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Synthesis and crystal structure of $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ and $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ †

Nikolaus Korber * and Andrea Fleischmann

Institut für Anorganische Chemie der Universität Regensburg, Universitätsstraße 31,
93053 Regensburg, Germany. Fax: +49 941 9431812;
E-mail: nikolaus.korber@chemie.uni-regensburg.de

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The reduction of an excess of Sn or Pb with a concentrated solution of Li in liquid ammonia yielded black crystals of $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ or $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ as main product, respectively. The compounds are isotypic and crystallise in space group $P2_1/c$. They contain the isolated Zintl anions Sn_9^{4-} and Pb_9^{4-}, which form slightly distorted monocapped square antiprisms. The lead compound is the first example of a "naked" Pb_9^{4-} cage without contacts to metal atoms.

Introduction

Most of the early work on the homoatomic polyanions of the heavier post-transition elements used anhydrous liquid ammonia as a solvent. Joannis observed the change of colour from deep blue to green accompanying the reaction of alkali metals with an excess of lead in this solvent,[1] and Kraus[2] and Smyth[3] were able to show by electrolytic investigations that similar solutions contained ionic alkali metal polystannides and polyplumbides. The composition of these compounds was established by Zintl and co-workers[4] using potentiometric titrations in liquid ammonia; they identified Na_4Sn_9 and Na_4Pb_9 as the species with the highest Group 14 metal content. In recognition of Zintl's pioneering work in this field, Laves and Kohlschütter later proposed the term "Zintl anions" for the homoatomic polyanions of the heavier post-transition elements.[5] Zintl and his co-workers also tried to obtain crystalline solids by evaporation of the solvent, but failed because of the tendency of the resulting compounds containing large amounts of ammonia of crystallisation to lose the solvent molecules at below room temperature. The low thermal stability of these ammoniates was probably the reason why the successful later crystallographic work by Kummer and Diehl[6] and Corbett[7] concentrated on ethylenediamine (en) as a solvent. However, this approach implied the necessity to abandon the direct reduction of the main group element by alkali metal solutions for the extraction of binary solids like Na_2Sn_5.[8] The use of 2,2,2-cryptand (2,2,2)[9] introduced by Corbett[7] as a sequestering ligand for the alkali metal cations in Zintl anion chemistry resulted in a major breakthrough followed by the structural characterisation of a number of homo- and hetero-atomic naked main group polyanions; this procedure has remained the method of choice until now.

As modern X-ray crystallography makes possible the structure determination even of thermally very unstable compounds, we are interested in investigating the crystalline, ammonia-rich products which are obtained using the original direct reduction approach in liquid ammonia. Until now, we have reported on the reactions of the Group 15 elements P, As and Sb with Li in liquid ammonia. We identified $[Li(NH_3)_4]_4[P_{14}]$,[10] $[Li(NH_3)_4]_3[As_7]\cdot NH_3$[10] and $[Li(NH_3)_4]_3[Li_2(NH_3)_2Sb_5]\cdot 2NH_3$[11] as the products with the highest main group element content per formula unit, which contain the polyanions P_{14}^{4-}, As_7^{3-} and Sb_5^{5-}. The novel cyclic Sb_5^{5-} has an unprecedented high charge-per-atom ratio for Zintl anions obtained from solution. The tetraamminelithium complex $[Li(NH_3)_4]^+$ occurring in the above named compounds is, even given its low stability, a useful counter ion, which is isoelectronic to the tetramethylammonium ion. While the latter standard voluminous non-co-ordinating counter ion cannot be introduced by direct reductions and has to be added in a metathesis reaction after a different reducing agent has been employed, in the lithium–ammonia system the reduced form $[Li(NH_3)_4]$ is known.[12] Thus, a straightforward reduction of main group elements using this "expanded metal" can be performed. A similar approach, which also circumvents the usual extraction of binary solids in the preparation of homoatomic Zintl anions, is the recent use of molten crown ether/alkali metal mixtures published by Fässler and Hoffmann.[13] In these reactions the alkali metal complexes used as counter ions in the generated Zintl anion compounds are also introduced in their reduced form as electrides or alkalides, opening an easy access to a number of polyanions like Sn_9^{4-}, As_7^{3-}, Sb_7^{3-} and Te_4^{2-}.

The present work reports on the reaction of solutions of lithium in liquid ammonia with an excess of Sn and Pb, respectively. The crystalline products $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ and $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ were characterised structurally by low-temperature X-ray crystallography.

