Zintl Ions

DOI: 10.1002/ange.200907228

$[Ag(Sn_9{-}Sn_9)]^{5-}$: A Homoleptic Silver Complex of A Dimeric Sn_9 Zintl Anion**

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Recently, homo- and heteroatomic Zintl anions have been rediscovered to serve as an elegant source for the synthesis of intermetalloid clusters.[1] In the ideal case these clusters appear as ligand-free species and show atom coordination patterns found in intermetallic compounds. For example, the anion $[Co@Ge_{10}]^{3-}$ displays Co–Ge and Ge–Ge distances as observed for the binary phase $CoGe_2$.[2] The largest structurally characterized ligand-free heteroatomic clusters are $[As@Ni_{12}@As_{20}]^{3-}$[3] and $[Au_3Ge_{45}]^{9-}$[4] which form through reactions of $[As_7]^{3-}$ and $[Ge_9]^{4-}$ polyanions, respectively. The bottom-up synthesis of intermetalloid clusters requires both cluster growth and bonding to a second metal. Such cluster growth is well documented for the tetrel atom clusters $[Ge_9]^{4-}$, and includes the formation of dimeric $Ge_9{-}Ge_9$,[5] rod-type trimeric $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$,[6] and tetrameric $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$ polyanions[7] as well as the anionic linear polymer chain $^1_\infty\{[Ge_9]\}^{2-}$.[8] Formation of exo-cluster bonds occurs by oxidative coupling reactions in competition with formation of stable radicals $[Ge_9^{\bullet}]^{3-}$.[9] Full oxidation of nine-atom clusters also offers the possibility of producing periodic, nanostructured materials.[10] A cluster exo-bonded to a ligand-free metal atom was observed for the first time in the mercury-linked polymer $^1_\infty[(\mu^2\text{-}Hg)(Ge_9)^{2-}]$.[11] Reactions with organometallic compounds presumably involve formation of an organometallic complex, as was shown in the sequence of the transformation of $[(cod)Ir(\eta^4\text{-}Sn_9)]^{3-}$ (cod = cyclooctadiene) into $[Ir@Sn_{12}]^{3-}$.[12] Homoleptic transition-metal complexes of germanide Zintl ions have also been observed in form of $[(\mu^2\text{-}Au)_3(\eta^3\text{-}Ge_9)_2]^{5-}$[13] and $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$[14] as well as the endohedral $[Pd_2@Ge_{18}]^{4-}$.[15]

In the case of homoatomic tin polyanions, the intermetalloid clusters $[Ni_2@Sn_{17}]^{4-}$,[16] $[Pt_2@Sn_{17}]^{4-}$,[17] $[Pd_2@Sn_{18}]^{4-}$,[18] and the above-mentioned $[Ir@Sn_{12}]^{3-}$[12] were recently been described. To form these clusters from the $[Sn_9]^{4-}$-containing starting materials again oxidative coupling must occur, along with defragmentation. However, up to now, the missing link of an oxidative coupling of two $[Sn_9]^{4-}$ anions to form a dimeric unit has not been reported, and so far there is no evidence for an $[Sn_9{-}Sn_9]^{6-}$ dimer analogous to $[Ge_9{-}Ge_9]^{6-}$. Until now, only the stable paramagnetic $[Sn_9]^{3-}$ has been reported.[9b,d,21c]

Herein we present the first oxidative coupling of $[Sn_9]^{4-}$ clusters to form a dimer with an Sn–Sn exo-cluster bond. This bond is additionally supported by a silver cation, and thus the title species is also a homoleptic Ag complex and the first cluster consisting of only silver and tin atoms.

The reaction of K_4Sn_9 in ethylenediamine with $(AgMes)_4$[19] (Mes = 2,4,6-$Me_3C_6H_4$) in the presence of 2,2,2-crypt was accompanied by immediate formation of a small amount of a dark precipitate, which was filtered off. After one week two fractions of crystalline material were obtained from the filtrate which could be separated mechanically and were identified as the already known paramagnetic $[K(2,2,2\text{-crypt})]_6[Sn_9]_2{\cdot}1.5\,en{\cdot}0.5\,tol$ (tol = toluene)[21] and as the new salt $[K\text{-}(2,2,2\text{-crypt})]_5[Ag(Sn_9{-}Sn_9)]{\cdot}en{\cdot}0.5\,tol$ (**1**) which contains the cluster anion $[Ag(Sn_9{-}Sn_9)]^{5-}$ (**1a**). Compound **1** was characterized by single-crystal X-ray diffraction and energy dispersive X-ray analysis (EDX). According to EDX analysis, the insoluble dark precipitate formed during the reaction has the same Ag/Sn ratio as **1**.

