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Reaction of Sn_4^{4-} in liquid ammonia: the formation of $Rb_6[(η^2-Sn_4)Zn(η^3-Sn_4)]·5NH_3$†

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The reaction of Rb_4Sn_4 with $ZnPh_2$ in liquid ammonia in the presence of [2.2.2]-cryptand yielded crystals of $Rb_6[(η^2-Sn_4)Zn(η^3-Sn_4)]·5NH_3$, which could be characterized by single crystal X-ray diffraction. This is the first example of a successful solution reaction of the highly charged tetrahedral Sn_4^{4-} anions. The homoleptic $[E_4ZnE_4]^{6-}$ complex (E = tetrel element) was previously known only for E=Ge and Si/Ge.

Homoatomic polyanions of group 14 or 15 are a very fascinating class of compounds as they can be considered as molecular, discrete building blocks of the main group elements.[1] These polyanions are known from solid state materials, where the term *Zintl* phases holds true.[2] Some of the *Zintl* phases are soluble in appropriate solvents like ethylenediamine or liquid ammonia and undergo versatile chemical transformations with different (post-) transition metal complexes as well as main group element compounds. These investigations have been limited to the well investigated E_9^{4-} (E=Si–Pb) anions and a large number of reaction products can be found in the literature.[1] In contrast, only very little is known about the solution behavior of the more highly reduced tetrahedral species E_4^{4-}, which exist in the binary *Zintl* phases A_4E_4 and $A_{12}E_{17}$.[2–9] Only very few compounds are reported for derivatives of these anions. By reacting $K_6Rb_6Si_{17}$ or $K_{14}ZnGe_{16}$, respectively, with MesCu in liquid ammonia compounds including the $[(MesCu)_2E_4]^{4-}$ (E=Si[10] or Ge[11]) anion could be crystallized. The use of mixed $K_{12}(Si,Ge)_{17}$ precursor materials reacted with diphenylzinc resulted in the formation of $K_6ZnSi_{4.1(1)}Ge_{3.9(1)}·11NH_3$.[12] The lack of similar results for the heavier homologues tin and lead is conspicuous. A possible explanation

could be that the potential precursor materials A_4E_4 were supposed to be insoluble until very recently.[11]

In preliminary investigations we were able to show that Rb_4Sn_4 is soluble in anhydrous liquid ammonia, which is the best solvent for these very air and moisture sensitive compounds.[13] However, ^{119}Sn NMR experiments on ammonia solutions of Rb_4Sn_4 demonstrated that the use of pure liquid ammonia, without any further additives, exclusively yields Sn_9^{4-} clusters by fast rearrangement of the tetrahedral species in solution. Fortunately, the tetrahedranide anions can be stabilized in solution by the use of [2.2.2]-cryptand. We now employ the thus acquired knowledge to investigate the chemical reactions of Sn_4^{4-} anions towards post-transition metal compounds. As a first result, we present here the formation of $Rb_6[(η^2-Sn_4)Zn(η^3-Sn_4)]·5NH_3$ (**1**) by reacting Rb_4Sn_4 with diphenylzinc in liquid ammonia in the presence of [2.2.2]-cryptand. The anionic moiety is represented by a $[(Sn_4)_2Zn]^{6-}$ (**1a**) unit, where a Zn^{2+} cation is coordinated by two Sn_4^{4-} anions (Fig. 1). The coordination of a post-transition metal (M) by two group 14 tetrahedra (E_4) to form dimers (M=Zn, E=Ge or Si/Ge),[11,12,14] one-dimensional strands (M=Au, E=Sn or Pb)[15,16]

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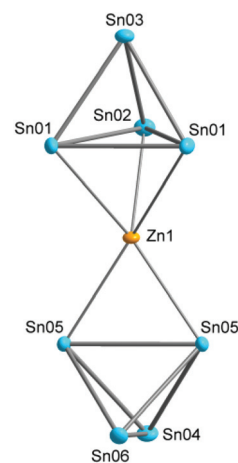[b]Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany

Fig. 1 Representation of the homoleptic complex **1a**. Anisotropic displacement ellipsoids are shown at 50% probability level.

Table 1 Zn^{2+} linked group 14 tetrahedra show different coordination numbers of Zn^{2+}

Compound	Anion	$CN(Zn^{2+})$
$Cs_6Ge_8Zn^{14}$	$[(\eta^3\text{-}Ge_4)\text{-}Zn(\eta^3\text{-}Ge_4)]^{6-}$	6
$A_{14}ZnGe_{16}$ (A = K, Rb)[11]	$[(\eta^2\text{-}Ge_4)\text{-}Zn(\eta^3\text{-}Ge_4)]^{6-}$	5
$K_6Zn(Si,Ge)_8\cdot11NH_3^{12}$	$[(\eta^2\text{-}(Si,Ge)_4)\text{-}Zn(\eta^2\text{-}(Si,Ge)_4)]^{6-}$	4
$Rb_6ZnSn_8\cdot5NH_3$	**$[(\eta^2\text{-}Sn_4)\text{-}Zn(\eta^3\text{-}Sn_4)]^{6-}$**	**5**