Results and discussion

The reaction of concentrated solutions of Li in anhydrous liquid ammonia with an excess of Sn at 233 K resulted in solutions which changed from the familiar deep blue of the alkali metal solutions to a deep red after approximately 24 h. Over the period of a week they had turned nearly black, and two products with distinctly different crystal shapes had precipitated. The major fraction (approximately 70%) was black prism-shaped crystals, which were shown by X-ray crystallography to contain Sn_9^{4-} anions. The minor fraction was black needles, on which only a preliminary crystallographic study could be performed, proving the presence of Sn_4^{4-} anions in this product. Subsequent experiments with a Li:Sn starting stoichiometry of 4:9 showed that some small amounts of the needle shaped product were always present as a by-product, while a Li:Sn ratio of 1:1 led to almost pure Sn_4^{4-} containing product.

Analogous reactions between Li and Pb in liquid ammonia produced very similar results; the initial colour of the solutions, after the blue of unchanged Li had disappeared, was a deep

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† Dedicated to Professor H. Brunner on the occasion of his 65th birthday.

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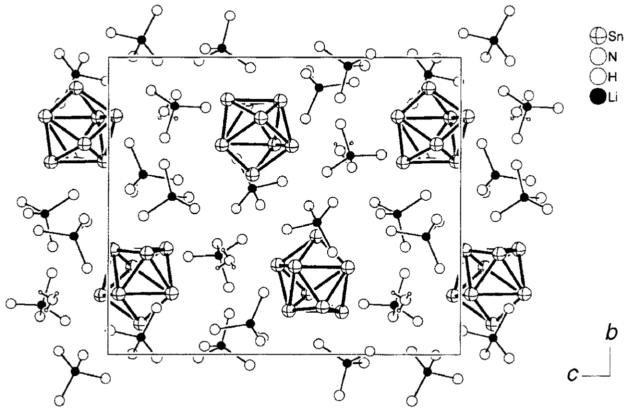

Fig. 1 Cut-out of the structure of $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ projected on the *b*–*c* plane.

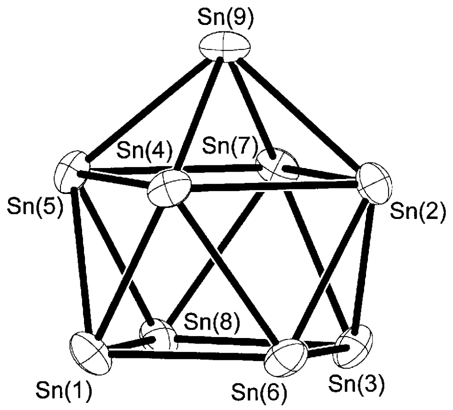

Fig. 2 ORTEP[16] plot of the Sn_9^{4-} cage in $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ (70% probability ellipsoids). Selected interatomic distances [Å]: Sn(1)–Sn(6) 2.9715(9), Sn(1)–Sn(8) 2.9508(7), Sn(1)–Sn(4) 2.9514(8), Sn(1)–Sn(5) 2.9759(7), Sn(2)–Sn(9) 2.9456(8), Sn(2)–Sn(3) 2.9649(8), Sn(2)–Sn(6) 2.9510(7), Sn(2)–Sn(4) 3.2165(8), Sn(2)–Sn(7) 3.1895(8), Sn(3)–Sn(7) 2.9660(7), Sn(3)–Sn(6) 2.9691(7), Sn(3)–Sn(8) 2.9470(9), Sn(4)–Sn(9) 2.9336(7), Sn(4)–Sn(6) 2.9532(8), Sn(4)–Sn(5) 3.1910(8), Sn(5)–Sn(9) 2.9468(9), Sn(5)–Sn(8) 2.9710(8), Sn(5)–Sn(7) 3.2315(8), Sn(7)–Sn(9) 2.9267(8) and Sn(7)–Sn(8) 2.9689(7).

green, which is in accordance with the early observations of Joannis.[1] The reactions also yielded needle- and prism-shaped crystals; only for the latter crystals a structure determination could be performed.