The anion $[Ag(Sn_9{-}Sn_9)]^{5-}$ (**1a**) is composed of a dimeric $[Sn_9{-}Sn_9]$ cluster with a covalent two-center, two-electron exo-cluster bond with a length of 2.987(1) Å corresponding to a slightly elongated Sn–Sn single bond (2.80 Å in α-Sn).[20] The two intact polyhedral $[Sn_9]$ clusters additionally coordinate to one Ag atom (Figure 1). All other Sn–Sn distances within the dimeric unit are in the normal range for $[Sn_9]$ clusters,[21] with the Sn–Sn cluster edges adjacent to the atoms of the exo bond being the shortest (2.858(1)–2.870(2) Å). This phenomenon of short intracluster contacts neighboring an exo bond is also found in $[Ge_9{-}Ge_9]^{6-}$ dimers. The two $[Sn_9]$

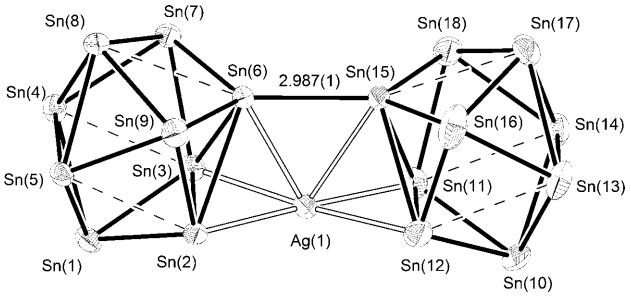

Figure 1. Structure of the $[Ag(Sn_9{-}Sn_9)]^{5-}$ ion (**1a**). Atoms are shown with 50% occupation probability. Selected distances [Å] and angles [°]:[22] Sn(6)–Sn(8) 3.486(1), Sn(3)–Sn(4) 3.369(1), Sn(2)–Sn(5) 3.282(1), Sn(15)–Sn(17) 3.409(1), Sn(11)–Sn(14) 3.353(1), Sn(12)–Sn(13) 3.318(1), average Sn–Ag 2.937(1); Sn(8)-Sn(6)-Sn(15) 159.29, Sn(8)-Sn(15)-Sn(17) 158.82.

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[**] This work was financially supported by the Deutsche Forschungsgemeinschaft (project number FA 198/6-1). We thank Dr. A. Schier for the revision of the manuscript and W. C. Heraeus GmbH for the donation of chemicals. J.-Q.W. is grateful to the Alexander von Humboldt Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200907228.

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clusters in the dimer have an almost identical topology close to a distorted tricapped trigonal prism with three elongated prismatic edges, shown as dashed lines in Figure 1.

The prism heights Sn(6)–Sn(8) (h_1), Sn(3)–Sn(4) (h_2), Sn(2)–Sn(5) (h_3) and Sn(15)–Sn(17) (h_4), Sn(11)–Sn(14) (h_5), Sn(12)–Sn(13) (h_6) with ratios $h_1/h_2/h_3 = 1.06:1.03:1$ and $h_4/h_5/h_6 = 1.03:1.01:1$, respectively, indicate that the tricapped prisms are distorted towards C_{2v}-symmetric monocapped square antiprisms with the open squares having short diagonals Sn(6)—Sn(8) and Sn(15)–Sn(17), respectively. Considering the Sn–Sn distances, the overall cluster charge of −5 in **1a** can formally be rationalized as a $[(Sn_9–Sn_9)^{6-}]$ dimer coordinating to Ag^+ with d^{10} configuration.

