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Directed Formation of an Organotin Sulfide Cavitand and Its Transformation into a Rugby-Ball-like Capsule

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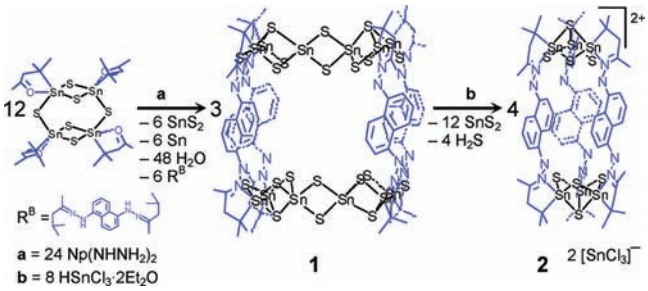
The formation of discrete macrocyclic organotransition-metal complexes has become a regular feature in the literature.[1] However, relatively little is known about the respective architectures created by main-group elements. This holds particularly for organotin compounds. Exceptions are rare and mentioned mainly for organostannoxane-type complexes,[2] the preparation of which is often hampered both by their tendency to grow into oligomers or polymers and by problems associated with their pure isolation.[3] The replacement of oxide by chalcogenide ligands decreases the polymerization tendency. Furthermore, such ensembles might exhibit multifaceted properties in addition to their structural diversity, such as microporosity, catalytic activity, or semiconductivity.[4−6]

One of our current aims is to find a directed approach toward organodecorated chalcogenidometallate clusters to produce molecular hybrid containers. Therefore, we have extended our recent studies on the synthesis and reactivity of a new class of functionalized chalcogenidometallate cages of the general type $[(RT)_4(\mu\text{-}E)_6]$ (R: R^1 = CMe_2CH_2COMe, R^2 = CH_2CH_2COOH; T = Ge, Sn; E = S)[7,8] toward larger aggregates through the use of bifunctional organic reagents. Herein, we report the systematic and effective synthesis and thorough characterization of an organotin sulfide cavitand and its unique transformation into a rugby-ball-like capsule in high yield under acidic conditions.

Treatment of $[(R^1Sn)_4(\mu\text{-}S)_6]$ with 2 equiv of 1,1′-(1,5-naphthalenediyl)bishydrazine in a 1:1 $CHCl_3$/DMF mixture at room temperature afforded $[R^B_4Sn_{12}S_{20}]\cdot 4DMF\cdot 3CHCl_3\cdot H_2O$ (**1**·4DMF·$3CHCl_3$·H_2O) in 59% yield. Subsequent addition of $HSnCl_3\cdot 2Et_2O$ followed by stirring for 0.5 h resulted in the in situ generation of $[R^B_3Sn_6S_8][(SnCl_3)_2]\cdot 3DMF\cdot 1.5H_2O$ (**2**·3DMF·$1.5H_2O$) in 80% yield (Scheme 1).

Scheme 1. Stepwise Syntheses of Compounds **1** and **2**



1 and **2** were characterized by single-crystal X-ray diffraction[9,10] (Figure 1) and spectroscopic analyses (see the Supporting Information). Both compounds comprise discrete molecules representing either a neutral cavitand (**1**) or a cationic capsule (**2**). The inorganic components of **1** and **2** are based on $[Sn_3S_4]$ defect heterocubane building units that are linked by 1,5-bis[(*E*)-2-(4-methylpentan-2-ylidene)hydrazinyl]naphthalene organic spacers (R^B).

In the structure of the cavitand **1**, each pair of $[Sn_3S_4]$ units is further linked by two μ-S bridges to form larger $[Sn_6S_{10}]$ clusters. Two $[Sn_6S_{10}]$ moieties are then bridged by four R^B spacers, resulting in the hybrid architecture. While the uncommon $[Sn_6S_{10}]$ thiostannate motif was also observed upon reaction of $[(R^1Sn)_4(\mu\text{-}S)_6]$ with phenylhydrazine, the reaction with hydrazine hydrate did not lead to any rearrangement of the Sn/S topology.[8] Hence, if R^B is regarded as a "doubled" $PhNHNH_2$, the result indicates a coherence between the steric demand of the organic group and the topology of the inorganic Sn/S skeleton.

