First Incorporation of the Tetrahedral $[Sn_4]^{4-}$ Cluster into a Discrete Solvate $Na_4[Sn_4]\cdot(NH_3)_{13}$ from Solutions of Na_4Sn_4 in Liquid Ammonia

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Treatment of solutions of Na_4Sn_4 in liquid ammonia with CuMes (Mes = mesityl) and 18-crown-6 afforded crystals of the composition $Na_4[Sn_4]\cdot(NH_3)_{13}$. The structure features anionic units $\{Na_7[Sn_4]_2\}$ and separate Na cations, both fully solvated by ammonia molecules.

Key words: Cluster Compounds, Zintl Anions, X-Ray Diffraction, Solubility, Tetrahedral Zintl Clusters, Tin Clusters

Introduction

The solution chemistry of nine-atomic group 14 Zintl clusters $[E_9]^{4-}$ (E = Si–Pb) shows a fascinating diversity. Mild oxidation or oxidative coupling of these clusters lead to free radicals or dimeric, oligomeric and polymeric structures of the elements [1 – 5]. Further oxidation even results in new element allotropes with tetrahedrally connected tetrel atoms [6], and structures that are exclusively built up from E_9 clusters are predicted to be stable [7, 8]. Additionally, E_9 clusters can serve as ligands in transition metal complexes or form more complex intermetalloidal clusters [1 – 5, 9, 10].

Regarding the chemistry of the tetrahedral group 14 Zintl clusters $[E_4]^{4-}$, the number of species isolated from solution-based reactions is rather limited, even though A_4E_4 Zintl phases (A = alkali metal) with tetrahedral units have been known since 1953 [11]. $[Pb_4]^{4-}$ is the only known tetrahedral cluster anion that has been extracted from an A_4E_4 phase. Crystals of

$Rb_4Pb_4(NH_3)_2$ were obtained from ammonia solutions of Rb_4Pb_4 [12].

Recently tetrahedral $[Si_4]^{4-}$ and $[Ge_4]^{4-}$ clusters as well as heteroatomic clusters with the composition $[Si_{4-x}Ge_x]^{4-}$ have been isolated from $A_{12}E_{17}$ – a Zintl phase that simultaneously contains four-atomic $[E_4]^{4-}$ and nine-atomic $[E_9]^{4-}$ clusters – as CuMes-stabilized complexes $[E_4(CuMes)_2]^{4-}$ (Mes = mesityl) [13 – 15]. Bare $[Sn_4]^{4-}$ clusters are further accessible from reactions of alkali metals and elemental Sn or Ph_4Sn in liquid ammonia [12]. Related reactions of alkali metals and elemental Sn in molten 18-crown-6, in contrast, lead to the formation of nine-atomic $[Sn_9]^{4-}$ clusters [16]. The isolation of a tetrahedral tetrastannide from an ammonia solution of A_4Sn_4 has not yet been described in the literature. In the course of our investigations on soluble tetrahedral E_4 clusters we report here on results of reactions of A_4Sn_4 (A = Na, K) phases and CuMes in liquid ammonia.

Results and Discussion

Addition of liquid ammonia to solid mixtures of freshly prepared A_4Sn_4 phases (A = Na, K), CuMes and 18-crown-6 yields deep-red suspensions. After storing these reaction mixtures at $-70\,^\circ$C for several weeks, black crystals with hexagonal symmetry can be isolated. In the case of A = K a single-crystal X-ray structure determination has revealed strongly disordered Sn_4 clusters and no further electron density indicative of Cu atoms [17]. From a mixture of Na_4Sn_4, 18-crown-6 and CuMes, black block-shaped crystals could be isolated after several weeks of storage. A structure determination led to the composition $Na_4Sn_4(NH_3)_{13}$ (**1**, Fig. 1 and Table 1). Next to two tetrahedral tetrastannide anions eight sodium atoms and 26 solvate ammonia molecules are present. Fragments of the initially used reactant $(CuMes)_4$ or the sequestering agent 18-crown-6 are absent. The bond lengths within the $[Sn_4]^{4-}$ polyanion range between 2.946(1) and 2.950(1) Å and perfectly match those in the starting material Na_4Sn_4 (Sn–Sn distance: 2.975(2) – 2.981(2) Å) [18] and also in $A_4Sn_4(NH_3)_2$ (A = Rb, Cs; Sn–Sn distance: 2.896(1) – 2.963(1) Å) [12]. The bond angles are in the narrow range between 59.97(1)° and 60.00° and show that the structure of the $[Sn_4]^{4-}$ clusters only
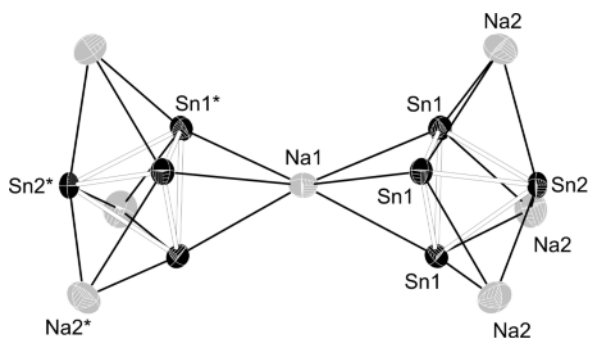
Fig. 1. Structure of two tetrahedral tetrastannide anions $[Sn_4]^{4-}$ and their direct sodium coordination sphere in $Na_4[Sn_4]\cdot(NH_3)_{13}$, **1**. Atoms are drawn at the 70 % probability level at 120 K. Solvate ammonia molecules are omitted for clarity.