The single crystal X-ray structural analysis showed the structures of the prism-shaped crystals of the tin and lead reductions to be isotypic. They are ionic solids of the composition $[Li(NH_3)_4]_4[E_9]\cdot NH_3$ (E = Sn or Pb) with well separated tetraamminelithium cations and E_9^{4-} anions (closest N···E distance 3.83 Å in the tin compound) (Fig. 1). The Zintl anions show the familiar monocapped square antiprismatic geometry. The dimensions of the Sn_9^{4-} cage (Fig. 2) are similar to those of previously determined structures.[13–15] However, it should be noted that only the first well resolved structure analysis of Sn_9^{4-} in $[Na(2,2,2)]_4[Sn_9]$ by Corbett and Edwards[14] is of truly "naked" anions without any contacts to metal cations, while K···Sn contacts are present in $[K(2,2,2)]_3K[Sn_9]$,[15] $[K(18\text{-crown-}6)]_3K[Sn_9]\cdot en$[13] and $[K(18\text{-crown-}6)]_4[Sn_9]$.[13] Fässler and Hoffmann have found that such contacts may cause significant distortions of Sn_9^{4-} away from the C_{4v} symmetry of an ideal monocapped square antiprism towards the tricapped trigonal prism geometry (point symmetry D_{3h}),[13] similar to the geometry of the less highly charged Sn_9^{3-} species.[17] For the description of this distortion, the diagonal distances Sn(6)–Sn(8) and Sn(3)–Sn(1) at the uncapped face of the cage and the torsion angle Sn(6)–Sn(3)–Sn(8)–Sn(1) have been established as useful criteria.[13] The diagonal distances are equal and the angle is zero for ideal C_{4v} geometry; distortion towards a tricapped prismatic shape of the cage implies differing diagonal distances and a torsion angle closer to the positive values of the corresponding torsion angles Sn(4)–Sn(1)–Sn(5)–Sn(9) and Sn(2)–Sn(9)–Sn(7)–Sn(3). In $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ the diagonal distances are Sn(1)···Sn(3) 4.143(1) Å and Sn(6)···Sn(8) 4.228(1) Å, which indicates a small but significant deviation from ideal C_{4v} symmetry, and agrees well with the analogous distances in $[Na(2,2,2)]_4[Sn_9]$ (4.163 and 4.205 Å).[14] The torsion angle Sn(6)–Sn(3)–Sn(8)–Sn(1) has a negative value of −1.06(2)° in $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$, which shows that this distortion occurs not towards D_{3h} symmetry but rather in the opposite direction, causing Sn(6)–Sn(8) to be not an outward but an inward facing edge. This is also true for $[Na(2,2,2)]_4[Sn_9]$; the torsion angle of −1.85° here indicates an even more pronounced negative deviation of the ideal planar arrangement. On the other hand, in $[K(18\text{-crown-}6)]_4[Sn_9]$ the Sn_9^{4-} cage has a corresponding torsion angle of 15°. To our knowledge, $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$ is the first compound without macrocyclic alkali metal ligands in which the Sn_9^{4-} anion has been proven to exist by X-ray crystallography; the structure of the closely related $[N(CH_3)_4]_4Sn_9$ prepared by Haushalter and co-workers was not determined due to thermal instability.[18]

The Pb_9^{4-} cage in $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ shows, due to the isotypic crystal structure, essentially the same structural features as those of Sn_9^{4-} in $[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$, if one allows for the generally larger Pb–Pb distances (numbering schema as in Fig. 2). The diagonal distances Pb(1)···Pb(3) 4.301(1) Å and Pb(6)···Pb(8) 4.414(1) Å and the torsion angle Pb(6)–Pb(3)–Pb(8)–Pb(1) −1.46(2)° at the base of the cage show the same deviation from C_{4v} symmetry. Nevertheless, $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ is the first compound characterised by X-ray structural analysis in which the Pb_9^{4-} cage has no contacts to metal atoms. In $[K(2,2,2)]_3K[Pb_9]$,[19] Pb_9^{4-} is co-ordinated by two K^+ ions in an infinite chain, while in $[K(2,2,2)]_4Cr(CO)_3Pb_9$[20] the chromium atom occupies the open face of the cage. In the binary solid K_4Pb_9, Pb_9^{4-} is present in two different geometries (monocapped square antiprism and an elongated tricapped trigonal prism)[21] due to numerous cation–anion contacts. However, the disturbance caused by the two potassium contacts in $[K(2,2,2)]_3K[Pb_9]$ is minimal, and the Pb–Pb distances in $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ are very similar to those in the latter compound. The distances vary from 3.053(1) to 3.068(1) Å for the contacts of apical Pb(9) (3.039(1) to 3.094(2) Å in $[K(2,2,2)]_3K[Pb_9]$). In the open square face Pb–Pb contacts were found to range from 3.069(1) to 3.094(1) Å (3.073(1) to 3.103(2) Å in $[K(2,2,2)]_3K[Pb_9]$), and in the capped square from 3.330(1) to 3.395(1) Å (3.317(2) to 3.434(2) Å in $[K(2,2,2)]_3K[Pb_9]$). The consistently lower spread for the sets of distances which should be equal in an ideal monocapped square antiprism in $[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$ indicates that the "naked" cage in this compound is closer to C_{4v} symmetry than the anion in $[K(2,2,2)]_3K[Pb_9]$.

