Syntheses and Crystal Structures of Ammoniates with the Phenyl-Substituted Polytin Anions $Sn_2Ph_4^{2-}$, *cyclo*-$Sn_4Ph_4^{4-}$, and $Sn_6Ph_{12}^{2-}$

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The reaction of diphenyltin dichloride with the binary *Zintl* phase K_4Sn_9 in the presence of excess lithium and 18-crown-6 in liquid ammonia led to the ammoniate $[K(18\text{-crown-}6)(NH_3)_2]_2Sn_2Ph_4$ (**1**). The analogous reaction with K_4Ge_9 and potassium in the absence of further alkali metal ligands resulted in the compound $[K_2(NH_3)_{12}]Sn_6Ph_{12} \cdot 4\,NH_3$ (**3**). $Cs_6[Sn_4Ph_4](NH_2)_2 \cdot 8\,NH_3$ (**2**) was prepared by reacting diphenyltin dichloride with a surplus of caesium in liquid ammonia. The low-temperature single-crystal structure determinations show all compounds to contain phenyl-substituted polyanions of tin. Compound **1** is built from $Sn_2Ph_4^{2-}$ anions consisting of Sn dumbbells with two Ph substituents at each Sn-atom. Compound **2** contains *cyclo*-$Sn_4Ph_4^{4-}$ anions formed by a four-membered tin ring in butterfly conformation with one Ph substituent at each Sn-atom in an (all-*trans*)-configuration. $Sn_6Ph_{12}^{2-}$ in **3** is a zig-zag Sn_6 chain with two substituents at each of the Sn-atoms. Both **1** and **3** have molecular counter cations, in the latter case the unprecedented dinuclear potassiumammine complex $[K_2(NH_3)_{12}]^{2+}$ is observed. Compound **2** shows a complicated three-dimensional network of Cs−Sn interactions.

Introduction. – Highly charged Sn polyanions like Sn_2^{6-} dumbbells (Li_7Sn_2) [1] as well as Sn_3^{7-} (Li_7Sn_3) [2] or Sn_5^{12-} chains ($Ca_{31}Sn_{20}$) [3] are only known in neat solids. Flat pentagonal rings of Sn_5^{6-} conforming to the rules of aromaticity have recently been characterized in the ternary phase Na_8BaSn_6 [4]. The high charges postulated by an ionic bonding model for these compounds are necessary for electron-precise polytin species and are of course simply the result of the position of tin in the periodic table. Unfortunately, these charges also make polytin chain or ring anions only observable in densely packed solids; a solution chemistry of these homoatomic species is highly unlikely.

Attaching covalently bound Ph substituents to the polyanions causes a reduction of the anionic charge and consequently provides an opportunity to expand the solution chemistry of tin *Zintl* anions, which predominantly has been restricted to cages like Sn_9^{4-} [5] or Sn_5^{2-} [6]. In 1997, *Jacobs* and co-workers reported the first Sn compound of this kind, $[Li(NH_3)_4]_2Sn_2Ph_4$ [7], which contains $Sn_2Ph_4^{2-}$ anions. It was synthesized by the reaction of diphenyltin dichloride with Li in liquid NH_3. A similar reaction of triphenylantimony with Li in THF in the presence of 12-crown-4 led to the compounds $[Li(12\text{-crown-}4)_2][SbPh_2] \cdot 1/3$ THF [8] and $[Li(12\text{-crown-}4)_2][Sb_3Ph_4] \cdot$ THF [8] with $SbPh_2^-$ and *catena*-$[Sb_3Ph_4]^-$ anions, respectively. Inspired by these earlier results, we were interested in further investigating homoatomic, Ph-substituted *Zintl* anions of the heavier main-group metals tin and antimony. The recently published compound

$\{[Li(NH_3)_4]_2[18\text{-crown-}6]\}[Li(NH_3)_4]_2(Sn_3Ph_6)_2 \cdot 4\,NH_3$ [9] contains larger *catena*-$Sn_3Ph_6^{2-}$ anions, which are stabilized in the solid state by novel voluminous $\{[Li(NH_3)_4]_2[18\text{-crown-}6]\}^{2+}$ divalent cations. The reduction of triphenylantimony with caesium yielded the compound $[Cs_6(PhSb_2)_2] \cdot 11\,NH_3$ [10] containing Sb_2Ph^{3-} anions, in which the Ph residue is fixed to one atom of a single-bonded diantimonide dumbbell.

