (m), 1636 (m), 1456 (w), 1433 (w), 1408 (w), 1386 (w), 1369 (w), 1330 (w), 1254 (m), 1223 (m), 1158 (w), 1141 (m), 1113 (s), 884 (m), 826 (m),
812 (w), 701 (w), 548 (m), 518 (s), 497 (w), 450 (m), 381 (s), 354 (s), 334 (m), 306 (s),
276 (w), 164 (w), 130 (s), 110 cm⁻¹ (s).

**Synthesis of \([R^2NI_{2}\{Sn(\mu-S)_{2}Cu(PPh_{2}Me)}]_{4}\cdot2THF, (3\cdot2THF)\):**

Treatment of a solution of compound 1 (0.092 g, 0.075 mmol) in THF (10 mL) with a solution of Na₂S·9H₂O (0.13 g, 0.510 mmol) in water (2 mL) resulted in the formation of compound 2 that is stable only for a few minutes. A solution of [CuCl(PPh₂Me)₃] (0.752 g, 1.074 mmol) in THF (8 mL) was added. The solution turned dark orange. It was stirred for 12 h and then filtered. Yellow crystals of 3 were obtained within one week upon layering the solution of 3 in THF over water. Yield: 0.064 g (0.0263 mmol, 35%).

\(^1\)H NMR (400 MHZ, CDCl₃, 25°C): \(\delta = 1.10\) (br, 8H; CH₂), 1.28 (br, 24H; Me and PMe)*, 1.63 (br, 24H; Me₂C), 7.30–7.43 ppm (br, 40H; Ar); \(^{13}\)C NMR (100 MHZ, CDCl₃, 25°C): \(\delta = 12.76\) (PMe), 22.75 (Me₂), 32.00 (Me), 37.33 (CSn), 47.70 (CH₂), 128.35, 128.48, 132.15, 134.99 (Ar), 140.1 ppm (C=N), (C=O not verified); \(^{31}\)P NMR (162 MHz, CDCl₃, 25°C): \(\delta = -25.8\) ppm; FT-IR (KBr, Nujol mull in polyethylene windows): \(\tilde{\nu} = 3350\) (w), 2923 (s), 2853 (s), 1679 (m), 1584 (w), 1572 (w), 1461 (s), 1435 (w), 1378 (s), 1303 (w), 1260 (w), 1213 (w), 1141 (w), 1097 (w), 1026 (w), 885 (s), 802 (m), 742 (m), 720 (w), 694 (s), 506 (s), 475 (w), 436 (w), 415 (w), 377 (w), 359 (m), 333 (s), 308 (w), 290 (w), 252 (w), 228 (w), 213 (w), 192 (w), 175 (w), 159 (w), 131 cm⁻¹ (w).

* The resonance of the CH₃ protons of the organic arms gets obscured by the CH₃ protons of the PPh₂Me ligands, and therefore it becomes difficult to be identified. However, the integration area accords to the number of protons calculated from the proposed structure.
Details of the X-ray diffraction measurement, structure solution and refinement

Data were collected on a diffractometer equipped with a STOE imaging plate detector system IPDS2T, using MoKα radiation with graphite monochromatization (λ = 0.71073 Å) at 100 K. Structure solution was performed by direct methods, full-matrix-least-squares refinement against \( F^2 \) using SHELXS-97 and SHELXL-97 software. Details of the data collection and refinement are given in Table S1. Selected bond lengths and bond angles are provided in Tables S2 and S4.