The cationic part of **2** is constructed from two of the $[Sn_3S_4]$ building units that are bridged by three organic spacers R^B to form an unprecedented capsule that is accompanied by two $[SnCl_3]^-$ counteranions. As in **1**, the connection of the R^B groups to the inorganic units comprises one covalent Sn−C bond and one intramolecular N → Sn Lewis base−Lewis acid interaction at each of the Sn atoms, resulting in an Sn−C_3−N five-membered ring.

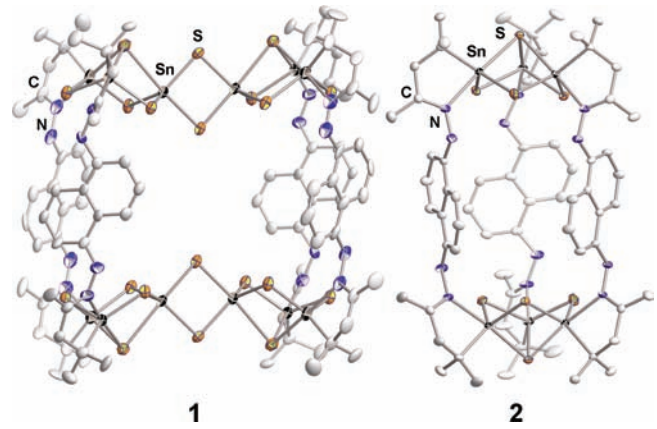


Figure 1. Molecular structures of compounds **1** and **2**. Hydrogen atoms and solvent and counterion molecules ($CHCl_3$, DMF, H_2O, $[SnCl_3]^-$) have been omitted for clarity. Thermal ellipsoids have been drawn at the 40% probability level.

As known for group-14 chalcogenidometallates, the pH controls the generation of particular cluster types.[7b,11] Here, lowering the pH of a solution of **1** initiates partial destruction of the $[Sn_6S_{10}]$ units involving the unshielded central $Sn_2(\mu\text{-}S)_2$ ring and adjacent S ligands, as can be inferred by analysis of the byproducts H_2S and SnS_2. Subsequently, the to date unknown intermediates are linked to form the capsule in **2**. Further preliminary investigations showed that the use of different protic acids (e.g., H_2SO_4, $HClO_4$, etc.) afforded the same structural motif as observed in compound **2** with different counteranions.

Positive-ion electrospray ionization mass spectrometry (ESI-MS) of a methanol solution of **2** shows an intense signal at *m*/*z* 1010.0, corresponding to the cation $[C_{66}H_{90}N_{12}S_8Sn_6]^{2+}$, which confirms that the capsule remains intact in the solution and even upon release

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of the encapsulated solvent molecule under ESI-MS conditions. This is of considerable interest for future investigations regarding molecular recognition by chalcogenidometallate organic hybrid compounds. First hints toward uptake of guest molecules as well as possible bond activation upon molecular embedding are given by the situation of the encapsulated solvent molecules.

Both compounds show specific host−guest interactions. Cavitand **1** hosts four DMF molecules within its cavity, whereas $CHCl_3$ molecules are located outside. In compound **2**, one of the three DMF molecules is encapsulated within the cationic capsule. Accordingly, the solid-state IR spectrum of **2** shows two different DMF carbonyl bands (1647.4 and 1658.1 cm^{-1}), confirming that at least one DMF molecule is in a different environment than the other two on the IR time scale.[12] The inclusion of DMF molecules within **1** and **2** involves two types of hydrogen bonding (Figure 2): first, C−H···π interactions between N−Me groups of the guest DMF and the aromatic walls, e.g., C01−H01···π (C···$\pi_{centroid}$ distance 3.7−3.8 Å),[13] and second, a bifurcated hydrogen bond[14] between a DMF oxygen atom and two adjacent hydrogen atoms of a hydrazone group, e.g., N4−H4···O1···H2−N2 in **1** and N2−H1···O1···H4−N4 in **2** [N···O distance 3.124(9)−3.146(9) Å].

