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

Mohammad Reza Halvagar, Zohreh Hassanzadeh Fard and Stefanie Dehnen*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany

email: dehnen@chemie.uni-marburg.de

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} mbar) for several hours. [$CuCl(PPh_2Me)_3$] and [$(R^1Sn)_4(\mu\text{-}S)_6$] ($R^1$ = CMe_2CH_2COMe) was prepared according to the reported methods.[1,2] $Na_2S\cdot9H_2O$ and carbohydrazide were purchased from Aldrich and used as received. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR measurements were carried out using a Bruker DRX 400 MHz spectrometer at 25ºC. In ^{1}H and ^{13}C NMR, the chemical shifts were quoted in ppm relative to the residual protons of deuterated solvents. In ^{31}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 $[(R^NSn_2)_2(\mu\text{-}S)_6]\cdot1.1MeOH\cdot1.9H_2O$, [**1**$\cdot1.1MeOH\cdot1.9H_2O$, R^N = $(CMe_2CH_2CMeNNH)_2CO$]:

[$(R^1Sn)_4(\mu\text{-}S)_6$] (0.05 g, 0.047 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}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.36 (br, 24H; Me_2C), 2.20 (br, 12H; Me), 2.77 (br, 8H; CH_2), 6.11 ppm (br, 4H; NH); ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 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), 1327 (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), 2913 (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 $[R^N_2\{Sn(\mu\text{-}S)_2Cu(PPh_2Me)\}_4]\cdot 2THF$*, (***3***·2THF)*:

Treatment of a solution of compound **1** (0.092 g, 0.075 mmol) in THF (10 mL) with a solution of $Na_2S\cdot 9H_2O$ (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 $[CuCl(PPh_2Me)_3]$ (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, $CDCl_3$, 25°C): δ = 1.10 (br, 8H; CH_2), 1.28 (br, 24H; Me and PMe)*, 1.63 (br, 24H; Me_2C), 7.30–7.43 ppm (br, 40H; Ar); ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 12.76 (PMe), 22.75 (Me_2), 32.00 (Me), 37.33 (CSn), 47.70 (CH_2), 128.35, 128.48, 132.15, 134.99 (Ar), 140.1 ppm (C=N), (C=O not verified); ^{31}P NMR (162 MHz, $CDCl_3$, 25°C): δ = −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 CH_3 protons of the organic arms gets obscured by the CH_3 protons of the PPh_2Me 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 MoKa 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.[3] 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.

Compound	**1**·1.1MeOH·1.9H$_2$O	**3**·2THF
empirical formula	$C_{27.1}H_{56.2}N_8O_5S_6Sn_4$	$C_{86}H_{116}Cu_4N_8O_4P_4S_8Sn_4$
fw /g·mol^{-1}	1241.26	2435.15
crystal color and shape	colorless cube	Yellow plate
crystal size /mm^3	0.19×0.13×0.08	0.38×0.08×0.07
radiation (λ /Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a /Å	11.614(2)	13.875(3)
b /Å	25.211(5)	20.617(4)
c /Å	16.472(3)	17.955(4)
β /deg	96.01(3)	93.05(3)
V /Å^3	4796.6(17)	5128.9(18)
Z	4	2
ρ_{calcd} /g·cm^{-3}	1.719	1.624
μ(Mo Kα) /mm^{-1}	2.360	2.047
abs correction type	numerical	numerical
min/max transmission	0.6627/0.8410	0.5101/0.8700
2θ range /deg	9.50-50.00	3.02-50.00
no. of measured reflns	18273	27791
R(int)	0.0274	0.0444
Ind. reflns / ind. reflns ($I > 2\sigma(I)$)	8325/7287	9038/6567
no. of parameters	489	568
R_1 ($I > 2\sigma(I)$) / wR_2 (all data)	0.0332/0.0799	0.0276/0.0490
S (all data)	1.167	0.999
largest diff. peak/hole /e$^-$·Å^{-3}	1.374/-1.028	1.475/-0.925

