The synthesis, properties and reactivity of group 11 organotin sulfide clusters \([ (R^1Sn)^4(SnCl)_2(CuPPh_3)_2S_8] \) (M = Cu, Ag), \([ (R^2Sn)_4(AgPPh_3)_4S_12] \) and \([ (R^3Sn)_4(AuPPh_3)_4S_4] \) with covalently bound, carbonyl or hydrazine-terminated ligands \( R^1 = CMe_2CH2C(Me)O \) or \( R^3 = CMe_2CH2C(Me)NNH_2 \) are reported.

The last few decades have afforded a large variety of ligand-protected chalcogenide clusters of group 11 metals. Ternary complexes and clusters were also reported, which often combined structural and physical properties of the binary components. Additionally, with regard to further reactivity, the introduction of functionalized phosphines was achieved. Consequently, the combination of functional organic ligand shells with finely tunable (ternary or multinary) inorganic cores, providing even more diversity, is thus of interest for diverse purposes, such as for optoelectronics or solar cell development. To address suitable functional materials, the synthesis and directed derivatization of clusters with covalently attached organic groups have currently been investigated in detail for polyoxometalates as well as for group 14/16 compounds, for instance.

The organic groups on the periphery of organogermanium and organotin sulfide complexes of the general type \([ (R^1T)_4(SnCl)_2(CuPPh_3)_2S_8] \) \((R^1 = functionalized organic ligand; R^T = CMe_2CH_2C(Me)O, HR^2 = C_2H_4COOH; T = Ge, Sn; x/y = 4/6, 6/10)\) are reactive towards hydrazine derivatives, which allowed further derivatizations of the organic ligand shell. Hereby, an extension of the ligand shell towards ligands such as \( R^3 = CMe_2CH_2C(Me)NNH_2, R^4 = \{CMe_2CH_2C(Me)NNH_2\}_2CO, \) or \( R^5 = CMe_2CH_2C(Me)NNC(2-py)_2 \) was achieved. Reactions with transition metal compounds additionally enabled the extension of the inorganic core to form the organofunctionalized ternary clusters \([ (R^2T)_2(CuPR_3)_4S_8] \), \([ (R^3Sn)_4(OMe)_4CuS_4] \), \([ (R^4Ge)_{12}PdS_{12}] \) and \([ (R^5Sn)_{12}Ag_{10}S_{20}] \). Bispyridine-decorated clusters \([ (R^3Sn)_4(ZnX)_4S_8] \) (\( X = \text{Cl}, \text{Br}, \text{I} \)) were obtained by slow diffusion of zinc halide solutions into solutions of the organotin sulfide cluster \([ (R^3Sn)_{10}] \). Further structurally characterized ternary group 11 metal/organotin sulfide clusters have so far been surrounded by unreactive organic groups, as in \([ (R^3Sn)_4(CuPPh_3)_4S_8] \), \([ (R^4Sn)_2Cu(PPh_3)_6SnIICu_4S_{12}] \), and the mixed-valence compound \([ (CH_2)_8Sn^{IV}_6(CuPPh_3)_3Sn^{II}_2Cu_4S_{12}] \). Ternary complexes containing Ag/Sn/S or Au/Sn/S cores have not been characterized yet using X-ray diffraction.‡

Recently we reported new functional organotin sulfide complexes of the type \([ (R^1,3Sn)_4S_4Cl] \) that exhibit defect heterocubane scaffolds with carbonyl and hydrazine groups. Herein, we show that these turned out to be suitable precursor complexes as well. \([ (R^1Sn)_4S_4Cl] \) (A) reacts with the group 11 metal complexes \([ Cu(PPh_3)_3Cl] \), \([ Ag(PPh_3)_3Cl] \) and \([ Au(PPh_3)_3Cl] \) in \( CH_2Cl_2 \) with \( (Me_3Si)_2S \), in the case of Ag and Au complexes with subsequent in situ derivatization by hydrazine hydrate (Scheme 1), to yield single crystals of the following compounds comprising ternary clusters \([ (R^1Sn)_4S_4Cl]_2(CuPPh_3)_2S_8] \), \([ (R^1Sn)_4S_4Cl]_2(1.4CH_2Cl_2) \), \([ (R^1Sn)_4S_4Cl]_2 (Me_3Si)_2S \) (hereafter denoted as 1), \([ (R^2Sn)_4(SnCl)_4Cu(PPh_3)_2S_8] \), \([ (R^3Sn)_4(SnCl)_4Cu(PPh_3)_2S_8] \) and \([ (R^4Sn)_4(SnCl)_4Cu(PPh_3)_2S_8] \) (3). The clusters exhibit