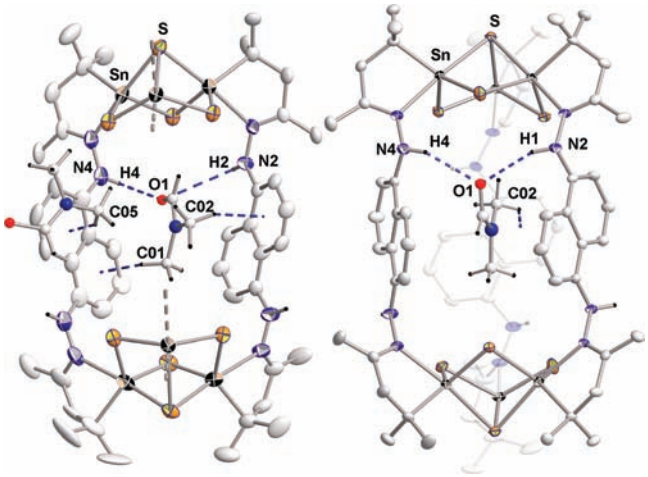

Figure 2. Hydrogen-bonding situations within (left) cavitand **1** and (right) capsule **2**. In **1**, only the asymmetric unit of the molecular structure (i.e., half of the cavitand) is shown; the continuation of the structure is indicated by dashed lines. Hydrogen atoms (except those of DMF molecules and hydrazone groups), solvent molecules outside the cavities, and counterions have been omitted. Thermal ellipsoids have been drawn at the 40% probability level.

The simultaneous donation of two hydrogen bonds in both compounds is reminiscent of the catalytic active site of urea/thiourea-based compounds, which are of considerable importance for the activation of proton acceptor substrates.[15] In view of the cavity sizes in **1** (402 $Å^3$) and **2** (134 $Å^3$)[16] and their stability in solution, these hydrogen-bonding endo-receptor compounds may enable the replacement of the DMF molecules by other guest substrates that complement the template in size, shape, and chemical functionalities.[17,18]

In conclusion, we have presented a directed and efficient synthetic procedure for the generation of an organotin sulfide cavitand that undergoes a unique transformation into a stable, rugby-ball-like capsule upon addition of protic acids. Further investigations to explore the catalytic activity of these compounds are currently underway.

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Supporting Information Available: Experimental details and spectroscopic data and CIF files for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Data were collected on diffractometer equipped with a STOE imaging plate detector system (IPDS2T) using Mo Kα radiation with graphite monochromatization ($\lambda = 0.71073$ Å) at 100 K. Structure solution was performed by direct methods with full-matrix least-squares refinement against F^2 using SHELXS-97 and SHELXL-97 software.[10] $[R^B_4Sn_{12}S_{20}]\cdot 4DMF\cdot 3CHCl_3\cdot H_2O$ (**1**·4DMF·3$CHCl_3$·H_2O): triclinic; $P\bar{1}$; $a, b, c = 15.727(3), 16.547(3), 18.515(4)$ Å; $\alpha, \beta, \gamma = 90.84(3), 92.62(3), 117.68(3)°$; $V = 4259.3(15)$ $Å^3$; $Z = 1$; R1 = 0.0749 [$I > 2\sigma(I)$], wR2 = 0.1691 (all data); GOF = 0.756. $[R^B_3Sn_6S_8][(SnCl_3)_2]\cdot 3DMF\cdot 1.5H_2O$ (**2**·3DMF·1.5H_2O): monoclinic; $P2_1/c$; $a, b, c = 19.434(4), 28.124(6), 19.367(4)$ Å; $\beta = 103.00(3)°$; $V = 10314(4)$ $Å^3$; $Z = 4$; R1 = 0.0470 [$I > 2\sigma(I)$], wR2 = 0.1157 (all data); GOF = 1.169.

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