Optimization of the structure of the anion by quantum chemical calculations led to a C_{2v}-symmetric structure with slightly larger interatomic distances than found in the crystal structure. On average, all calculated interatomic distances are elongated by approximately 0.08 Å, with a maximum deviation of 0.2 Å for the Sn(6)–Sn(15) exo bond. The mean difference in the bond angles is 1.0°. The shorter Sn–Sn distances adjacent to the exo bond of **1a** are also verified by the calculations. Furthermore, the anion appears to be a stable unit, as indicated by the HOMO–LUMO gap of 1.77 eV. The calculated natural charge of +0.4 for Ag supports its formal description as Ag^+. The d^{10} configuration of transition metal atoms has also been found in various other examples of endo- und exohedral clusters such as $[(\mu^2\text{-Au})_3(\eta^3\text{-Ge}_9)_2]^{5-}$,[13] $[Cu(\eta^4\text{-Ge}_9)(\eta^1\text{-Ge}_9)]^{7-}$,[14] $[Pd_2@Ge_{18}]^{4-}$,[15] and $[Ir@Sn_{12}]^{3-}$.[12]

The number of compounds with Ag–Sn bonds is quite limited.[23] In **1a**, the silver atom is connected to six tin atoms. The Ag–Sn distances range from 2.880(2) to 3.010(1) Å and are longer than typical single bonds[23] but lie in the range of those observed in silver complexes of stanna-*closo*-dodecaborate with $d(Ag–Sn) = 2.7607(9)–3.127(1)$ Å[24] and compare well to those in intermetallic phases such as $SrAg_2Sn_2$ ($d(Ag–Sn) = 2.795(4)$ Å).[40] Considering only the four shortest Ag–Sn contacts [Sn(2), Sn(3), Sn(11), Sn(12)] results in a rectangular-planar coordination of the silver atom. Such planar coordination of Ag^+ is not frequent, but has recently also been observed and discussed for other d^{10} homoleptic complexes: In $[Hg(\eta^2\text{-Sn}_9)_2]^{6-}$ Hg^{2+} is coordinated to four Sn atoms of the two separate $[Sn_9]^{4-}$ clusters. Two longer Hg–Sn contacts complete the coordination sphere of the Hg atom.[25] Quantum chemical calculations for the structurally characterized $[Ag(\eta^2\text{-P}_4)_2]^+$[26] and $[Au_3Ge_{45}]^{9-}$ also reveal the stability of rectangular planar coordination geometry of Ag^+ and Au^+, respectively. For the Au^I model compound $[(\eta^2\text{-Ge}_4)_2Au]^{7-}$ the D_{2h} conformation is preferred over the D_{2d} conformation by only 6 kJ mol^{-1}.[4]

Apparently, the silver atom has a great impact on the structure of the cluster **1a**, since the two $[Sn_9]$ units show a sterically less favorable *cisoid* conformation, whereas the $[Ge_9]$ clusters in the related $[Ge_9–Ge_9]^{6-}$ dimer always exhibit a *transoid* arrangement (Figure 2), despite the fact that the Sn(8)-Sn(6)-Sn(15) and Sn(17)-Sn(15)-Sn(6) angles of 159.3 and 158.8°, respectively, are rather similar to the Ge(8)-Ge(6)-Ge(6′) angles of 162.2°. The Sn(8)-Sn(6)-Sn(15)-Sn(17) torsion angle of 11.5° in **1a** reveals a small deviation from C_{2v} symmetry due to twisting around the exo bond. Most reported dimeric clusters, such as digerma-*closo*-dodecaborate $[(Ge_2B_{10}H_{10})_2]^{2-}$[27] and distanna-*closo*-dodecaborate $[(Sn_2B_{10}H_{10})_2]^{2-}$[28] also prefer a *transoid* conformation. Quantum-chemical calculations on a hypothetical "naked" $[(Sn_9–Sn_9)]^{6-}$ dimer show that a *transoid* (C_{2h}) conformation is energetically slightly more stable by about 5 kJ mol^{-1} than a *cisoid* (C_{2v}) arrangement, but the incorporation of Ag^+ between the two interconnected $[Sn_9]$ units in **1a** apparently forces the dimeric unit into the sterically more crowded *cisoid* conformation.