![Scheme 1 Synthesis of compounds 1–6](image)

\( R^1 = CMe_2CH_2C(Me)O, R^2 = CMe_2CH_2C(Me)NNH_2 \)
The observation of formal Sn$^{II}$ and Sn$^{IV}$ atoms is in agreement with natural charges, obtained by natural population analyses (NPA)\(^\text{18}\) of the DFT wave function, which was calculated by simultaneous optimization of the geometric and electronic structure using the program system TURBOMOLE.\(^\text{19}\) The formal Sn$^{IV}$ atoms exhibit charges of +1.38 and +1.47, which are larger than the +0.88 charge calculated for the formal Sn$^{II}$ atoms by a factor of 1.6 to 1.7. Details of the DFT calculations are provided in the ESI.\(^\dagger\)

Neither variation of the stoichiometry of the starting materials nor attempts to replace the Cl$^{-}$ ligand have led to the isolation of further clusters until now. An analogous reaction with 1.0 eq. [Cu(PPh$_3$)$_2$Cl]$_2$, however, yielded 1[[R$^{5}$Sn]$^2$S$_2$] (2). The structural parameters of the two large co-crystallizing clusters in 2 are similar to those observed in 1·4 CH$_2$Cl$_2$ (see ESI) and [[R$^{5}$Sn]$^2$S$_2$].\(^\text{20}\)

Upon reaction with [Ag(PPh$_3$)$_3$Cl] and (Me$_3$Si)$_2$S at −78 °C in CH$_2$Cl$_2$ and subsequent, careful warming-up to room temperature, a colorless precipitate was obtained, which was re-dissolved by addition of excess of CH$_2$Cl$_2$. Layering with $n$-hexane afforded [[R$^{5}$Sn]$^2$(SnCl)$_2$(AgPPh$_3$)$_2$]$^2$[[R$^{5}$Sn]$^2$S$_2$]$^3$ (3[[R$^{5}$Sn]$^2$S$_2$]] as light yellow crystals. The ternary cluster is isostructural to that in 2, hence the structural parameters are similar to those observed in 1 or 2, except the expected elongation of M–S, M–P and M–Sn bonds (Ag1–Sn3 2.6803(3) Å) for M = Ag in comparison with M = Cu, and a larger Sn–M–P angle (1: 115.40(3) for M = Cu; 3: 131.23(2) for M = Ag). For the selected structural parameters and NPA results see the ESI.\(^\dagger\)

Addition of hydrazine hydrate to the re-dissolved solution, and subsequent layering with $n$-hexane produced orange crystals of the hydrazine functionalized cluster [[R$^{5}$Sn]$^2$(Ag$_2$S)$_2$]$^3$. 3.5CH$_2$Cl$_2$ (4·3.5CH$_2$Cl$_2$). 4 consists of three [[R$^{5}$Sn]$^2$(μ-S)$_2$]$^2$ units and two [[R$^{5}$Sn]$^2$(μ-S)$_2$]$^2$(μ-S)$_2$] moieties that are linked by ten Ag atoms (see Fig. 2). All Sn atoms exhibit trigonal bipyramidal coordination, with N and S atoms in the axial positions. Four Ag atoms (Ag1, Ag5, Ag7, Ag10) are coordinated in a linear manner, while six other Ag atoms exhibit trigonal planar coordination. Closest Ag···Ag distances are in the range of 2.935(3) Å to 3.260(7) Å. Eight of the Ag atoms are connected this way, with a central butterfly-like arrangement and to adjacent Ag···Ag units, while one Ag···Ag unit is further apart. The cluster possesses pseudo-C$_2$-symmetry. The pseudo-C$_2$-axis runs through the centers of the Ag···Ag four-ring and the separate Ag···Ag dimer. In contrast to known silver sulfide clusters,\(^\text{2a}\) the cluster does not additionally contain stabilizing phosphate groups attached to the silver atoms. N–Sn coordination of the bidentate organic ligands seems to provide sufficient kinetic stabilization.

