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Communication

A Heterometallic, Heterovalent Cu^I/Sn$^{II/IV}$/S Cluster with an Unprecedented Cu$_4$Sn Core and Stannacyclopentane Units

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[(Ph$_3$PCu^I)$_6$\{(CH$_2$)$_4$Sn^{IV}S$_2$\}$_6$Cu$^I_4$Sn^{II}], a walnut-type, heterometallic, heterovalent cluster, as confirmed by density functional theory calculations, was obtained under reductive solvothermal conditions and features an unprecedented metalloid core within a metal sulfide shell and an organic surface.

Multinary, heterometallic chalcogenide compounds often combine characteristics of the underlying binary phases. In this way, fine tuning of chemical or physical properties, in particular optoelectronics and magnetism, can be realized.[1] Very promising combinations are those of coinage metal chalcogenides with main-group (semi)metals of groups 13 or 14:[2] devices based on InCuSe$_2$ (CIS), for instance, have the highest solar cell efficiency for photovoltaic cells;[3] diverse Cu$_x$SnS$_y$ phases, such as Cu$_2$SnS$_3$[4] or Cu$_4$SnS$_6$,[5] show metallic conductivity.

This concept not only has been the subject of the investigation of numerous solid-state chalcogenides but also has led to active research in the field of ternary or multinary cluster compounds and complexes of the general type [(L$_m$)M$_x$(L$'_n$)M$'_y$(R)E$_z$]^q. In these, M and M$'$ are different (semi)metal atoms with or without additional coordination by ligands L or L$'$, E represents a coordinating, mostly bridging chalcogen atom S, Se, or Te with or without organic groups R, and q replaces a possible charge. Recent examples are [Zn$_3$Hg$_7$Se$_4$(SePh)$_{12}$(P^{n}Pr$_3$)$_4$],[6] [Ag$_{26}$In$_{18}$S$_{36}$Cl$_6$(dppm)$_{10}$-

(thf)$_4$][InCl$_4$(thf)$_2$],[7] [K$_{10}$(ROH)$_x$][M$_4$Sn$_4$E$_{17}$] (R = H, Me; $x \geq 0$; M = Fe, Co),[8] or [Na$_{10}$(H$_2$O)$_6$][Co$_5$Sn$_5$S$_{20}$],[8h,9] all of which respond with particular optoelectronic properties to the mixed metallic situation.

In order to prepare volatile hybrid compounds for vapor deposition, as was first reported for precursors of CuInE$_2$ (E = S, Se),[10] or metallorganic frameworks based on ternary complexes, we currently study reactions of organotin compounds with transition-metal complexes. We obtained heterometallic, heterovalent cluster [(Ph$_3$PCu)$_6$\{(CH$_2$)$_4$SnS$_2$\}$_6$Cu$_4$Sn] (**1**) from Cl$_3$Sn−(CH$_2$)$_4$SnCl$_3$,[11] [CuCl(Ph$_3$P)$_3$], and Na$_2$S·9H$_2$O under solvothermal conditions in MeOH. The organotin(IV) compound was partially reduced by S^{2-} ions; additionally, a yet unprecedented cyclization of a butyl rest occurred at the Sn atom upon Sn−C bond cleavage. Equation 1 provides a possible reaction scheme for the formation of **1** and all of the identified byproducts (see the Supporting Information). **1** crystallizes as light-orange-yellow crystals in the monoclinic space group P2$_1$/n.[12–14] Figure 1 shows the molecular structure of **1**.

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(12) Crystal structure analysis (CCDC 682542): IPDS2, 100 K, Mo Kα, C$_{132}$H$_{138}$Cu$_{10}$P$_6$S$_{12}$Sn$_7$, monoclinic, P2$_1$/n, a = 1762.27(5) pm, b = 2268.14(4) pm, c = 1883.53(5) pm, β = 115.099(2)°, Z = 2. The structure was solved by direct methods[13] and refined against all F^2 data with full-matrix least-squares methods[14] to residuals wR = 0.0768 (all 14 367 independent reflections) and R = 0.0377 [8789 F$_o$ data >3σ(F)].