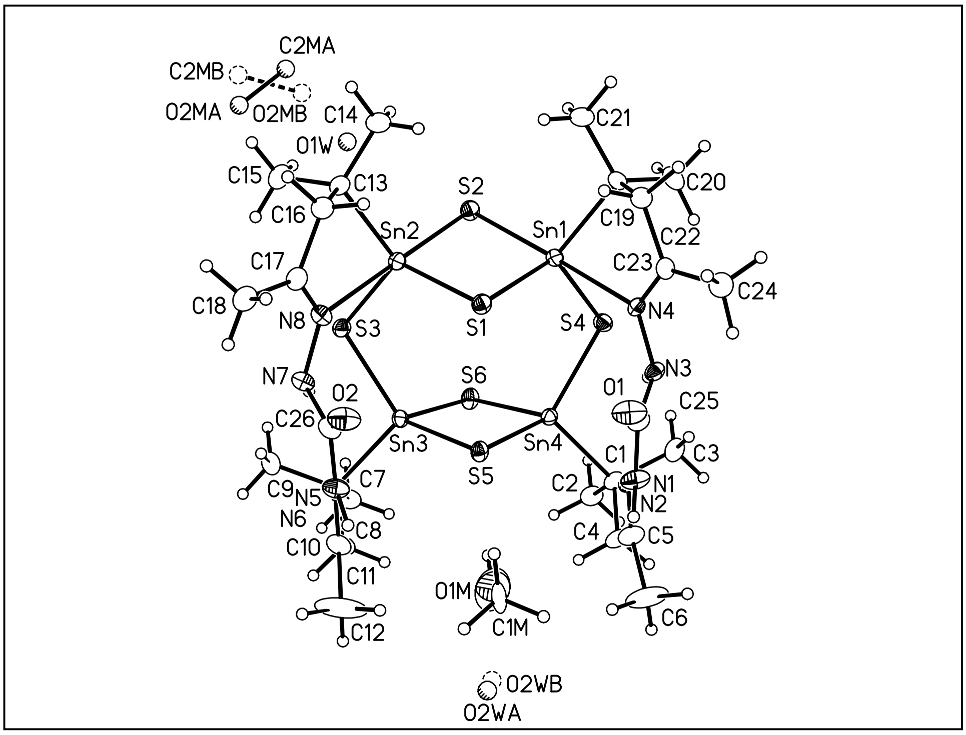
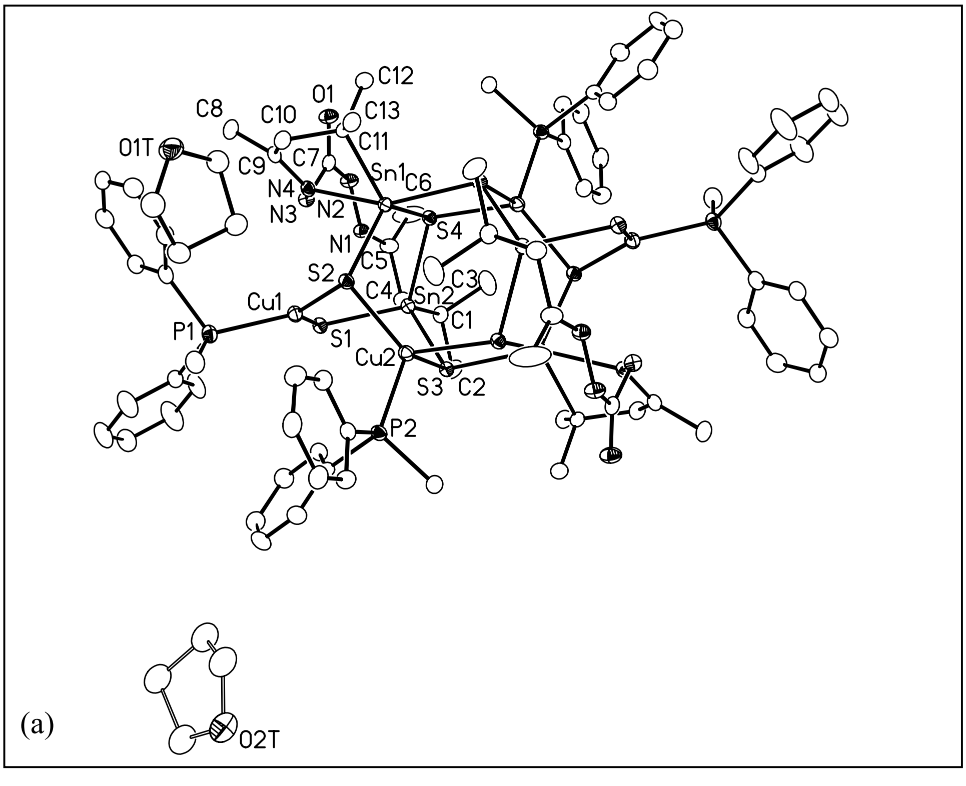