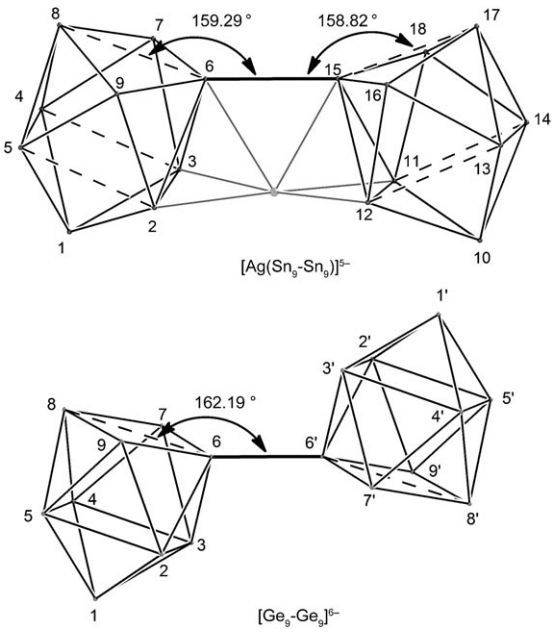

Figure 2. Comparison of the structures of $[Ag(Sn_9–Sn_9)]^{5-}$ and $[Ge_9–Ge_9]^{6-}$.[5]

In an analogous reaction of $(AgMes)_4$ with $[Ge_9]^{4-}$ the transfer of one mesityl group to the $[Ge_9]$ cluster takes place with formation of the mono-alkylated $[Ge_9(Mes)]^{3-}$ cluster unit,[29] and the related reaction of $[Sn_9]^{4-}$ with CuMes leads to a $[Cu@Sn_9]^{3-}$ cluster with an endohedral Cu atom,[30] which can be described as a Cu^I complex of an $[Sn_9]^{4-}$ cluster.

In the present case, oxidation of the $[Sn_9]^{4-}$ cluster is observed, and subsequently dimerization of the oxidation product—the paramagnetic $[Sn_9]^{3-}$ unit, which was actually found in the second product of the reaction—occurs. Interestingly, the dimerization of paramagnetic species $[E_9]^{3-}$ has never been observed for E = Si, Ge, Sn, and Pb before in the presence of 2,2,2-crypt. In the reaction presented herein, isolation of the dimer as the $[K(2.2.2\text{-crypt})]^+$ salt is attributed to the presence of Ag^+ ions in the solution.

Experimental Section

All manipulations and reactions were performed in an argon atmosphere by standard Schlenk line or glove box techniques. "K_4Sn_9" was synthesized by heating a stoichiometric mixture of elemental K and Sn at 550 °C for 20 h in a stainless steel tube. Ethylenediamine (Merck, 99 %) was distilled over CaH_2 and stored in

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an Ar-filled Schlenk tube. 2,2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]-hexacosane, Merck, 98%) was vacuum-dried for 8 h prior to use. $(AgMes)_4$ was prepared as reported.[19] K_4Sn_9 (125 mg, 0.1 mmol) was dissolved in 2 mL of ethylenediamine. After stirring for 0.5 h, the dark red K_4Sn_9 solution was filtered onto solid $(AgMes)_4$ (23 mg, 0.025 mmol). The resulting dark-brown solution was stirred for 3 h, filtered, and layered with a solution of 2,2,2-crypt (150 mg, 0.4 mmol) in toluene (5 mL). Over one week, two kinds of crystals appeared: large, brick-shaped, black crystals, which were shown to be $[K(2,2,2\text{-crypt})]_6[Sn_9]_2 \cdot 1.5\,en \cdot 0.5\,tol$[21d] (yield ca. 23 mg, ca. 10%), and small needle-shaped dark-red crystals, which were identified as the title compound $[K\text{-}(2.2.2)crypt]_5[Ag(Sn_9{-}Sn_9)] \cdot en \cdot 0.5\,tol$ (**1**) (yield ca. 50 mg, ca. 23%). Quantitative EDX analysis of the crystals of **1** showed the presence of K, Ag, and Sn, with an approximate ratio of K/Ag/Sn = 5:1:18.