Table S1 Crystallographic and refinement details of 1 and 3 at 100 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1-1.1MeOH·1.9H2O</th>
<th>3-2THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>( \text{C}<em>{27.1}\text{H}</em>{56.2}\text{N}_8\text{O}_5\text{S}_6\text{Sn}_4 )</td>
<td>( \text{C}<em>{86}\text{H}</em>{116}\text{Cu}_4\text{N}_8\text{O}_4\text{P}_4\text{S}_8\text{Sn}_4 )</td>
</tr>
<tr>
<td>fw /g·mol(^{-1})</td>
<td>1241.26</td>
<td>2435.15</td>
</tr>
<tr>
<td>crystal color and shape</td>
<td>colorless cube</td>
<td>Yellow plate</td>
</tr>
<tr>
<td>crystal size /( \text{mm}^3 )</td>
<td>0.19×0.13×0.08</td>
<td>0.38×0.08×0.07</td>
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<tr>
<td>radiation (λ /Å)</td>
<td>Mo Kα, 0.71073</td>
<td>Mo Kα, 0.71073</td>
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<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>( \text{P}2_1/\text{n} )</td>
<td>( \text{P}2_1/\text{n} )</td>
</tr>
<tr>
<td>( a /\text{Å} )</td>
<td>11.614(2)</td>
<td>13.875(3)</td>
</tr>
<tr>
<td>( b /\text{Å} )</td>
<td>25.211(5)</td>
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<td>( c /\text{Å} )</td>
<td>16.472(3)</td>
<td>17.955(4)</td>
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<td>( \beta /\text{deg} )</td>
<td>96.01(3)</td>
<td>93.05(3)</td>
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<tr>
<td>( V /\text{Å}^3 )</td>
<td>4796.6(17)</td>
<td>5128.9(18)</td>
</tr>
<tr>
<td>( Z )</td>
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<td>2</td>
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<td>( \rho_{\text{calc}} /\text{g} \cdot \text{cm}^{-3} )</td>
<td>1.719</td>
<td>1.624</td>
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<td>( \mu (\text{Mo Kα}) /\text{mm}^{-1} )</td>
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<td>2.047</td>
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<td>numerical</td>
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<td>0.5101/0.8700</td>
</tr>
<tr>
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<td>3.02-50.00</td>
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<tr>
<td>no. of measured reflns</td>
<td>18273</td>
<td>27791</td>
</tr>
<tr>
<td>( R(\text{int}) )</td>
<td>0.0274</td>
<td>0.0444</td>
</tr>
<tr>
<td>Ind. reflns / ind. reflns (( I &gt; 2\sigma(I) ))</td>
<td>8325/7287</td>
<td>9038/6567</td>
</tr>
<tr>
<td>no. of parameters</td>
<td>489</td>
<td>568</td>
</tr>
<tr>
<td>( R_1 (I &gt; 2\sigma(I)) / wR_2 ) (all data)</td>
<td>0.0332/0.0799</td>
<td>0.0276/0.0490</td>
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<tr>
<td>( S ) (all data)</td>
<td>1.167</td>
<td>0.999</td>
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<tr>
<td>largest diff. peak/hole /e(^{-1}\cdot\text{Å}^{-3} )</td>
<td>1.374/-1.028</td>
<td>1.475/-0.925</td>
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Figure S1 Molecular structure of 1·1.1MeOH·1.9H₂O with atom labeling scheme. Thermal ellipsoids have been drawn at the 40% probability level and H atoms are denoted as spheres of arbitrary radius. The disordered part is shown with dashed lines.
Figure S2 Molecular structure of 3·2THF with atom labeling scheme. Thermal ellipsoids have been drawn at the 40% probability level. (a) The C atoms of the PPh₂Me ligand and THF molecules are not labeled. The unlabeled part is generated with the symmetry operation \([i] \cdot -x+1, -y+1, -z+1\). H atoms are omitted for clarity. (b) The phenyl rings and methyl group of the PPh₂Me ligand and THF molecules are not drawn. (c) The organic moieties are not drawn. (d) Hydrogen-bonded chains in 3, extending along [001]. Hydrogen bonds are denoted with dashed lines. Only relevant atoms are shown for clarity.
Table S2  Selected bond lengths, bond angles [Å, °] in 1·1.1MeOH·1.9H2O.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Bond Angles</th>
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<tr>
<td>S5-Sn3</td>
<td>2.4057(14)</td>
</tr>
<tr>
<td>S5-Sn4</td>
<td>2.4059(13)</td>
</tr>
<tr>
<td>S6-Sn3</td>
<td>2.4340(13)</td>
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<td>S6-Sn4</td>
<td>2.4425(14)</td>
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<td>S3-Sn3</td>
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<tr>
<td>S3-Sn2</td>
<td>2.4502(13)</td>
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<tr>
<td>S4-Sn4</td>
<td>2.4046(13)</td>
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<td>S2-Sn2</td>
<td>2.4476(13)</td>
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<td>S2-Sn1</td>
<td>2.4566(14)</td>
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<td>Sn4-C1</td>
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<td>Sn3-C7</td>
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<td>Sn2-C13</td>
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<td>Sn2-N8</td>
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<td>N1-N2</td>
<td>1.394(6)</td>
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<td>N2-H2</td>
<td>0.89(2)</td>
</tr>
<tr>
<td>N3-N4</td>
<td>1.401(5)</td>
</tr>
<tr>
<td>N3-H3</td>
<td>0.896(19)</td>
</tr>
<tr>
<td>N5-N6</td>
<td>1.391(6)</td>
</tr>
<tr>
<td>N6-H6</td>
<td>0.91(2)</td>
</tr>
<tr>
<td>N7-N8</td>
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</tr>
<tr>
<td>N7-H7</td>
<td>0.901(19)</td>
</tr>
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<tr>
<td>Sn3-S6-Sn4</td>
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<tr>
<td>Sn3-S3-Sn2</td>
<td>108.64(5)</td>
</tr>
<tr>
<td>Sn4-S4-Sn1</td>
<td>109.54(5)</td>
</tr>
<tr>
<td>Sn2-S1-Sn1</td>
<td>87.73(4)</td>
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Table S3  Hydrogen bonding parameters [Å, °] in 1·1.1MeOH·1.9H2O. Symmetry code: (i) -x+2, -y, -z+1.