Fig. 2. Unit cell of the crystal structure of $Na_4[Sn_4]\cdot(NH_3)_{13}$, **1**. Na atoms are drawn at the 70 % probability level at 120 K. Sn_4 tetrahedra are depicted with grey color. The N atoms of ammonia molecules are shown as open circles.

slightly deviates from an ideal tetrahedron $(60°)$. Each face of the $[Sn_4]^{4-}$ tetrahedron is capped by a sodium atom (Na1, Na2) with Sn–Na distances ranging between 3.321(3) and 3.423(1) Å (Fig. 1, compare Na–Sn distances in solid Na_4Sn_4: 3.355 – 3.534 Å) [18]. Na1 coordinates to two triangular faces of two $[Sn_4]^{4-}$ clusters with the triangles having an eclipsed conformation. The coordination sphere of the Na1 and Na2 atoms is completed by three solvate ammonia molecules each. A further Na atom is present in the crystal structure (Na3, see Fig. 2). Na3 coordinates to the N atoms of five ammonia molecules and shows no direct interaction with the Sn atoms of the $[Sn_4]^{4-}$ clusters. The Na–N distances in the range between 2.405(9) and 3.001(18) Å are indicative of coordinating ammonia molecules rather than amide ions. Thus a four-fold negative charge results for the cluster. In Na_4Sn_4 each alkali metal atom directly coordinates to the Sn atoms of tetrahedral Sn_4 clusters [18]. The structural motif $[Na_7Sn_8]^-$ (see Fig. 1) is unique for tetrahedral Zintl clusters isolated from solution reactions, but equivalents are already known in the neat solids $NaRb_7Si_8$ or $NaRb_7Ge_8$ [19, 20].

Conclusion

We investigated the solubility of A_4Sn_4 phases (A = Na, K) in liquid ammonia. In the presence of CuMes and 18-crown-6, Na_4Sn_4 was found to be soluble with formation of deep-red suspensions, from which crystals of the composition $Na_4Sn_4(NH_3)_{13}$ can be grown. The role of CuMes and the sequestering

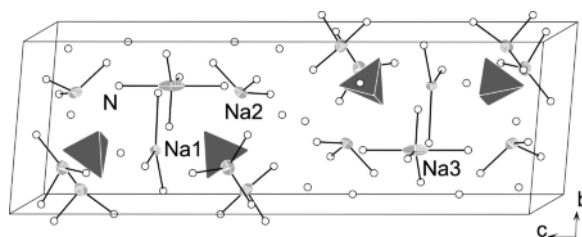Table 1. Selected crystallographic and refinement data for compound **1**.

	1
Empirical formula	$H_{39}N_{13}Na_4Sn_4$
Formula weight, g mol^{-1}	788.16
Temperature, K	120(2)
Crystal size, mm^3	$0.3 \times 0.2 \times 0.2$
Crystal system	hexagonal
Space group	$P6_3/m$
Unit cell dimensions	
a, Å	10.5623(4)
b, Å	10.5623(4)
c, Å	29.6365(16)
Volume, Å^3 / Z	2863.3(2) / 4
Calculated density, g cm^{-3}	1.83
Absorption coefficient, mm^{-1}	3.5
$F(000)$, e	1496
θ range, deg	3.04–26.23
Refl. measured / unique / R_{int}	28083 / 1972 / 0.0599
Completeness, %	99.7
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1972 / 0 / 73
Goodness-of-fit on F^2	1.058
R_1 / wR_2 [$I > 2\sigma(I)$]	0.040 / 0.115
R_1 / wR_2 (all data)	0.056 / 0.120
Largest diff. peak / hole, e Å^{-3}	3.948 / −0.671

agent for the formation of soluble Sn_4 clusters is currently under investigation.

Experimental Section

General

All experiments were performed under argon atmosphere using standard Schlenk and glove box techniques. CuMes was prepared according to literature [21]. 18-Crown-6 was sublimed under dynamic vacuum at 80 °C. Liquid ammonia was dried and stored over sodium metal.

Precursor synthesis

The binary Zintl phases A_4Sn_4 (A = Na, K) [18, 22–24] were synthesized in fused tantalum tubes filled with a mixture of 184 mg (8.00 mmol) Na and 950 mg (8.00 mmol) Sn or 313 mg (8.00 mmol) K and 950 mg (8.00 mmol) Sn. Each tantalum tube was heated to 500 °C for 48 h and afterwards cooled to room temperature with a rate of 1.0 °C min^{-1}.