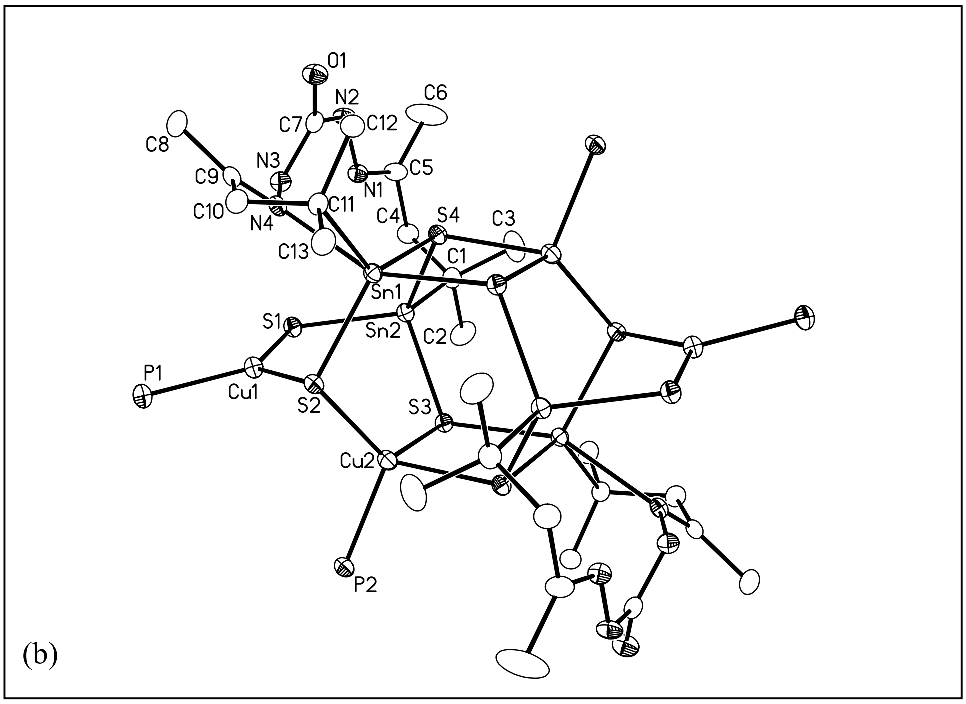
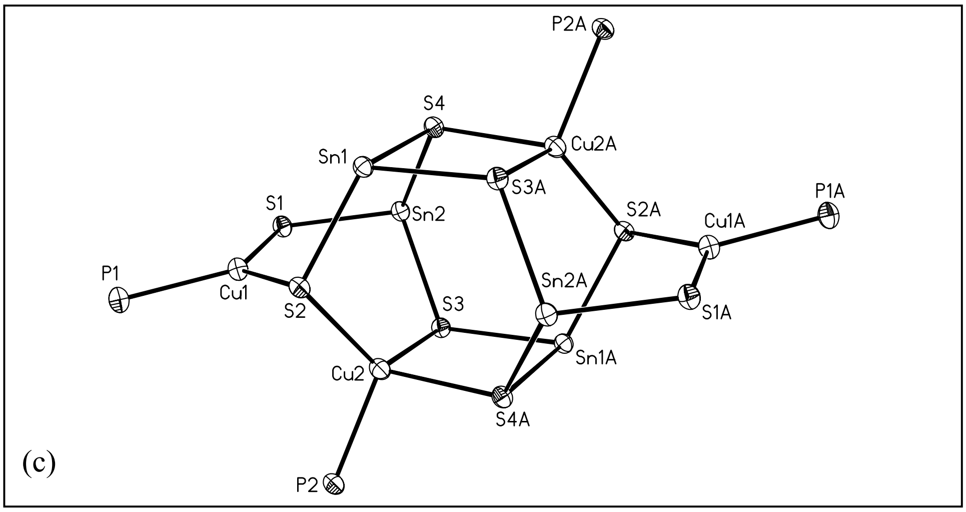