The $Li(NH_3)_4^+$ counter ions are roughly tetrahedral, their observed structural features being in agreement with previously determined values.[11] The N atom of the single ammonia molecule of solvation has two distances to adjacent N atoms (3.223(1) and 3.257(7) Å for the lead compound and 3.218(1) and 3.237(6) Å for the tin), which may indicate weak hydrogen bonding (the corresponding distances in cubic solid ammonia are 3.38 Å[22]).

The synthesis and structure determination of $[Li(NH_3)_4]_4[E_9]\cdot NH_3$ (E = Sn or Pb) prove that direct reduction of post transition elements by lithium in liquid ammonia is a workable alternative to the extraction of binary solids with organic solvents and cryptands for the preparation of Zintl ion compounds. If one is prepared to accept the necessity of low temperature conditions, the simplicity of this approach as well as the low costs involved facilitate not only the characterisation of but further chemistry with these excellent homoatomic building blocks.

Experimental

All manipulations were carried out under dry argon in all-glass reaction and handling vessels that were dried *in vacuo*. Ammonia (Bayer AG) was made anhydrous by distilling it first from sodium, then from potassium, and was stored as a potassium–ammonia solution at 195 K. Lithium grains (Aldrich) and tin and lead shot (Kraemer&Martin) were dried *in vacuo* at 333 K for 2 days and stored under argon.

General procedure for $[Li(NH_3)_4]_4[E_9]\cdot NH_3$ (E = Sn or Pb)

Into a Schlenk-type reaction vessel 0.02 mol of Sn or Pb and the stoichiometric amount of Li were placed. *ca.* 30 mL ammonia were frozen into the vessel at 77 K. The vessel was allowed to warm slowly to 233 K. The reactions were complete after *ca.* two weeks at 233 K. Upon removal of the solvent the compounds apparently lose the ammonia of solvation; the crystalline products turn into amorphous powders, which were extremely sensitive to air and moisture.

For the crystal preparation we adapted the technique described by Kottke and Stalke[23] to our needs. Small amounts of the reaction products were transferred directly from the liquid ammonia into perfluoroether (RS 3000 and RS 216, Riedel de Haen) which was cooled to 213 K by a stream of cold nitrogen. Single crystals suitable for X-ray structure analysis were selected with the help of a microscope and picked up on the tip of a capillary mounted on a goniometer head. The crystals were then immediately submerged in liquid nitrogen and transferred to the diffractometer.

Crystal data and structure refinement

$[Li(NH_3)_4]_4[Sn_9]\cdot NH_3$. $H_{51}Li_4N_{17}Sn_9$, $M = 1385.55$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.529(1)$, $b = 17.700(1)$, $c = 21.190(1)$ Å, $\beta = 98.93(1)°$, $V = 3901.2(4)$ Å^3, $Z = 4$, μ(Mo-Kα) = 5.68 mm^{-1}, reflections measured 25889, independent reflections 6728 ($R_{int} = 0.063$), $T = 123(2)$ K. The H atoms were located by Fourier difference synthesis; those bound to N atoms attached to Li were refined in a riding mode and the H atoms of the NH_3 molecule of solvation were refined free (SHELXL 97[24]). The final $wR2$ value was 0.0568 [corresponds to a conventional R value of 0.0329 using only reflections with $I > 2\sigma(I)$].

$[Li(NH_3)_4]_4[Pb_9]\cdot NH_3$. $H_{51}Li_4N_{17}Pb_9$, $M = 2182.05$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.611(1)$, $b = 17.864(1)$, $c = 21.414(2)$ Å, $\beta = 99.05(1)°$, $V = 4008.6(5)$ Å^3, $Z = 4$, μ(Mo-Kα) = 37.67 mm^{-1}, reflections measured 19948, independent reflections 7491 ($R_{int} = 0.076$), $T = 123(2)$ K. The final $wR2$ value was 0.0753 [corresponds to a conventional R value of 0.0378 using only reflections with $I > 2\sigma(I)$].

CCDC reference number 186/2307.

See http://www.rsc.org/suppdata/dt/b0/b008123j/ for crystallographic files in .cif format.

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