Powder X-ray diffraction

Phase analysis of A_4Sn_4 was performed using a Stoe STADI P diffractometer (Ge(111) monochromator; Cu$K_{\alpha 1}$ radiation) equipped with a linear position-sensitive detector. For sample preparation the products were finely ground in an agate mortar and filled into sealed glass capillaries. The sample was measured in Debye-Scherrer mode ($2\theta_{max} = 60°$). Data analysis was carried out using the Stoe WINXPOW software package [25].

Compound 1

Na$_4$Sn$_4$ (42.5 mg; 0.075 mmol), 18-crown-6 (36 mg; 0.135 mmol) and MesCu (14 mg; 0.075 mmol) were weighed into a Schlenk tube and dissolved in approximately 1 mL of liquid ammonia at −78 °C. The resulting deep-red suspension was kept at −70 °C. 1 crystallized as black blocks after 19 weeks with approximately 25 % yield. The analogous reaction leads in the case of A = K to a few crystals with hexagonal symmetry [17].

Single-crystal structure determination

The air- and moisture-sensitive as well as thermally very unstable crystal of 1 was transferred from the mother liquor into perfluoropolyalkyl ether oil at 213 K under a cold stream of N$_2$. The selected single crystal was fixed in a glass capillary and positioned in a cold stream of N$_2$ (120 K) using the crystal cap system. Data collection: Oxford-Diffraction Xcalibur3 diffractometer (MoK_α radiation). The structure was solved by Direct Methods (SHELXS-97) [26] and refined by full-matrix least-squares calculations against F^2 (SHELXL-97) [27].

Further details of the crystal structure investigation of 1 can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository number CSD-425862 (1).

[1] J. D. Corbett, *Chem. Rev.* **1985**, *85*, 383.

[2] J. D. Corbett, *Structure and Bonding* **1997**, *87*, 157.

[3] T. F. Fässler, *Coord. Chem. Rev.* **2001**, *215*, 347.

[4] S. Scharfe, T. F. Fässler, *Philosoph. Trans.* **2010**, *368*, 1265.

[5] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50*, 3630.

[6] A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, Y. Grin, *Nature* **2006**, *443*, 320.

[7] T. F. Fässler, *Angew. Chem. Int. Ed.* **2007**, *46*, 2572.

[8] A. J. Karttunen, T. F. Fässler, M. Linnolahti, T. A. Pakkanen, *Chem. Phys. Chem.* **2010**, *11*, 1944.

[9] J. M. Goicoechea, S. C. Sevov, *Organometallics* **2006**, *25*, 4530.

[10] *Zintl Ions: Principles and Recent Developments*, Book Series: Structure and Bonding, Ed.: T. F. Fässler, Volume **140**, Springer-Verlag, Heidelberg, **2011**.

[11] R. E. Marsh, D. P. Shoemaker, *Acta Crystallogr.* **1953**, *6*, 197.

[12] K. Wiesler, K. Brandl, A. Fleischmann, N. Korber, *Z. Anorg. Allg. Chem.* **2009**, *635*, 508.

[13] M. Waibel, F. Kraus, S. Scharfe, B. Wahl, T. F. Fässler, *Angew. Chem. Int. Ed.* **2010**, *49*, 6611.

[14] M. Waibel, G. Raudaschl-Sieber, T. F. Fässler, *Chem. Eur. J.* **2011**, *17*, 13391.

[15] S. Stegmaier, M. Waibel, A. Henze, L.-A. Jantke, A. J. Karttunen, T. F. Fässler, *J. Am. Chem. Soc.* **2012**, *134*, 14450.

[16] T. F. Fässler, R. Hoffmann, *Angew. Chem. Int. Ed.* **1999**, *38*, 543.

[17] Hexagonal cell parameters: $a = b = 13.0480(2)$, $c = 39.029(1)$ Å, $V = 5754.5(3)$ Å^3.

[18] M. Baitinger, Y. Grin, R. Kniep, H. G. v. Schnering, *Z. Kristallogr.* **1999**, *214*, 453.

[19] T. Goebel, Y. Prots, A. Ormeci, O. Pecher, F. Haarmann, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1.

[20] J. Llanos, R. Nesper, H. G. v. Schnering, *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 998.

[21] E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *Organometallics* **1989**, *8*, 1067.

[22] M. Baitinger, Y. Grin, R. Kniep, H. G. v. Schnering, *Z. Kristallogr.* **1999**, *214*, 457.

[23] I. F. Hewaidy, E. Busmann, W. Klemm, *Z. Anorg. Allg. Chem.* **1964**, *328*, 283.

[24] W. Müller, K. Volk, *Z. Naturforsch.* **1977**, *32b*, 709.

[25] WinXPow (version 2.08), Stoe & Cie GmbH, Darmstadt (Germany) **2003**.

[26] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.

[27] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.