Figure S1 Molecular structure of **1**·1.1MeOH·1.9H$_2$O with atom labeling scheme. Thermal ellipsoids have been drawn at the 40% probability level and H atoms are denoted as spheres of arbitrary radius. The disordered part is shown with dashed lines.




O1
N2
C6
C7
C12
C8
N3
C5
C9
N1
C10
C11
N4
C4
S4
C3
C13
C1
Sn1
S1
Sn2
C2
P1
Cu1
S2
S3
Cu2
P2
(b)


P2A
S4
Cu2A
Sn1
S3A
S1
Sn2
S2A
P1A
Cu1A
P1
Cu1
S2
Sn2A
S3
S1A
Sn1A
Cu2
S4A
(c)
P2

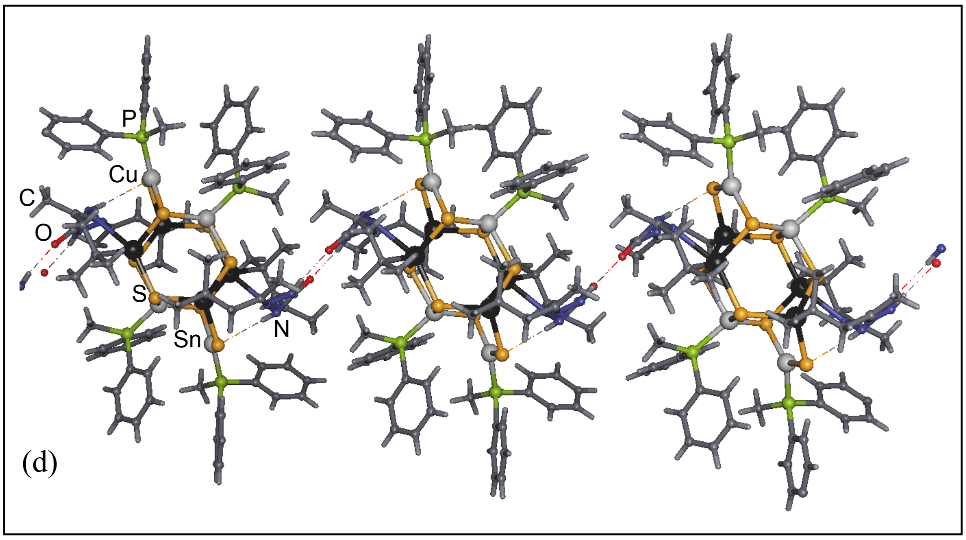


Figure S2 Molecular structure of **3**·2THF with atom labeling scheme. Thermal ellipsoids have been drawn at the 40% probability level. (a) The C atoms of the PPh_2Me ligand and THF molecules are not labeled. The unlabeled part is generated with the symmetry operation [i] -*x*+1, -*y*+1, -*z*+1. H atoms are omitted for clarity. (b) The phenyl rings and methyl group of the PPh_2Me 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 $\mathbf{1}\cdot1.1\mathrm{MeOH}\cdot1.9\mathrm{H_2O}$.