In our search for additional Ph-substituted polytin anions, we focused our work on the reaction of the starting material diphenyltin dichloride with alkali metals as reducing agents, in some cases in the presence of binary *Zintl* phases like K_4Sn_9 or K_4Ge_9.

Results and Discussion. – *Crystal Structure of* $[K(18\text{-crown-}6)(NH_3)_2]_2Sn_2Ph_4$ (**1**). The compound $[K(18\text{-crown-}6)(NH_3)_2]_2Sn_2Ph_4$ is built of $Sn_2Ph_4^{2-}$ anions, K^+ cations encapsulated by crown ether molecules, and NH_3 molecules of crystallization coordinating to the alkali metal from above and below the plane of the crown ether.

Comparison of the $Sn_2Ph_4^{2-}$ anion (*Fig. 1*) with the same anion found in the compound $[Li(NH_3)_4]_2[Sn_2Ph_4]$ [7] shows high conformity in terms of the geometrical data. Both anions display a staggered conformation of the two covalently bound Ph substituents on each Sn atom. Due to the site symmetry, the torsion angle between two opposed Ph residues in $[K(18\text{-crown-}6)(NH_3)_2]_2Sn_2Ph_4$ is 180°. The Sn−Sn bond length, 2.909(1) Å in our compound, agrees well with the 2.905(3) Å found in $[Li(NH_3)_4]_2[Sn_2Ph_4]$ [7], and is similar to the distances in Sn_9^{4-} *Zintl* ions (2.928(6)–3.308(5) Å) [5][11]. Comparison with non-ionic compounds like Sn_2Ph_6 (2.77 Å) [12] and with the elemental grey tin modification (2.810 Å) [13] indicates a remarkable bond lengthening in the $Sn_2Ph_4^{2-}$ anions, presumably due to the repulsive forces caused by the negative charge located at each Sn-atom. *Fig. 2* shows the packing of the anions and the $[K(18\text{-crown-}6)(NH_3)_2]^+$ cationic potassium–crown ether–ammonia complexes.

The formation of H-bonds between the NH_3 molecules coordinating to the alkali metal cations and the O-atoms of the crown ether molecules leads to one-dimensionally infinite cationic chains parallel to the crystallographic [110] direction. The H-bonds were detected by the *Platon* Program for Windows [14], the relevant distances and angles are given in the caption of *Fig. 2*.

Additionally, H-bonds between the $Sn_2Ph_4^{2-}$ anions and the NH_3 molecules of crystallization can be observed. The distance between the N-atom and the negatively charged Sn-atom measures 4.065(5) Å. The H−Sn distance *d*(H1A#3−Sn1#1) is with 3.34(2) Å significantly shorter than the sum of the *Van der Waals* radii[1]), the angle N1#3−H1A#3−Sn1#1 is 140.4°.

Crystal Structure of $Cs_6[Sn_4Ph_4](NH_2)_2 \cdot 8\,NH_3$ (**2**). In this compound, four-membered Ph-substituted tin rings as shown in *Fig. 3* form the anionic part of the structure. They are coordinated by Cs^+ cations with numerous direct ion-pairing contacts. The crystal structure at first seemed to show a discrepancy with respect to the expected charge of the anion and the number of counter ions present. Since each Sn-atom carries one covalently bound Ph residue and forms additionally two bonds to the neighboring Sn-atoms, the $(8-N)$ rule predicts one negative charge per Sn-atom and consequently a

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[1]) $W(Sn) = 2.2$ Å; $W(H) = 1.4$ Å [15].