The employment of a related gold complex, [Au(PPh$_3$)$_2$Cl], along with (Me$_3$Si)$_2$S in the reaction with A afforded single crystals of the complex [[R$^{5}$Sn]$^2$(AuPPh$_3$)$_2$]$^2$[[R$^{5}$Sn]$^2$S$_2$]$^3$ (5). Moreover, addition of hydrazine hydrate to the reaction mixture yielded the hydrazine functionalized derivative [[R$^{5}$Sn]$^2$(μ-S)$_2$]$^2$]]AuPPh$_3$(μ-S)$_2$]$_2$: 5CH$_2$Cl$_2$ (6·5CH$_2$Cl$_2$) (see Fig. 3). In the present case, the derivatization of the organic ligand did not affect the molecular structure of the complex. In 5 and 6, a central [[R$^{5}$Sn]$^2$(μ-S)$_2$]$^2$ unit (cf. ref. 21) is terminated by two [Au(PPh$_3$)(μ-S)]$^2$ units. As in 1–4,
selected structural parameters [Å, °]: Sn–C 2.3865(16)–2.6987(17), Sn–C 2.170(6)–2.187(7), Sn–N 2.362(5)–2.456(5), Ag–S 2.3666(16)–2.9040(16), Ag–Ag 2.9353(7)–3.3260(7), S–Sn–S 89.57(5)–122.29(6), S–Ag–Sn 85.13(5)–146.30(6), Ag–S–Sn 81.50(5)–144.91(7), C–Sn–N 71.6(2)–75.8(2).

Organodecorated Sn atoms exhibit a trigonal bipyramidal coordination environment, while all Au atoms show linear coordination. The structural parameters of the central part are similar in both complexes, but the orientation of the attached {Au(PPh₃)(µ-S)} units is different. In 5, they point away from the central Sn₂S₂ ring, with a C1–Sn1–S2–Au1 trans arrangement, whereas in 6, the corresponding atoms show a cis arrangement. While interatomic distances are similar in both complexes, the Sn1–S2–Au1 and S2–Au1–P1 angles show notable differences in both complexes, indicating the influence of the functional group included in the organic ligand.

In summary, a series of ternary group 11 organotin sulfide clusters have been synthesized and structurally characterized. The presence of the functional group included in the organic ligand.

![Fig. 2](image_url) Molecular structure of the inorganic core of 4 along the pseudo-C₂ axis (ellipsoids drawn at 50% probability). Ag–Ag contacts below 3.4 Å are drawn as dashed red lines. Selected structural parameters [Å, °]: Sn–S 2.3865(16)–2.5987(17), Sn–C 2.170(6)–2.187(7), Sn–N 2.362(5)–2.456(5), Ag–S 2.3666(16)–2.9040(16), Ag–Ag 2.9353(7)–3.3260(7), S–Sn–S 89.57(5)–122.29(6), S–Ag–Sn 85.13(5)–146.30(6), Ag–S–Sn 81.50(5)–144.91(7), C–Sn–N 71.6(2)–75.8(2).

![Fig. 3](image_url) Molecular structures of 5 (left) and 6 (right) without H atoms (ellipsoids drawn at 50% probability). b = –x, 2–y, 1–z; c = 2–x, 1–y, –z. Selected structural parameters [Å, °]: 5: Sn–S 2.380(2)–2.463(2), Sn1–C1 2.189(8), Sn1–O1 2.714(6), Au1–S2 2.291(2), Au1–P1 2.260(2), Sn1–S1–Sn1 86.30(7), S1–Sn1–S1 93.70(7), Sn1–S2–Au1 96.63(9), S2–Au1–P1 178.29(9), 6: Sn–S 2.383(3)–2.525(3), Sn1–C1 1.2186(14), Sn1–Ni 1.2479(11), Au1–S2 2.298(3), Au1–P1 2.250(3), Sn1–S1–Sn1 89.06(11), S1–Sn1–S1 90.94(11), Sn1–S2–Au1 103.86(13), S2–Au1–P1 172.84(12).

Accordingly, the products exhibit different compositions and topologies. Unexpectedly, the reaction with the Cu and Ag precursors induced in situ reduction of one third of the Sn atoms under Sn–Cu and Sn–Ag bond formation. It was shown for the first time that a functionalized ternary M–Sn–S complex could undergo further derivatization.

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Notes and references

‡ X-ray crystallographic data: Data collection on a STOE IPDS2 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 100 K. Structure solution and refinement by direct methods and full matrix least-squares on F², respectively; SHELXTL software.²²


17 Another example for the generation of formal Sn²⁺ during cluster formation from a Sn⁰ precursor was reported in ref. 14 for the compound [(CH₃)₂Sn₆V₃(CuPPh₃)₅Sn₆CuV₃S₂]. [(CH₃)₂Sn₆Cu] also exhibits Sn³⁺–Sn⁰ bonds, see R. E. Allan, A. Bashall, J. S. Palmer, M. McPartlin, M. E. G. Mosquera, J. M. Rawson, A. E. H. Wheatleya, P. A. K. Pannell and T. R. All, Chem. Comm., 1997, 1997.


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