$$10[Cu^ICl(PPh_3)_3] + 18Na_2S \cdot 9H_2O +$$
$$6Cl_3Sn^{IV}C_4H_8Sn^{IV}Cl_3 \xrightarrow{\text{MeOH, 110 °C (4 days)}}$$

$$[(Ph_3PCu^I)_6\{(CH_2)_4Sn^{IV}S_2\}_6Cu^I_4Sn^{II}] + \frac{6}{8}S^0_8 + 5Sn^{II}Cl_2 +$$
$$\underset{\mathbf{1}\ (23.3\%)}{} 36NaCl + 24PPh_3 + 162H_2O \quad (1)$$

The core of the heterometallic sulfide cluster comprises a yet unprecedented arrangement of four Cu atoms and one Sn atom in a distorted trigonal-bipyramidal manner, with six of the nine edges left unbridged. It was necessary to assign a statistical disorder (not shown in Figure 1) to the atoms of the central unit within the otherwise strictly located cluster atoms. An additionally observed rotational disorder of three of the four Cu atoms (Cu4−Cu6) around the Sn4···Cu7 axis with 8.8(1)% occupation further indicates a large flexibility of this heterometallic core unit. For clarity, the disorder will be disregarded during further discussion of the structure.
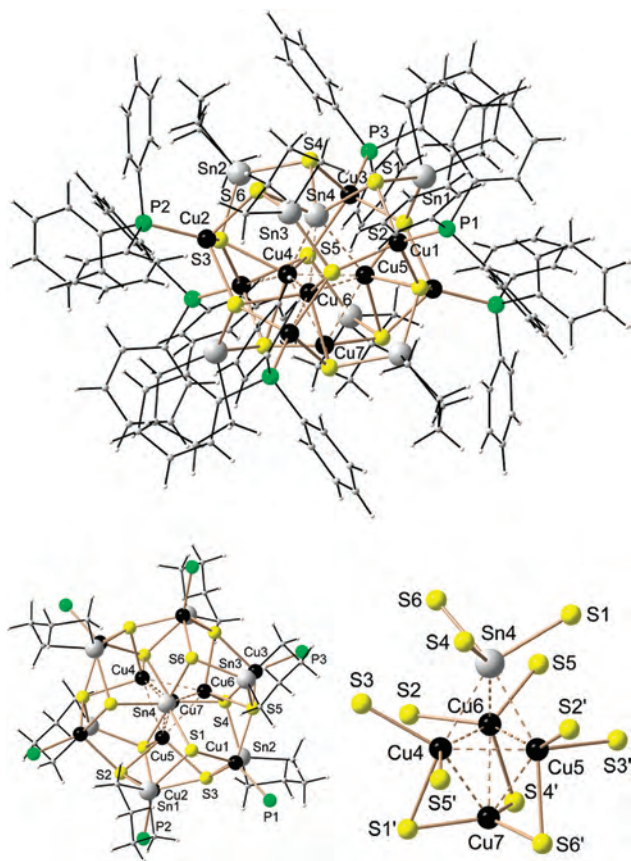
The Cu_4Sn core is linked to the surface of the cluster by S atoms that belong to the six n-BuSnS$_2$ units [Cu(4−6)−S 243.5(2)−257.7(2) pm, Cu7−S 218.1(2)−223.8(2) pm, and Sn4−S 251.9(1)−255.2(2) pm]. Being three-coordinate (S1, S4, and S6) or four-coordinate (S1′, S6′, S4′, S2, S3, and S5), the S atoms bridge to one further Sn atom and one CuPPh$_3$ unit or to one Sn atom and two further CuPPh$_3$ units [Sn(1−3)−S 237.3(2)−243.8(1) pm and Cu(1−3)−S 237.7(1)−242.7(2)

pm]. In this way, all inner Cu atoms show distorted trigonal-planar (Cu7) or trigonal-pyramidal [Cu(4−6) and Sn1] coordination by S atoms besides three (Cu7 and Sn1) or four (Cu4−Cu6) metal−metal contacts [Cu−Cu 257.5(2)−262.7(2) pm and Cu−Sn 262.6(1)−263.7(1) pm]. In addition, Cu4−Cu6 that form the equatorial plane of the Cu$_4$Sn trigonal pyramid are each involved in one further, unusually short Cu−Cu contact [232.9(1)−238.8(1) pm] in the more dominant rotational disorder positions.