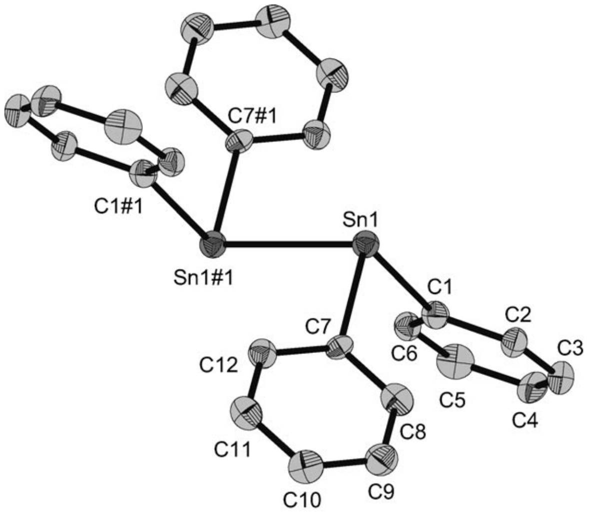

Fig. 1. *ORTEP Plot of the $Sn_2Ph_4^{2-}$-anion in $[K(18\text{-crown-}6)(NH_3)_2]_2Sn_2Ph_4$.* Distances [Å] and angles [°] in the $Sn_2Ph_4^{2-}$-anion: Sn1–Sn1#1 = 2.909(1), Sn1–C1 = 2.251(6), C1–C2 = 1.423(8), C2–C3 = 1.370(8), C3–C4 = 1.397(8), C4–C5 = 1.396(9), C5–C6 = 1.401(9), C6–C1 = 1.408(7), Sn1–C7 = 2.264(5), C7–C8 = 1.377(8), C8–C9 = 1.426(7), C9–C10 = 1.379(9), C10–C11 = 1.404(9), C11–C12 = 1.418(7), C12–C7 = 1.417(8); Sn1#1–Sn1–C1 = 97.86(1), Sn1–C1–C6 = 121.9(4), Sn1–C1–C2 = 122.0(4), C1–C2–C3 = 122.6(6), C2–C3–C4 = 120.9(6), C3–C4–C5 = 118.3(6), C4–C5–C6 = 120.7(6), C5–C6–C1 = 121.7(5), C6–C1–C2 = 115.7(5), Sn1#1–Sn1–C7 = 96.92(1), Sn1–C7–C12 = 119.2(4), Sn1–C7–C8 = 122.9(4), C7–C8–C9 = 122.3(5), C8–C9–C10 = 120.1(6), C9–C10–C11 = 118.9(5), C10–C11–C12 = 120.7(5), C11–C12–C7 = 120.5(5), C12–C7–C8 = 117.6(5). Probability factor 50%; symmetry operation for generating equivalent atoms: #1: $1-x$, $1-y$, $1-z$.

fourfold negative charge for the whole anion. However, the asymmetric unit contains three Cs^+ cations besides two Ph-substituted Sn-atoms and five N-atoms, which would usually be assigned to NH_3 molecules of crystallization; the ring anions are generated by the twofold rotation axes of space group *Fdd*2. Given the good agreement of the Sn–Sn bond lengths with the previously observed Ph-substituted polytin anions (see below), and the even distribution of these bond lengths within the anion, the presence of a $Sn_4Ph_4^{6-}$ anion seemed to be highly unlikely, while a $Sn_4Ph_4^{4-}$ anion, though a new species, was well within the predictions of *Zintl* ion chemistry. The most probable solution to this charge problem was the presence of amide anions in the structure; amides are common by-products in the liquid ammonia chemistry of alkali metal solutions [16].

Unfortunately, the localization of H-atoms in ammoniates by X-ray methods is usually not very reliable. In this case, only a small number of the H-atoms could be isotropically refined. However, the careful inspection of the Cs-coordination sphere of the five crystallographically inequivalent N-atoms in the asymmetric unit yields convincing structural evidence for the assignment of one of these atoms to an amide ion (*Fig. 4*).

The NH_3 molecules N1 and N4 show a coordination sphere of two, the N3 and N5 molecules a coordination sphere of three Cs^+ cations with distances in the range of 3.27(4)–3.73(4) Å, while the N2-atoms are coordinated by four cations with distances