Single-crystal X-ray diffraction data of **1** were collected on a Stoe IPDS-IIT image plate diffractometer at the window of a rotating anode (Bruker AXS; FR951) with graphite-monochromatized $Mo_{K\alpha}$ (0.71073 Å) radiation at 150 K. Numerical absorption corrections were applied (X-Shape/X-Red).[31] The structure was solved by direct methods and was refined on F^2 by using the SHELXTL V6.1 package.[32] Crystal data: $M_r = 4428.40$, triclinic space group $P\bar{1}$, $a = 13.932(3)$, $b = 19.877(4)$, $c = 29.050(6)$ Å, $\alpha = 106.98(3)$, $\beta = 96.09(3)$, $\gamma = 99.49(3)°$, $V = 7487(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.96$ g cm^{-3}, $\mu = 3.3$ mm^{-1}; 44569 measured and 20585 independent reflections, $R_{int} = 0.0366$; $R_1 = 0.039$ and $wR_2 = 0.102$ for $I \geq 2\sigma(I)$, $R_1 = 0.053$ and $wR_2 = 0.107$ for all data. Min./max. residual electron density: $-1.641/2.819$ e Å^3. CCDC 757104 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The quantum chemical calculations were carried out with Gaussian 03.[33] The negative charge of the anionic clusters was compensated by the polarizable continuum model (PCM) as implemented in Gaussian 03 with dichloromethane ($\varepsilon_r = 8.93$) as solvent. For the hybrid DFT calculations the B3LYP[34] exchange correlation functional was used. For tin and silver atoms the core electrons were replaced by the small-core scalar-relativistic effective-core potentials, namely, ECP28MDF for Ag[35] and Sn.[36] Basis sets with cc-pVTZ quality were used for the calculations.[37,38] The natural charges were obtained by a natural population analysis implemented into the NBO 3.0[39] program. Preliminarily, the coordinates derived from the crystal structure determination of $[Ag(Sn_9{-}Sn_9)]^{5-}$ were optimized to their energetic minimum. Due to only slight deviations the obtained structure was restricted to C_{2v} symmetry. The analysis of the Hessian matrix showed no imaginary values and therefore confirmed the optimized structures to be stationary points on the potential-energy hypersurface. Furthermore, the structures of the hypothetical $[(Sn_9{-}Sn_9)]^{6-}$ dimers in *cisoid* (C_{2v}) and *transoid* (C_{2h}) conformation also proved to be local minima. The coordinates of the optimized structures can be obtained from the Supporting Information.

Received: December 22, 2009
Revised: March 24, 2010
Published online: July 27, 2010

Keywords: cluster compounds · heterometallic complexes · silver · tin · Zintl anions

[1] a) T. F. Fässler, S. D. Hoffmann, *Angew. Chem.* **2004**, *116*, 6400–6406; *Angew. Chem. Int. Ed.* **2004**, *43*, 6242–6247; b) S. C. Sevov, J. M. Goicoechea, *Organometallics* **2006**, *25*, 5678–5692; c) S. Scharfe, T. F. Fässler, *Phil. Trans. R. Soc. London Ser. A* **2010**, *368*, 1265–1284.

[2] a) J.-Q. Wang, S. Stegmaier, T. F. Fässler, *Angew. Chem.* **2009**, *121*, 2032–2036; *Angew. Chem. Int. Ed.* **2009**, *48*, 1998–2002; b) N. Korber, *Angew. Chem.* **2009**, *121*, 3262–3264; *Angew. Chem. Int. Ed.* **2009**, *48*, 3216–3217.

[3] M. J. Moses, J. C. Fettinger, B. W. Eichhorn, *Science* **2003**, *300*, 778–781.

[4] A. Spiekermann, S. D. Hoffmann, T. F. Fässler, I. Krossing, U. Preiss, *Angew. Chem.* **2007**, *119*, 5404–5407; *Angew. Chem. Int. Ed.* **2007**, *46*, 5310–5313.

[5] a) L. Xu, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 9245–9246; b) R. Hauptmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2266–2278; c) C. Suchentrunk, J. Daniels, M. Somer, W. Carrillo-Cabrera, N. Korber, *Z. Naturforsch. B* **2005**, *60*, 277–283; d) A. Nienhaus, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1752–1758.

[6] a) A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 10990–10991; b) L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149–1153.

[7] a) A. Ugrinov, S. C. Sevov, *Inorg. Chem.* **2003**, *42*, 5789–5791; b) L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977–1981.

