

First Incorporation of the Tetrahedral $[\text{Sn}_4]^{4-}$ Cluster into a Discrete Solvate $\text{Na}_4[\text{Sn}_4] \cdot (\text{NH}_3)_{13}$ from Solutions of Na_4Sn_4 in Liquid Ammonia

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Treatment of solutions of Na_4Sn_4 in liquid ammonia with CuMes (Mes = mesityl) and 18-crown-6 afforded crystals of the composition $\text{Na}_4[\text{Sn}_4] \cdot (\text{NH}_3)_{13}$. The structure features anionic units $[\text{Na}_7[\text{Sn}_4]_2]^-$ 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 $[\text{E}_9]^{4-}$ ($\text{E} = \text{Si}–\text{Pb}$) 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 intermetallic clusters [1–5, 9, 10].

Regarding the chemistry of the tetrahedral group 14 Zintl clusters $[\text{E}_4]^{4-}$, the number of species isolated from solution-based reactions is rather limited, even though A_4E_4 Zintl phases ($\text{A} = \text{alkali metal}$) with tetrahedral units have been known since 1953 [11]. $[\text{Pb}_4]^{4-}$ is the only known tetrahedral cluster anion that has been extracted from an A_4E_4 phase. Crystals of

$\text{Rb}_4\text{Pb}_4(\text{NH}_3)_2$ were obtained from ammonia solutions of Rb_4Pb_4 [12].

Recently tetrahedral $[\text{Si}_4]^{4-}$ and $[\text{Ge}_4]^{4-}$ clusters as well as heteroatomic clusters with the composition $[\text{Si}_{4-x}\text{Ge}_x]^{4-}$ have been isolated from $\text{A}_{12}\text{E}_{17}$ – a Zintl phase that simultaneously contains four-atomic $[\text{E}_4]^{4-}$ and nine-atomic $[\text{E}_9]^{4-}$ clusters – as CuMes-stabilized complexes $[\text{E}_4(\text{CuMes})_2]^{4-}$ (Mes = mesityl) [13–15]. Bare $[\text{Sn}_4]^{4-}$ 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 $[\text{Sn}_9]^{4-}$ 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 ($\text{A} = \text{Na}, \text{K}$) phases and CuMes in liquid ammonia.

Results and Discussion

Addition of liquid ammonia to solid mixtures of freshly prepared A_4Sn_4 phases ($\text{A} = \text{Na}, \text{K}$), CuMes and 18-crown-6 yields deep-red suspensions. After storing these reaction mixtures at -70°C for several weeks, black crystals with hexagonal symmetry can be isolated. In the case of $\text{A} = \text{K}$ 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 $\text{Na}_4\text{Sn}_4(\text{NH}_3)_{13}$ (**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 $(\text{CuMes})_4$ or the sequestering agent 18-crown-6 are absent. The bond lengths within the $[\text{Sn}_4]^{4-}$ 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 $\text{A}_4\text{Sn}_4(\text{NH}_3)_2$ ($\text{A} = \text{Rb}, \text{Cs}$; Sn–Sn distance: 2.896(1)–2.963(1) Å) [12]. The bond angles are in the narrow range between $59.97(1)^\circ$ and 60.00° and show that the structure of the $[\text{Sn}_4]^{4-}$ clusters only

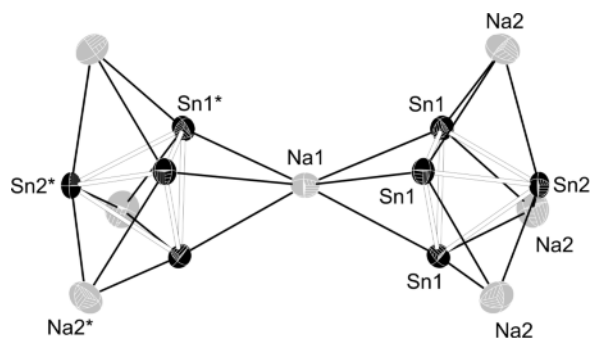


Fig. 1. Structure of two tetrahedral tetrastannide anions $[\text{Sn}_4]^{4-}$ and their direct sodium coordination sphere in $\text{Na}_4[\text{Sn}_4] \cdot (\text{NH}_3)_{13}$, **1**. Atoms are drawn at the 70% probability level at 120 K. Solvate ammonia molecules are omitted for clarity.

slightly deviates from an ideal tetrahedron (60°). Each face of the $[\text{Sn}_4]^{4-}$ 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 $[\text{Sn}_4]^{4-}$ 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 $[\text{Sn}_4]^{4-}$ 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 $[\text{Na}_7\text{Sn}_8]^-$ (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 ($\text{A} = \text{Na}, \text{K}$) 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 $\text{Na}_4\text{Sn}_4(\text{NH}_3)_{13}$ can be grown. The role of CuMes and the sequestering

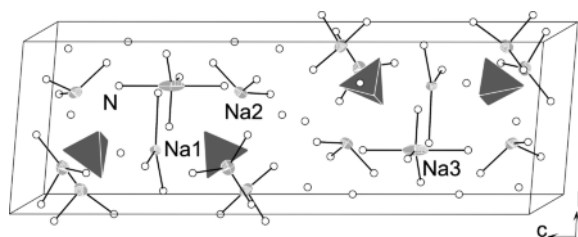


Fig. 2. Unit cell of the crystal structure of $\text{Na}_4[\text{Sn}_4] \cdot (\text{NH}_3)_{13}$, **1**. Na atoms are drawn at the 70% probability level at 120 K. Sn_4 tetrahedra are depicted with grey color. The N atoms of ammonia molecules are shown as open circles.

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

	1
Empirical formula	$\text{H}_{39}\text{N}_{13}\text{Na}_4\text{Sn}_4$
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, $\text{\AA}^3 / Z$	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 \AA^{-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; $CuK_{\alpha 1}$ 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 ($2\theta_{\max} = 60^\circ$). Data analysis was carried out using the Stoe WINXPow software package [25].

Compound 1

Na_4Sn_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).

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- [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, $V = 5754.5(3)$ Å³.
- [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.