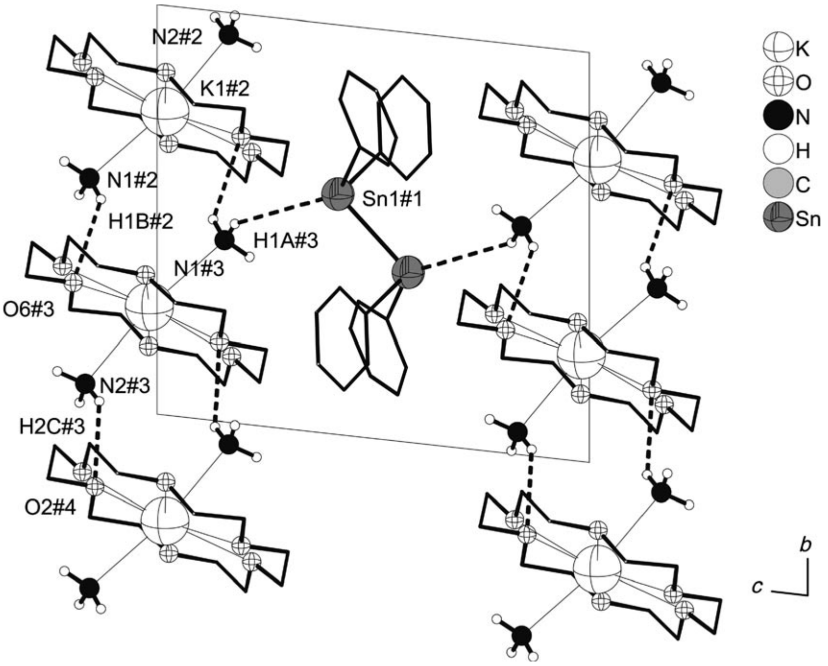

Fig. 2. *Section of the structure of [K(18-crown-6)(NH_3)$_2$]$_2$$Sn_2Ph_4$.* Distances [Å] and angles [°] within the cationic chains: N2#2–K1#2 = 2.836(5), N1#2–K1#2 = 2.852(4), H1B#2–O6#3 = 2.55(1), N1#2–O6#3 = 3.234(6), H2C#3–O2#4 = 2.52(1), N2#3–O2#4 = 3.248(7), N2#3–O2#4 = 3.248(7); N1#2–H1B#2–O6#3 = 134.0, N2#3–H3C#3–O2#4 = 139.4. Symmetry operations for generating equivalent atoms: #1 = $1-x$, $1-y$, $1-z$; #2: $-x$, $1-y$, $1-z$; #3: x, y, $1+z$; #4: $1-x$, $-y$, $1-z$.

of 3.01(1), 3.13(3), 3.38(2), and 3.63(1) Å. Consequently, the N2-atoms show the largest number of Cs contacts and, with 3.01(1) and 3.13(3) Å, the shortest distances between Cs^+ cations and N-atoms in this structure, which is exactly what one would expect for the interaction between two oppositely charged ions as compared with the ion–dipole interaction between Cs^+ and an NH_3 molecule. The mean Cs–N distance in $CsNH_2 \cdot NH_3$ is 3.586 Å [17], which supports our interpretation of the structural data. According to *Wades* rules [18], the number of Sn-atoms and the number of valence electrons within the $Sn_4Ph_4^{4-}$ anion may be correlated by the equation $2n+8=16$ (n = skeleton atoms), which predicts a *hypho*-cluster. Consequently, the butterfly geometry of the tin ring can also be seen as a pentagonal bipyramid with three unoccupied vertices, two equatorial and one apical.

The (all-*trans*)-configuration of the Ph residues in the $Sn_4Ph_4^{4-}$ anion has also been observed in the iso-electronic compounds R_4Sb_4 and R_4Bi_4 (R = $(Me_3Si)_2CH$) [19]. The Sn–Sn distances within the $Sn_4Ph_4^{4-}$ anion lie in the range of 2.897(1)–2.918(9) Å, which agrees well with the distances for other Ph-substituted polytin anions in $[Li(NH_3)_4]_2[Sn_2Ph_4]$ (2.905(3) Å) or $[K(18\text{-crown-}6) \cdot 2\,NH_3]_2Sn_2Ph_4$ (2.909(1) Å), or even with the distances in *Zintl* cage anions like Sn_9^{4-} (2.928(6)–3.308(5) Å) [5] or Sn_5^{2-} (2.85–3.10 Å) [20]. The observed bond lengthening compared to the 2.810 Å