[8] a) C. Downie, Z. Tang, A. M. Guloy, *Angew. Chem.* **2000**, *112*, 346–348; *Angew. Chem. Int. Ed.* **2000**, *39*, 337–340; b) C. Downie, J.-G. Mao, H. Parmer, A. M. Guloy, *Inorg. Chem.* **2004**, *43*, 1992–1997; c) A. Ugrinov, S. C. Sevov, *C. R. Chim.* **2005**, *8*, 1878–1882.

[9] a) C. Belin, H. Mercier, V. Angilella, *New J. Chem.* **1991**, *15*, 931–938; b) T. F. Fässler, M. Hunziker, *Inorg. Chem.* **1994**, *33*, 5380–5381; c) T. F. Fässler, U. Schütz, *Inorg. Chem.* **1999**, *38*, 1866–1870; d) T. F. Fässler, M. Hunziker, M. E. Spahr, H. Lueken, H. Schilder, *Z. Anorg. Allg. Chem.* **2000**, *620*, 692–700.

[10] a) A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, Y. Grin, *Nature* **2006**, *443*, 320–323; b) M. G. Kanatzidis, G. S. Armatas, *Science* **2006**, *313*, 817–820; c) D. Sun, A. E. Riley, A. J. Cadby, E. K. Richmann, S. D. Korlann, S. H. Tolbert, *Nature* **2006**, *441*, 1126–1130; d) T. F. Fässler, *Angew. Chem.* **2007**, *119*, 2624–2628; *Angew. Chem. Int. Ed.* **2007**, *46*, 2572–2575.

[11] A. Nienhaus, R. Hauptmann, T. F. Fässler, *Angew. Chem.* **2002**, *114*, 3352–3355; *Angew. Chem. Int. Ed.* **2002**, *41*, 3213–3215.

[12] J.-Q. Wang, S. Stegmaier, B. Wahl, T. F. Fässler, *Chem. Eur. J.* **2010**, *16*, 1793–1798.

[13] A. Spiekermann, S. D. Hoffmann, F. Kraus, T. F. Fässler, *Angew. Chem.* **2007**, *119*, 1663–1666; *Angew. Chem. Int. Ed.* **2007**, *46*, 1638–1640.

[14] S. Scharfe, T. F. Fässler, *Eur. J. Inorg. Chem.* **2010**, 1207–1213.

[15] J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2005**, *127*, 7676–7677.

[16] E. N. Esenturk, J. C. Fettinger, B. W. Eichhorn, *J. Am. Chem. Soc.* **2006**, *128*, 12–13.

[17] B. Kesanli, J. E. Halsig. P. Zavalij, J. C. Fettinger, Y. F. Lam, B. W. Eichhorn, *J. Am. Chem. Soc.* **2007**, *129*, 4567–4574.

[18] a) Z.-M. Sun, H. Xiao, J. Li, L.-S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 9560–9561; b) F. S. Kocak, P. Zavalij, Y.-F. Lam, B. W. Eichhorn, *Inorg. Chem.* **2008**, *47*, 3515–3520.

[19] E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastinit, *Organometallics* **1989**, *8*, 1067–1079.

[20] J. L. Wardell in *Encyclopedia of Inorganic Chemistry*, *2nd ed.*, *Vol. 9* (Ed.: R. B. King), Wiley, New York, **2005**, pp. 1.

[21] a) T. F. Fässler, M. Hunziker, *Z. Anorg. Allg. Chem.* **1996**, *622*, 837–844; b) J. D. Corbett, P. A. Edwards, *J. Am. Chem. Soc.* **1977**, *99*, 3313–3317; c) S. C. Critchlow, J. D. Corbett, *J. Am. Chem. Soc.* **1983**, *105*, 5715–5716; d) R. Burns, J. D. Corbett, *Inorg. Chem.* **1985**, *24*, 1489–1492; e) R. Hauptmann, R. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2220–2224; f) N. Korber, A. Fleischmann, *J. Chem. Soc. Dalton Trans.* **2001**, 383–385; g) R. Hauptmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1500–1504.