or oligomers (M=Cd, E=Pb)[17] is a well-known structural characteristic. A size effect seems to play a major role, as similar anionic moieties are reported for mixed alkali metal silicides and germanides, where the two tetrahedra are bridged by the smaller alkali metal.[18–23] Concerning zinc, such compounds which include the structural characteristic $[E_4ZnE_4]^{6-}$ are exclusively known for E=Ge in solid state reaction generated compounds[11,14] or are obtained by reaction in solution for E=Si/Ge (mixed).[12] The tetrahedra show a versatile coordination behavior towards the central atom by using two triangular faces, two edges or the combination of one triangular face and one edge giving coordination numbers of four to six for the Zn^{2+} cation (Table 1). It has to be noted that in the herein presented compound the junction of a (post-)transition metal and Sn_4^{4-} in general succeeded for the first time, and concerning zinc no comparable material is known either from solid state/melt reactions or from solution experiments. With respect to the interaction of tin *Zintl* clusters and zinc, *closo*-$[Sn_9ZnR]^{3-}$ (R = Ph, Mes, ^iPr) containing compounds are the only reported materials.[24,25]

The asymmetric unit of **1** consists of six tin atoms, one Zn atom, six Rb cations and four ammonia molecules.‡ Several of the atoms are located on special position 4i of space group $I2/m$ (four tin atoms, the Zn atom, five Rb cations and three nitrogen atoms). The Rb atom on the general position shows a site occupancy factor of 0.5, so that the electron count is balanced and gives a charge of minus six for the **1a** unit, in agreement with the formulation as Sn_4^{4-} and Zn^{2+} ions. In this anionic moiety, two Sn_4^{4-} tetrahedra coordinate to the Zn^{2+} cation and form a homoleptic complex. One triangular face of the first tetrahedron coordinates to the Zn atom; additionally one edge of the second tetrahedron coordinates in a η^2-like fashion, which gives a total coordination number of five for the Zn atom. The same coordination number is observed in the related germanium compound $A_{14}ZnGe_{16}$. The Sn–Sn bond lengths of the triangular face respectively edge which are capped by Zn^{2+} are significantly elongated compared to uncoordinated Sn_4^{4-} anions in solvate structures. The remaining Sn–Sn distances show the expected values for this class of compounds.[26] The Sn–Zn distances lie between 2.7554(7) Å and 2.8063(6) Å and therefore are very close to the values of the $[Sn_9ZnR]^{3-}$ compounds (d_{Av}(Sn–Zn) = 2.78 Å).[24,25] Fig. 1 shows **1a**, and the relevant distances are given in Table 2.

As the asymmetric unit consists of six tin atoms, four of which are located in special positions, each tetrahedron only shows four instead of six unique distances. The coordination sphere of the anion is completed by 16 Rb^+ cations at Rb–Sn

Table 2 Selected bond lengths for **1a**

Bond	Distance (Å)
Sn01–Sn01	3.0140(4)
Sn01–Sn02	3.0439(5)
Sn01–Sn03	2.8822(5)
Sn02–Sn03	2.8735(6)
Sn04–Sn05	2.8974(5)
Sn04–Sn06	2.9324(6)
Sn05–Sn05	3.0628(4)
Sn05–Sn06	2.9013(5)
Zn1–Sn01	2.8063(6)
Zn1–Sn02	2.7554(7)
Zn1–Sn05	2.7874(6)

distances between 3.685(7) Å and 4.3798(3) Å (the discrepancy in the accuracy of the bond distances arises due to modeling some of the Rb positions with fractional occupancies) which interconnect the **1a** anions to form a three dimensional network of cations and anions. The coordination sphere of the Rb atoms is saturated by two to three ammonia molecules at distances between 2.90(4) Å and 4.036(7) Å. Considering the Rb–ammonia network within the given distances, one dimensional strands along the crystallographic *b*-axis can be described, which are interconnected due to the Rb^+–Sn_4^{4-} interaction, resulting in a three dimensional network of cations, anions and ammonia molecules.

According to our stoichiometric approach to Rb_4Sn_4 : $ZnPh_2$: [2.2.2]-crypt of 1 : 1 : 1 one would expect unreacted $ZnPh_2$, benzene and [2.2.2]-cryptand to remain in solution. In contrast, the results of ^{13}C and $^1H,^{13}C$ HSQC NMR investigations showed only the presence of benzene and cryptand. Careful examination of the reaction precipitate showed the presence of further crystals, very similar in shape and color to those of **1**. Single crystal X-ray determination showed the compound to be a zincate with the composition (Rb@crypt)-$ZnPh_3\cdot NH_3$ (**2**), which contains the well-known zincate anion $[ZnPh_3]^-$.[27] This allows for the remaining phenyl substituents as well as the excessive $ZnPh_2$. The requirement of excess $ZnPh_2$ needs to be proven. No bulk characterization of **1** was possible due to fast and irreversible decomposition at temperatures above −20 °C. Despite much effort, no ^{119}Sn signal could be detected so far, which probably indicates low concentrations or high fluxonality of **1** in solution. Similar observations were previously reported by other groups.†[24]

Conclusions

We present here the first successful chemical transformation of the highly charged tin *Zintl* anions Sn_4^{4-} using the binary solid state material Rb_4Sn_4, [2.2.2]-cryptand and diphenylzinc in liquid ammonia solution. The presence of these anions in solution could be proven only very recently; the herein shown possibility of reacting them may open the door to a versatile solution chemistry of tetrahedral tin *Zintl* anions Sn_4^{4-}.

Notes and references

‡Further details of the crystal structure investigation of **1** may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata(at)fiz-karlsruhe(dot)de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD 426039.

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