At the $Cu_6(SnS_2)_6$ metal chalcogenide surface embedding the inner Cu$_4$Sn unit, the cluster is decorated by a ligand shell of six Ph$_3$P groups at the Cu atoms and six n-Bu groups at the Sn atoms, which are part of the six [{cyclo-(CH$_2$)$_4$Sn}S$_2$]$^{2-}$ ligands. The formation of the latter was obviously advantaged over growing two separate clusters at both ends of the originally reacted Cl$_3$Sn−(CH$_2$)$_4$−SnCl$_3$ unit. As rationalized by density functional theory (DFT)[15] calculations employing the *RIDFT* approximation[16] of the program system *TURBOMOLE*,[17] the uncommon cyclization of Cl$_3$Sn−(CH$_2$)$_4$−SnCl$_3$ preliminarily producing SnCl$_4$ and {cyclo-(CH$_2$)$_4$Sn}Cl$_2$ (eq 2) is *not* enthalpically favored.[18] Therefore, it was rather driven by the reductive sulfidic conditions that led to formation of elemental sulfur and reduction of Sn^{IV}Cl$_4$ to Sn^{II}Cl$_2$. Consequently, this might enable further reactivity of **1** involving the {cyclo-(CH$_2$)$_4$Sn} unit. The Sn−C bond cleavage might have been induced thermally or catalytically by Cu$^+$ ions. Whether to be an intramolecular or intermolecular process is currently under investigation.
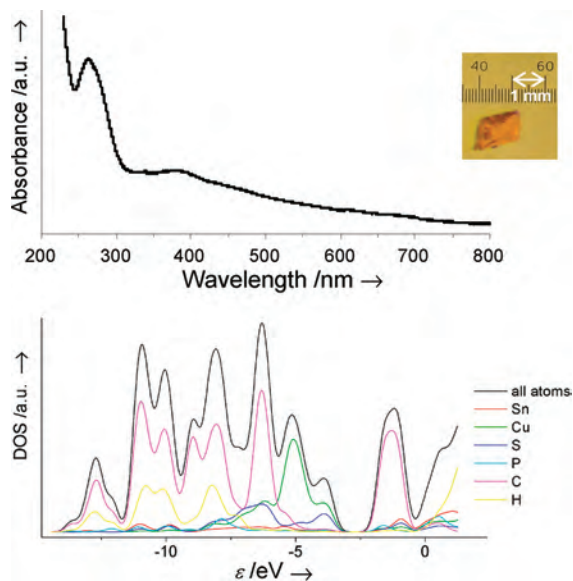
$$Cl_3Sn(CH_2)_4SnCl_3 \rightarrow \{cyclo-(CH_2)_4Sn\}Cl_2 + SnCl_4$$
$$\Delta E_{DFT,0K} = +48.4\ \text{kJ} \cdot \text{mol}^{-1} \quad (2)$$
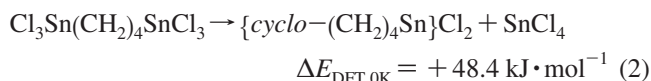
Only a few compounds have been published to date that are directly related to **1**; however, none of them feature a Cu^I/Sn$^{II/}$IV combination and none possess direct M−M interactions. Examples are [(Me$_2$PhPCu^I)$_6$(PhSn^{IV}S$_3$)$_2$],[19] the cation in [Sn$^{IV}_3$Cu$^I_4$(S$_2$C$_2$H$_4$)$_6$(μ_3-O)(PPh$_3$)$_4$](ClO$_4$)$_2$·3CH$_2$Cl$_2$,[20] and the quaternary Mo^{VI}/Cu^I/Sn^{IV}/S anion in [Et$_4$N]$_4$[(OMoS$_3$Cu$_2$)$_2$(μ-

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Figure 1. Molecular structure of **1**, disregarding the disorder of the central Cu$_4$Sn^{II} fragment (top). Color code: C, gray (small spheres); H, white. [(PCu)$_6$(C$_4$H$_8$Sn)$_6$Cu$_4$Sn] framework viewed down the pseudo-C_3 axis and inner Cu$_4$Sn fragment within its coordination environment (bottom).

Figure 2. Solid-state UV−visible spectrum, recorded as a suspension of single crystals in nujol oil and a picture of a single crystal of **1** (top). Calculated DOS indicating atomic orbital contributions of the different atoms to the frontier orbitals (bottom).