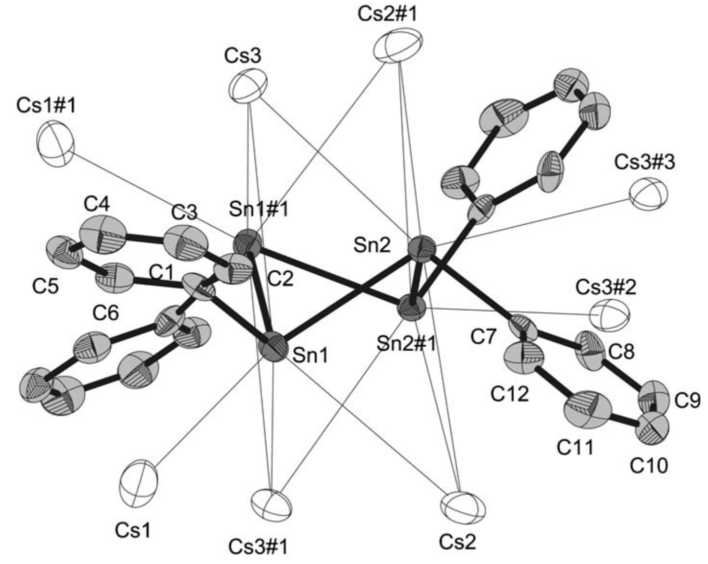

Fig. 3. *Cs-Coordination sphere of the* $Sn_4Ph_4^{4-}$ *anion in* $Cs_6[Sn_4Ph_4](NH_2)_2\cdot 8\,NH_3$. Selected distances [Å] and angles [°] within the anion: Sn1–Sn1#1 = 2.917(1), Sn1–Sn2 = 2.918(9), Sn2–Sn2#1 = 2.897(1), Sn1–C1 = 2.260(9), C1–C2 = 1.39(1), C2–C3 = 1.43(1), C3–C4 = 1.36(2), C4–C5 = 1.40(1), C5–C6 = 1.42(3), C6–C1 = 1.38(2), Sn2–C7 = 2.253(9), C7–C8 = 1.41(1), C8–C9 = 1.41(2), C9–C10 = 1.39(2), C10–C11 = 1.35(1), C11–C12 = 1.44(4), C12–C7 = 1.39(1), Sn2–Sn1–Sn1#1 = 77.71(2), Sn1–Sn2–Sn2#1 = 78.02(2), C1–Sn1–Sn1#1 = 104.7(2), C1–Sn1–Sn2 = 103.4(2), C1–C2–C3 = 121.9(2), C2–C3–C4 = 120.0(1), C3–C4–C5 = 120.5(1), C4–C5–C6 = 117.5(1), C5–C6–C1 = 123.7(9), C6–C1–C2 = 116.5(9), C7–Sn2–Sn1 = 106.96, C7–Sn2–Sn2#1 = 100.8(2), C7–C8–C9 = 121.6(9), C8–C9–C10 = 120.7(1), C9–C10–C11 = 119.5(1), C10–C11–C12 = 119.9(2), C11–C12–C7 = 122.2(1), C12–C7–C8 = 116.0(9). Distances within the Cs-coordination sphere of the $Sn_4Ph_4^{4-}$ anion: Sn1–Cs1 = 4.200(1), Sn2–Cs3#3 = 4.564(9), Sn1#1–Cs3 = 3.989(9), Sn1–Cs3 = 4.343(8), Sn2–Cs3 = 3.979(8), Sn1–Cs2 = 4.095(1), Sn2–Cs2 = 4.301(9), Sn2#1–Cs2 = 4.197(1). Probability factor: 50%; symmetry operations for the generation of equivalent atoms: #1: $-x, -y, z$; #2: $x-0.25, -y-0.25, 0.25+z$; #3 $= 0.25-x, 0.25+y, 0.25+z$.

within the elemental grey tin modification [13] is again explained by the negative charges formally located at each Sn-atom.

As can be seen in *Fig. 5*, the Sn-atoms of *cyclo*-$Sn_4Ph_4^{4-}$ ions have a number of direct contacts to surrounding Cs^+ ions. If distances up to 4.564 Å are considered, the Cs-coordination sphere around the anion consists of four Cs^+ cations in an η_3-like coordination to the four-membered ring and four cations with only a single tin contact, while the Ph residues are situated in the free space between the η_3- and η_1-like bound cations. These cation–anion interactions lead to a three-dimensional network.