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[22] Selected bond lengths [Å] and angles [°]: Ag(1)–Sn(2) 2.897(2), Ag(1)–Sn(3) 2.9192(9), Ag(1)–Sn(6) 2.988(1), Ag(1)–Sn(11) 2.880(2), Ag(1)–Sn(12) 2.929(1), Ag(1)–Sn(15) 3.010(1), Sn(1)–Sn(2) 2.951(1), Sn(1)–Sn(3) 2.935(1), Sn(2)–Sn(3) 3.153(1), Sn(2)–Sn(6) 3.172(1), Sn(2)–Sn(5) 3.282(1), Sn(3)–Sn(6) 3.134(1), Sn(4)–Sn(5) 3.089(1), Sn(6)–Sn(7) 2.858(1), Sn(6)–Sn(9) 2.870(2), Sn(6)–Sn(15) 2.987(1), Sn(11)–Sn(12) 3.154(1), Sn(11)–Sn(15) 3.160(1), Sn(12)–Sn(15) 3.1342(9), Sn(15)–Sn(16) 2.858(1), Sn(15)–Sn(18) 2.863(2); Sn(2)-Ag(1)-Sn(3) 65.66(3), Sn(2)-Ag(1)-Sn(6) 65.21(3), Sn(3)-Ag(1)-Sn(6) 64.08(3), Sn(6)-Ag(1)-Sn(15) 59.74(3), Sn(15)-Sn(6)-Ag(1) 60.50(3), Sn(6)-Sn(15)-Ag(1) 59.76(3).

[23] a) M. Barrow, H.-B. Bürgi, M. Camalli, F. Caruso, E. Fischer, L. M. Venanzi, L. Zambonelli, *Inorg. Chem.* **1983**, *22*, 2356–2362; b) B. Findeis, L. H. Gade, I. J. Scowen, M. McPartlin, *Inorg. Chem.* **1997**, *36*, 960–961; c) P. B. Hitchcock, M. F. Lappert, L. J.-M. Piersens, *Organometallics* **1998**, *17*, 2686–2688; d) H. V. R. Dias, A. E. Ayers, *Polyhedron* **2002**, *21*, 611–618; e) A. E. Ayers, H. V. R. Dias, *Inorg. Chem.* **2002**, *41*, 3259–3268.

[24] S. Hagen, H. Schubert, C. Maichle-Mössmer, I. Pantenburg, F. Weigend, L. Wesemann, *Inorg. Chem.* **2007**, *46*, 6775–6784.

[25] L. Yong, M. B. Boeddinghaus, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1293–1296.

[26] I. Krossing, *J. Am. Chem. Soc.* **2001**, *123*, 4603–4604.

[27] C. Nickl, D. Joosten, K. Eichele, C. Maichle-Mössmer, K. W. Törnroos, L. Wesemann, *Angew. Chem.* **2009**, *121*, 8061–8065; *Angew. Chem. Int. Ed.* **2009**, *48*, 7920–7923.

[28] D. Joosten, I. Pantenburg, L. Wesemann, *Angew. Chem.* **2006**, *118*, 1103–1105; *Angew. Chem. Int. Ed.* **2006**, *45*, 1085–1087.

[29] J. Q. Wang, T. F. Fässler, unpublished results.

[30] S. Scharfe, T. F. Fässler, S. Stegmaier, S. D. Hoffman, K. Ruhland, *Chem. Eur. J.* **2008**, *14*, 4479–4482.

[31] a) X-RED (1.26)s Data Reduction Program, Stoe & Cie, Darmstadt, Germany, **2004**; b) X-SHAPE (2.05)s Crystal Optimization for Numerical Absorption Correction, Stoe & Cie, Darmstadt, Germany, **2004**.

[32] G. M. Sheldrick, SHELXTL, version 6.1, Brucker-Nonius AXS, Madison, WI, **2000**.

[33] Gaussian 03 (Revision E.01), M. J. Frisch, et al., see Supporting Information.

[34] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[35] D. Figgen, G. Rauhut, M. Dolg, H. Stoll, *Chem. Phys.* **2005**, *311*, 227–244.

[36] B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563–2569.

[37] K. A. Peterson, C. Puzzarini, *Theor. Chem. Acc.* **2005**, *114*, 283–296.

[38] K. A. Peterson, *J. Chem. Phys.* **2003**, *119*, 11099–11112.

[39] a) J. E. Carpenter, F. Weinhold, *J. Mol. Struct.* **1988**, *169*, 41–62; b) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066–4073; c) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[40] W. Dörrscheidt, N. Niess, H. Schäfer, *Z. Naturforsch. B* **1976**, *32*, 985–988.

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