

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 intermetallic 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 reagent ($CuMes)_4$ 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) $^{\circ}$ and 60.00 $^{\circ}$ and show that the structure of the $[Sn_4]^{4-}$ clusters only

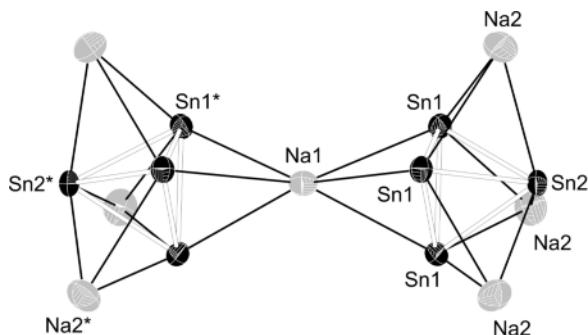


Fig. 1. Structure of two tetrahedral tetrastannide anions $[\text{Sn}_4]^{4-}$ and their direct sodium coordination sphere in $\text{Na}_4[\text{Sn}_4]\cdot(\text{NH}_3)_{13}$, **1**. Atoms are drawn at the 70 % probability level at 120 K. Solvate ammonia molecules are omitted for clarity.

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 $A_4\text{Sn}_4$ phases ($A = \text{Na, K}$) 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 $\text{Na}_4\text{Sn}_4(\text{NH}_3)_{13}$ can be grown. The role of CuMes and the sequestering

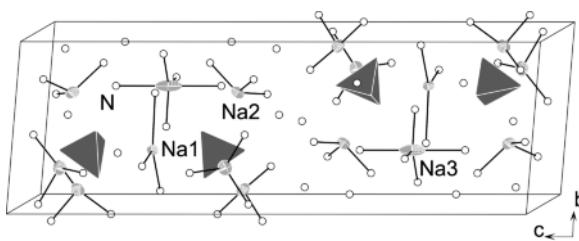


Fig. 2. Unit cell of the crystal structure of $\text{Na}_4[\text{Sn}_4]\cdot(\text{NH}_3)_{13}$. 1. Na atoms are drawn at the 70 % probability level at 120 K. Sn_4 tetrahedra are depicted with grey color. The N atoms of ammonia molecules are shown as open circles.

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 × 0.2 × 0.2
Crystal system	hexagonal
Space group	$P\bar{6}_3/m$
Unit cell dimensions	
<i>a</i> , Å	10.5623(4)
<i>b</i> , Å	10.5623(4)
<i>c</i> , Å	29.6365(16)
Volume, Å ³ / <i>Z</i>	2863.3(2) / 4
Calculated density, g cm ⁻³	1.83
Absorption coefficient, mm ⁻¹	3.5
<i>F</i> (000), e	1496
θ range, deg	3.04–26.23
Refl. measured / unique / <i>R</i> _{int}	28083 / 1972 / 0.0599
Completeness, %	99.7
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1972 / 0 / 73
Goodness-of-fit on <i>F</i> ²	1.058
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.040 / 0.115
<i>R</i> ₁ / <i>wR</i> 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; $CuK\alpha_1$ 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-Diffracton Xcalibur3 diffractometer ($MoK\alpha$ 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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