Crystal Structure of $[K_2(NH_3)_{12}]Sn_6Ph_{12}\cdot 4\,NH_3$ (**3**). The $Sn_6Ph_{12}^{2-}$ anion (*Fig. 6*) in $[K_2(NH_3)_{12}]Sn_6Ph_{12}\cdot 4\,NH_3$ is up to now the largest molecular anion that has been synthesized in the chemistry of Ph-substituted *Zintl* anions. Six Sn-atoms, which are arranged in zig-zag fashion, build up the backbone of the anion, and each Sn-atom carries two covalently bound Ph residues. The organic substituents are arranged in an (all-*trans*)-configuration with a corresponding mean torsion angle of 175.61°. The distance

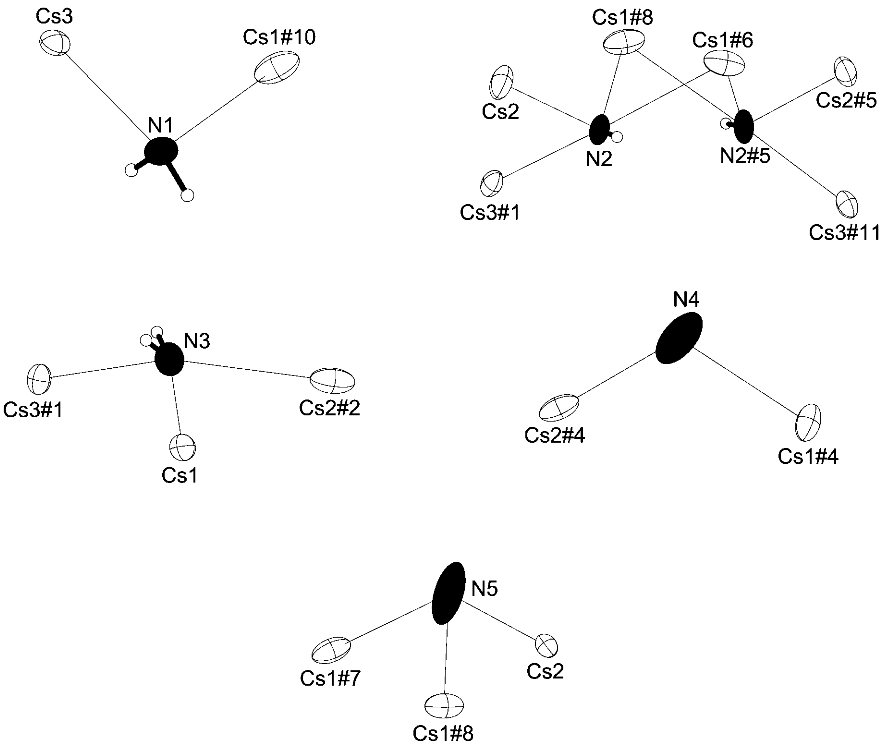

Fig. 4. *Cs-Coordination spheres of each of the five crystallographically independent N-atoms.* Selected distances [Å]: N1–Cs3 = 3.39(1), N1–Cs1#10 = 3.36(2), N2–Cs2 = 3.01(1), N2–Cs3#1 = 3.38(2), N2–Cs3#8 = 3.13(3), N2–Cs1#6 = 3.63(1), N3–Cs3#1 = 3.65(3), N3–Cs1 = 3.65(2), N3–Cs2#2 = 3.73(4), N4–Cs2#4 = 3.44(2), N4–Cs1#4 = 3.83(2), N5–Cs1#7 = 3.37(5), N5–Cs1#8 = 3.27(4), N5–Cs2 = 3.45(1). Symmetry operations for the generation of equivalent atoms: #1: $-x$, $-y$, z; #2: $-x-0.25$, $y+0.25$, $z-0.25$; #4: $x+0.25$, $-y+0.75$, $z-0.25$; #5: $-0.5-x$, $0.5-y$, z; #6: $-0.25+x$, $0.75-y$, $0.25+z$; #7: $x-0.25$, $-y+0.75$, $z+0.25$; #8: $-x-0.25$, $y-0.25$, $z+0.25$; #10: $x+0.25$, $-y+0.25$, $z+0.25$; #11: $-0.5+x$, $0.5+y$, z.

between the two central Sn1-atoms is with 2.8212(4) Å the shortest Sn–Sn distance within the anion and closest to the value for elemental tin (2.810 Å [13]), which is only to be expected given the absence of formal charges on both atoms. In contrast to that, the distance between the terminal Sn3-atoms bearing the formal negative charge and the Sn2-atoms is 2.8688(4) Å, which is shorter than the values for $Sn_2Ph_4^{2-}$ or $Sn_4Ph_4^{4-}$ anions (see above) but in good agreement with the corresponding distances in the *catena*-$Sn_3Ph_6^{2-}$ anion of the compound $\{[Li(NH_3)_4]_2[18\text{-crown-}6]\}[Li(NH_3)_4]_2(Sn_3Ph_6)_2 \cdot 4\,NH_3$ [9] (2.8669(8) and 2.8719(8) Å), in which also a formally negatively charged Sn-atom is bound to a central four-bonded, neutral atom. The value for the bond between Sn2 and Sn3 falls with 2.8404(4) Å, exactly between the value for the two neighboring bonds, as expected.