$Sn_2S_6)]$.[21] Additionally to these examples of molecular Cu^I/Sn^{IV}/S complexes, two coordination polymers were reported lately, the thermal treatment of which evolved nearly organic-free Cu_2SnS_3 besides SnS: $(DBUH)CuSnS_3$ (DBU = 1,8-diaza-bicyclo[5.4.0]undec-7-ene) and $(1,4-dabH_2)Cu_2SnS_4$ (1,4-dab = 1,4-diaminobutane).[22] Other main-group (semi)metal atoms are present in $[DmpGe(\mu_3-S)_3]_4Ni_6$ (Dmp = 2,6-dimesitylphenyl),[23] $[As(C_6H_5)_4]_2[Cu_6In_4(SeC_6H_5)_{16}Cl_4]$, or $[As(C_6H_5)_4][Cu_7In_4-(SeC_6H_5)_{20}]$.[24] These results and the preparation of **1** show the high potential of organometallic group 13 or 14 precursors for efficient access to heterometallic chalcogenide complexes, however, only leading to a mixed-valence Sn^{II}/Sn^{IV} situation employing the reaction conditions given in eq 1.

Single crystals of **1** have been investigated by means of optical absorption spectroscopy (Figure 2). Because all metal atoms involved possess a complete d^{10} shell (formal Cu^I, Sn^{II}, and Sn^{IV}), only $S(p) \rightarrow M(s,p)$ charge-transfer processes are expected concerning the cluster core. One observes a relatively weak, broad absorption with a smooth onset at 750 nm (1.65 eV), an inconspicuous shoulder around 446 nm (2.78 eV), and a maximum at 376 nm (3.30 eV), in accordance with the orange-yellow color of the crystals. A more significant maximum due to intraligand $\pi \rightarrow \pi^*$ excitation at the phenyl groups is observed in the UV region at 263 nm (4.71 eV).[25]

Probably the most peculiar feature of **1** is the inner Cu_4Sn unit, containing direct M−M contacts, some of which are not even clamped by bridging ligands (Sn−Cu2,3,4). Metalloid Cu/Sn clusters are known from laser evaporation experiments that produced, however, tin-rich clusters $[Cu_xSn_y]^+$ ($x = 1,..., 5$; $y = 10,..., 27$).[26] The Sn atom in **1**, which is involved in the central cluster unit, formally possesses oxidation state II+. While producing **1** in amounts suitable for further experimental analyses (Mössbauer spectroscopy and thermogravimetric investigations), DFT investigations[27] were performed in order to rationalize the unusual structural and electronic features. The molecular structure of **1** is well reproduced by the calculations (see the Supporting Information): $\Delta d = 0.8−11.9$ pm for all bonds except three Cu−Cu distances involving atomic positions that show rotational disorder; for the latter, Δd is also acceptable (16.5−21.3 pm), taking into account that the experimental positions of the respective atoms may vary in a range estimated to 16 pm owing to the observed disorder. On the basis of the reasonably calculated structure, population analyses (Mulliken for DOS and NPA for natural charges)[28] were carried out to rationalize both the optical absorption behavior and the mixed-valence situation. As shown in Figure 2 (bottom), the population of the highest occupied orbitals (ca. −7 eV to HOMO at −3.611 eV) is dominated by contributions of C(p) atomic orbitals, followed by contributions of Cu(d) and S(p) atomic orbitals. The first lowest unoccupied orbitals show essentially a C(p) contribution. Therefore, the above-mentioned intraligand $\pi \rightarrow \pi^*$ transition is certainly predominant. Further charge-transfer processes between metal and chalcogenide atoms (MLCT and LMCT) are secondary, which is in good agreement with the experimental findings: maximum absorbances and band widths of the UV−visible signals accord well with the calculated values of the DOS and the energy range of the DOS concerning the same involved atom type. Analyzing the natural charges, the Sn atoms at the periphery indeed show approximately twice the value ($+1.50 \pm 0.02$) of the core Sn atom ($+0.72$), exhibiting a charge similar to that observed for the Cu atoms ($+0.69 \pm 0.07$; note that these charges do *not* represent formal oxidation states). According to these results, Cu atoms are not involved in the mixed valency, whereas one formal Sn^{II} center is present in the heterometallic Cu_4Sn core besides six formal Sn^{IV} centers at the cluster surface.

The potential use of **1** in the generation of ternary mixed-valence chalcogenide films is under exploration.

Supporting Information Available: CIF files, details of syntheses, X-ray diffractometry, EDX and UV−visible spectroscopy, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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