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

Markus Waibel and Thomas F. Fässler
Department Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. T. F. Fässler. Tel: (+49) 89-289-13186.
E-mail: thomas.faessler@lrz.tum.de
89-289-13131. Fax: (+49) 89-289-13186.

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Treatment of solutions of \(\text{Na}_4\text{Sn}_4\) in liquid ammonia with CuMes (Mes = mesityl) and 18-crown-6 afforded crystals of the composition \(\text{Na}_4[\text{Sn}_4]^{-}\)·(\(\text{NH}_3\))\(_3\). The structure features anionic units \([\text{Na}_3\text{Sn}_4]^{-}\) 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 \([\text{E}_2]^{3-}\) (\(\text{E} = \text{Si–Pb}\)) 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 \(\text{E}_2\) clusters are predicted to be stable [7, 8]. Additionally, \(\text{E}_2\) 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 \([\text{E}_4]^{4-}\), the number of species isolated from solution-based reactions is rather limited, even though \(\text{As}_2\text{E}_4\) Zintl phases (\(\text{A} = \text{alkali metal}\)) with tetrahedral units have been known since 1953 [11]. \([\text{Pb}_4]^{3-}\) is the only known tetrahedral cluster anion that has been extracted from an \(\text{As}_4\text{E}_4\) phase. Crystals of \(\text{Rb}_3\text{Pb}_4(\text{NH}_3)_2\) were obtained from ammonia solutions of \(\text{Rb}_3\text{Pb}_4\) [12].

Recently tetrahedral \([\text{Si}_4]^{4-}\) and \([\text{Ge}_4]^{4-}\) clusters as well as heteroatomic clusters with the composition \([\text{Si}_4\text{–}_{x}\text{Ge}_4]^{4-}\) have been isolated from \(\text{A}_2\text{E}_4\text{F}_{12}\) – a Zintl phase that simultaneously contains four-atomic \([\text{E}_4]^{4-}\) and nine-atomic \([\text{E}_3]^{4-}\) 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\(_4\)Sn 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 \([\text{Sn}_9]^{3-}\) clusters [16]. The isolation of a tetrahedral tetrastannide from an ammonia solution of \(\text{A}_4\text{Sn}_4\) has not yet been described in the literature. In the course of our investigations on soluble tetrahedral \(\text{E}_4\) clusters we report here on results of reactions of \(\text{A}_4\text{Sn}_4\) (\(\text{A} = \text{Na, K}\)) phases and CuMes in liquid ammonia.

Results and Discussion

Addition of liquid ammonia to solid mixtures of freshly prepared \(\text{A}_4\text{Sn}_4\) phases (\(\text{A} = \text{Na, K}\)), CuMes and 18-crown-6 yields deep-red suspensions. After storing these reaction mixtures at \(70\text{°C}\) 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 \(\text{Sn}_9\) clusters and no further electron density indicative of Cu atoms [17]. From a mixture of \(\text{Na}_4\text{Sn}_4\), 18-crown-6 and CuMes, black block-shaped crystals could be isolated after several weeks of storage. A structure determination led to the composition \(\text{Na}_3\text{Sn}_4(\text{NH}_3)_3\) (I, 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 \([\text{Sn}_4]^{3-}\) polyanion range between 2.946(1) and 2.950(1) Å and perfectly match those in the starting material \(\text{Na}_4\text{Sn}_4\) (Sn–Sn distance: 2.975(2) – 2.981(2) Å) [18] and also in \(\text{As}_4\text{E}_4(\text{NH}_3)_2\) (\(\text{A} = \text{Rb, Cs}\); 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 \([\text{Sn}_4]^{3-}\) clusters only...
Note

Fig. 1. Structure of two tetrahedral tetrastannide anions \([\text{Sn}_4]^4^−\) and their direct sodium coordination sphere in \(\text{Na}_4[\text{Sn}_4](\text{NH}_3)_{13}\). I. 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 \(\text{Na}_4\text{Sn}_4\): 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 \(\text{Na}_4\text{Sn}_4\) each alkali metal atom directly coordinates to the Sn atoms of tetrahedral Sn3 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 \(\text{NaRb}_7\text{Si}_8\) or \(\text{NaRb}_7\text{Ge}_8\) [19, 20].

Conclusion

We investigated the solubility of \(\text{A}_4\text{Sn}_4\) phases (\(\text{A} = \text{Na, K}\)) in liquid ammonia. In the presence of CuMes and 18-crown-6, \(\text{Na}_4\text{Sn}_2\) 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 agent for the formation of soluble Sn4 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 A₄Sn₄ (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 A₄Sn₄ was performed using a Stoe STADI P diffractometer (Ge(111) monochromator; CuKα 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 (2θmax = 60°).

Data analysis was carried out using the Stoe W XPOW software package [25].

Compound 1

Na₄Sn₄ (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 N₂. The selected single crystal was fixed in a glass capillary and positioned in a cold stream of N₂ (120 K) using the crystal cap system. Data collection: Oxford-Diffraction Xcalibur3 diffractometer (MoKα radiation). The structure was solved by Direct Methods (SHELXS-97) [26] and refined by full-matrix least-squares calculations against F² (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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