The asymmetric unit of the title compound contains one Sn_3Ph_6 fragment, one K^+ cation and eight NH_3 molecules of crystallization. Six of these NH_3 molecules coordi-

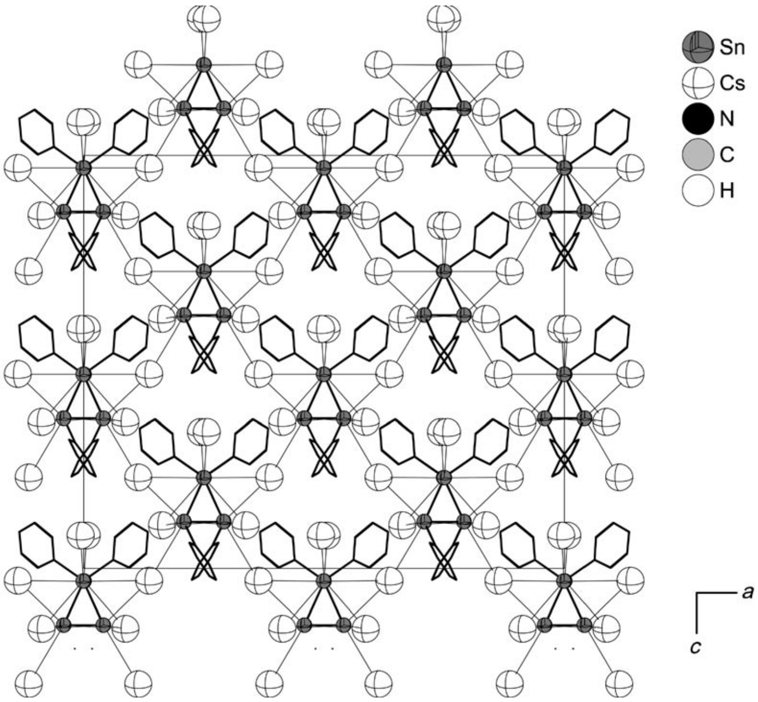

Fig. 5. *Unit cell of $Cs_6[Sn_4Ph_4](NH_2)_2 \cdot 8\,NH_3$; projection on the* ac*-plane.* The H- and N-atoms are omitted for clarity.

nate to K^+ ions to yield by symmetry cationic $[K_2(NH_3)_{12}]^{2+}$ complexes, which are shown in *Fig. 7*.

Inside this binuclear cationic complex, seven NH_3 molecules coordinate to each K^+ cation, with two of them acting as bridging ligands. To our knowledge, this is the first reported homoleptic ammine complex of the K^+ cation.

The phenylated polytin anions and the $[K_2(NH_3)_{12}]^{2+}$ complexes build up a rather distorted NaCl-like packing with irregular distances between the centres of the species in the range of 8.769(1)–11.620(7) Å.

Fig. 8 represents the unit cell of $[K_2(NH_3)_{12}]Sn_6Ph_{12} \cdot 4\,NH_3$ with the cationic complexes shown as edge-connected irregular polyhedra. The structure of $[K_2(NH_3)_{12}]Sn_6Ph_{12} \cdot 4\,NH_3$ is built of one-dimensionally infinite chains resulting from H-bonds between the $Sn_6Ph_{12}^{2-}$ anions and the cationic complexes. Both terminal Sn-atoms serve as acceptor atoms and two crystallographically inequivalent NH_3 molecules, coordinating the K^+ cations, as donor atoms (resulting distances and angles: Sn–H = 3.10(4), 3.250(1) Å, N–H = 3.922(3), 3.968(2) Å; N–H–Sn = 139.3(1), 175.1(3)°). Additionally, four NH_3 molecules of solvation per formula unit are present within the crystal structure and show no remarkable interactions to the ionic species.