S5-Sn3	2.4057(14)	Sn2-S2-Sn1	86.00(4)
S5-Sn4	2.4059(13)	C1-Sn4-S4	106.49(14)
S6-Sn3	2.4340(13)	C1-Sn4-S5	118.31(14)
S6-Sn4	2.4425(14)	S4-Sn4-S5	118.70(4)
S3-Sn3	2.4048(12)	C1-Sn4-S6	111.15(13)
S3-Sn2	2.4502(13)	S4-Sn4-S6	107.52(5)
S4-Sn4	2.4046(13)	S5-Sn4-S6	93.50(4)
S4-Sn1	2.4472(13)	C7-Sn3-S3	106.33(13)
S1-Sn2	2.4080(14)	C7-Sn3-S5	116.53(13)
S1-Sn1	2.4184(13)	S3-Sn3-S5	119.38(4)
S2-Sn2	2.4476(13)	C7-Sn3-S6	110.61(14)
S2-Sn1	2.4566(14)	S3-Sn3-S6	109.47(5)
Sn4-C1	2.197(4)	S5-Sn3-S6	93.72(4)
Sn3-C7	2.191(5)	C13-Sn2-S1	112.73(15)
Sn2-C13	2.187(5)	C13-Sn2-S2	107.56(14)
Sn2-N8	2.451(4)	S1-Sn2-S2	93.27(4)
Sn1-C19	2.191(5)	C13-Sn2-S3	116.12(14)
Sn1-N4	2.420(4)	S1-Sn2-S3	120.86(5)
N1-N2	1.394(6)	S2-Sn2-S3	101.67(4)
N2-H2	0.89(2)	C13-Sn2-N8	72.50(16)
N3-N4	1.401(5)	S1-Sn2-N8	85.24(10)
N3-H3	0.896(19)	S2-Sn2-N8	178.38(10)
N5-N6	1.391(6)	S3-Sn2-N8	79.67(10)
N6-H6	0.91(2)	C19-Sn1-S1	116.12(14)
N7-N8	1.413(6)	C19-Sn1-N4	72.58(16)
N7-H7	0.901(19)	S1-Sn1-N4	82.71(10)
		C19-Sn1-S4	112.67(14)
Sn3-S5-Sn4	86.61(4)	S1-Sn1-S4	120.46(4)
Sn3-S6-Sn4	85.18(4)	N4-Sn1-S4	81.26(10)
Sn3-S3-Sn2	108.64(5)	C19-Sn1-S2	107.87(14)
Sn4-S4-Sn1	109.54(5)	S1-Sn1-S2	92.79(4)
Sn2-S1-Sn1	87.73(4)	N4-Sn1-S2	175.06(10)
		S4-Sn1-S2	102.86(5)

Table S3 Hydrogen bonding parameters [Å, °] in $\mathbf{1}\cdot1.1\mathrm{MeOH}\cdot1.9\mathrm{H_2O}$. Symmetry code: (i) *-x*+2, *-y*, *-z*+1.

D–H···A	D–H	H···A	D···A	D–H···A
N2–H2···O2^{i}	0.89	2.09	2.953(6)	162
N3–H3···S4	0.896	2.52	3.265(4)	141
N6–H6···O1^{i}	0.91	2.07	2.948(6)	161
N7–H7···N5	0.901	2.18	2.638(6)	111
N7–H7···S3	0.901	2.57	3.261(4)	133
O1M–H11M···S5	0.87	2.40	3.241(7)	165

Table S4 Selected bond lengths, bond angles [Å, °] in **3**·2THF. Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1.

C11-Sn1	2.205(3)	Sn2-S3-Sn1^{i}	117.79(4)
N1-N2	1.381(4)	Cu2^{i}-S4-Sn1	93.13(4)
N3-N4	1.409(4)	Cu2^{i}-S4-Sn2	116.26(4)
N4-Sn1	2.505(3)	Sn1-S4-Sn2	104.54(4)
S1-Cu1	2.2340(12)	P1-Cu1-S1	116.98(4)
S1-Sn2	2.3398(11)	P1-Cu1-S2	115.53(4)
S2-Cu1	2.2683(11)	S1-Cu1-S2	127.49(4)
S2-Cu2	2.2945(11)	P2-Cu2-S2	114.22(4)
S2-Sn1	2.3628(10)	P2-Cu2-S3	111.47(4)
S3-Cu2	2.4116(12)	S2-Cu2-S3	120.21(4)
S3-Sn2	2.4218(10)	P2-Cu2-S4^{i}	101.54(4)
S3-Sn1^{i}	2.5427(11)	S2-Cu2-S4^{i}	116.08(4)
S4-Cu2^{i}	2.4268(11)	S3-Cu2-S4^{i}	89.41(4)
S4-Sn1	2.4410(11)	C11-Sn1-S2	108.44(10)
S4-Sn2	2.4423(10)	C11-Sn1-S4	127.70(10)
Cu1-P1	2.2248(12)	S2-Sn1-S4	118.96(4)
Cu2-P2	2.2488(11)	C11-Sn1-N4	72.65(12)
Cu2-S4^{i}	2.4268(11)	S2-Sn1-N4	95.33(7)
Sn1-S3^{i}	2.5427(11)	S4-Sn1-N4	81.87(7)
		C11-Sn1-S3^{i}	96.79(10)
C9-N4-Sn1	111.8(2)	S2-Sn1-S3^{i}	111.26(3)
N3-N4-Sn1	127.6(2)	S4-Sn1-S3^{i}	86.12(3)
Cu1-S1-Sn2	104.46(4)	N4-Sn1-S3^{i}	153.39(7)
Cu1-S2-Cu2	91.54(4)	C1-Sn2-S1	114.11(10)
Cu1-S2-Sn1	101.44(4)	C1-Sn2-S3	110.11(9)
Cu2-S2-Sn1	108.71(4)	S1-Sn2-S3	102.91(3)
Cu2-S3-Sn2	105.45(4)	C1-Sn2-S4	106.00(10)
Cu2-S3-Sn1^{i}	90.99(4)	S1-Sn2-S4	114.12(3)
		S3-Sn2-S4	109.58(4)