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<tr>
<th>D–H···A</th>
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<th>H···A</th>
<th>D···A</th>
<th>D–H···A</th>
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<tr>
<td>N2–H2···O2'</td>
<td>0.89</td>
<td>2.09</td>
<td>2.953(6)</td>
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</tr>
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<td>N3–H3···S4</td>
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<td>N7–H7···N5</td>
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<tr>
<td>O1M–H11M···S5</td>
<td>0.87</td>
<td>2.40</td>
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</table>
Table S4 Selected bond lengths, bond angles [Å, °] in 3·2THF. Symmetry codes: (i) -x+1, -y+1, -z+1.

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<th>Bond/Angle</th>
<th>Distance</th>
<th>Symmetry Code</th>
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<td>C11-Sn1</td>
<td>2.205(3)</td>
<td>Sn2-S3-Sn1 i</td>
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<td>N1-N2</td>
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<td>N3-N4</td>
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<td>Cu2-S4-Sn2</td>
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<td>N4-Sn1</td>
<td>2.505(5)</td>
<td>Sn1-S4-Sn2</td>
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<td>S1-Cu1</td>
<td>2.2340(12)</td>
<td>P1-Cu1-S1</td>
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<td>P1-Cu1-S2</td>
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<td>S2-Cu1</td>
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<td>S1-Cu1-S2</td>
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<td>S2-Cu2</td>
<td>2.2945(11)</td>
<td>P2-Cu2-S2</td>
</tr>
<tr>
<td>S2-Sn1</td>
<td>2.3628(10)</td>
<td>P2-Cu2-S3</td>
</tr>
<tr>
<td>S3-Cu2</td>
<td>2.4116(12)</td>
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</tr>
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<td>S3-Sn2</td>
<td>2.4218(10)</td>
<td>P2-Cu2-S4 i</td>
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<td>S3-Sn1 i</td>
<td>2.5427(11)</td>
<td>S2-Cu2-S4 i</td>
</tr>
<tr>
<td>S4-Cu2 i</td>
<td>2.4268(11)</td>
<td>S3-Cu2-S4 i</td>
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<td>S4-Sn1</td>
<td>2.4410(11)</td>
<td>C11-Sn1-S2</td>
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<td>2.4423(10)</td>
<td>C11-Sn1-S4</td>
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<td>Cu2-S3-Sn2</td>
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<td></td>
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Table S5 Hydrogen bonding parameters [Å, °] in 3·2THF. Symmetry code: (i) -x+2, -y+1, -z+1.

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>D–H</th>
<th>H···A</th>
<th>D···A</th>
<th>D–H···A</th>
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<tbody>
<tr>
<td>N2–H2N–O1 i</td>
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<td>N3–H3N–S1</td>
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<td>2.48</td>
<td>3.300(3)</td>
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S9
**ESI-MS spectra of 1 and 2**

Mass spectrometry (MS) was performed using a Finnigan MAT 95S. Electron Stoss Ionisation (ITMS-ESI) spectra were obtained by using solvent as the carrier gas.

**Figure S3** High resolution image of the mass spectrometry peaks corresponding to \([\text{R}^2\text{Sn}_2\text{]}\text{(\text{\mu-S})}_6\) (1), m/z: 1172.84 (M+1), \(M = C_{26}H_{48}N_8O_2S_6Sn_4\). The calculated isotope distribution pattern is shown below the measured peak.
Figure S4 High resolution image of the mass spectrometry peaks corresponding to Na$_2$[R$^\text{3}$SnS$_2$(μ-S)$_2$] (2), m/z: 662.85 (M–1), M = C$_{13}$H$_{24}$N$_4$O$_1$S$_4$Sn$_2$Na$_2$. The calculated isotope distribution pattern is shown below the measured peak.
References