Table S5 Hydrogen bonding parameters [Å, °] in **3**·2THF. Symmetry code: (i) -*x*+2, -*y*+1, -*z*+1.

D–H···A	D–H	H···A	D···A	D–H···A
N2–H2N···O1^{i}	0.895	1.99	2.856(4)	163
N3–H3N···S1	0.889	2.48	3.300(3)	153

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.

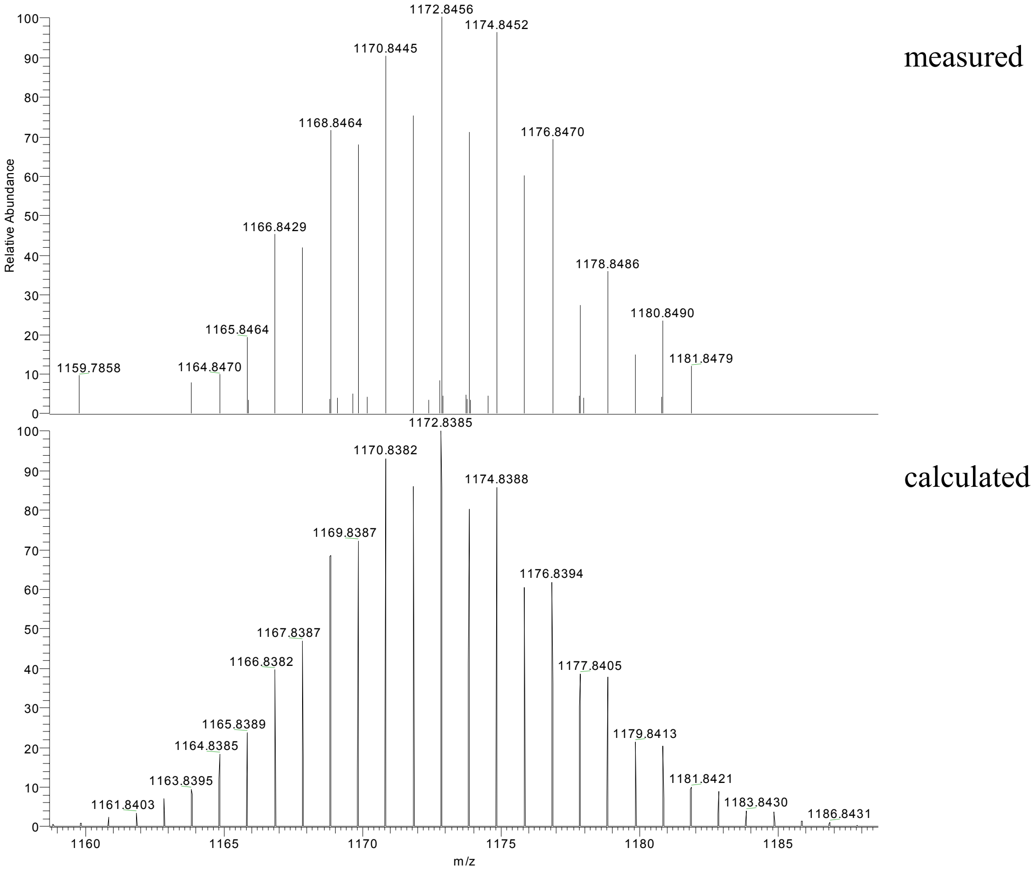


Figure S3 High resolution image of the mass spectrometry peaks corresponding to $[(R^{N}Sn_2)_2(\mu\text{-}S)_6]$ (**1**), m/z: 1172.84 $(M+1)^+$, M = $C_{26}H_{48}N_8O_2S_6Sn_4$. The calculated isotope distribution pattern is shown below the measured peak.

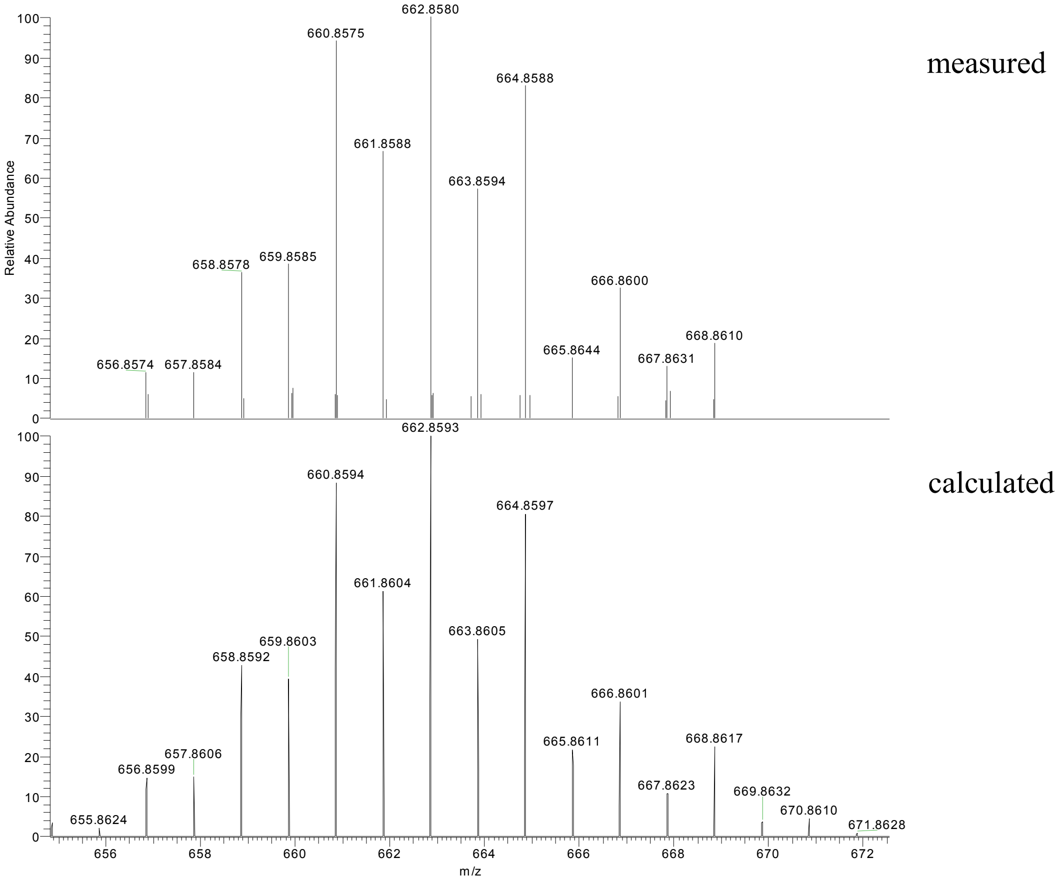


Figure S4 High resolution image of the mass spectrometry peaks corresponding to $Na_2[R^N(SnS)_2(\mu\text{-}S)_2]$ (**2**), m/z: 662.85 (M–1), M = $C_{13}H_{24}N_4O_1S_4Sn_2Na_2$. The calculated isotope distribution pattern is shown below the measured peak.

References

[1] D. J. Fife, W. M. Moore, and K. W. Morse, *Inorg. Chem*. 1984, **23**, 1684.

[2] Z. Hassanzadeh Fard, L. Xiong, C. Müller, M. Holyńska, and S. Dehnen, *Chem. Eur. J.*, 2009, **15**, 6595.

[3] G. M. Sheldrick, SHELXTL 5.1, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719–1173, USA, 1997.