Conclusions. – The three new compounds with different Ph-substituted polytin anions presented here lead to two conclusions concerning further investigations. Firstly,

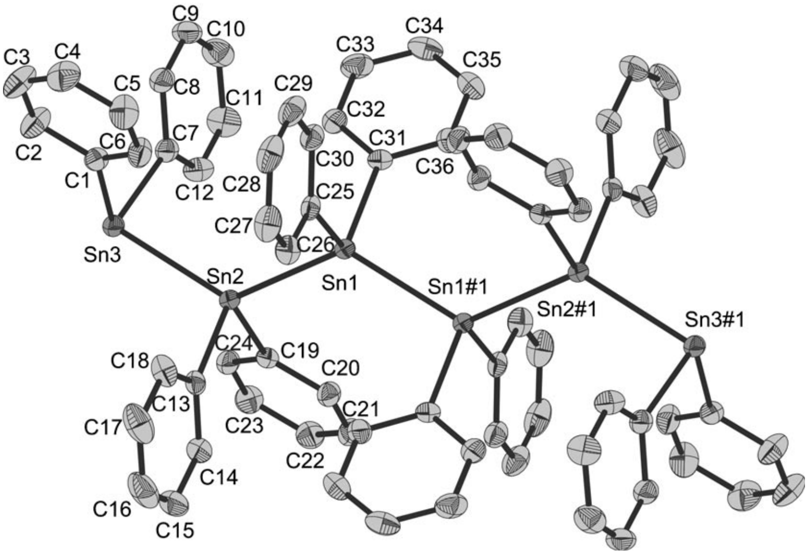

Fig. 6. *ORTEP Plot of the* $Sn_6Ph_{12}^{2-}$*-anion in* $[K_2(NH_3)_{12}]Sn_6Ph_{12}\cdot 4\,NH_3$. Selected distances [Å] and angles [°]: Sn1#1–Sn1 = 2.8212(4), Sn1–Sn2 = 2.8404(4), Sn2–Sn3 = 2.8688(4), Sn1–C31 = 2.172(2), C31–C32 = 1.403(3), C32–C33 = 1.394(3), C33–C34 = 1.389(4), C34–C35 = 1.385(4), C35–C36 = 1.392(3), C36–C31 = 1.401(3), Sn1–C25 = 2.182(2), C25–C26 = 1.400(3), C26–C27 = 1.397(3), C27–C28 = 1.383(4), C28–C29 = 1.390(4), C29–C30 = 1.393(3), C30–C25 = 1.400(3), Sn2–C19 = 2.175(2), C19–C20 = 1.407(3), C20–C21 = 1.388(3), C21–C22 = 1.394(3), C22–C23 = 1.391(3), C23–C24 = 1.388(3), C24–C19 = 1.404(3), Sn2–C13 = 2.184(2), C13–C14 = 1.402(3), C14–C15 = 1.396(3), C15–C16 = 1.382(4), C16–C17 = 1.385(5), C17–C18 = 1.389(4), C18–C13 = 1.403(3), Sn3–C7 = 2.217(2), C7–C8 = 1.407(3), C8–C9 = 1.396(3), C9–C10 = 1.383(4), C10–C11 = 1.389(4), C11–C12 = 1.396(3), C12–C7 = 1.397(3), Sn3–C1 = 2.218(2), C1–C2 = 1.405(3), C2–C3 = 1.401(4), C3–C4 = 1.375(4), C4–C5 = 1.387(4), C5–C6 = 1.391(3), C6–C1 = 1.397(3); Sn1–Sn2–Sn3 = 128.025(9), Sn2–Sn1–Sn1#1 = 125.909(11), C25–Sn1–C31 = 102.97(8), C13–Sn2–C19 = 99.53(8), C1–Sn3–C7 = 97.11(8). Probability factor 50%; symmetry operation for the generation of equivalent atoms: #1: $-1-x$, $-1-y$, $-z$.

the use of monotin starting materials like Ph_2SnCl_2 in reducing NH_3 solutions is a versatile route to organo-substitued polytin anions. Secondly, our original concept of including substituents in order to synthesize lower charged molecular *catena*- and *cyclo*-polytin anions in solutions seems to work; it remains to be seen just how much this route may be tuned for still larger polytin species or somewhat higher charged rings or chains.

Experimental Part

General. All experiments described below were performed in a purified Ar atmosphere by using *in vacuo*-dried vessels and glove box techniques. NH_3 (*Bayer AG*) was made anh. by distilling it from Na and was stored as a sodium–ammonia solution at −78°. The binary phase K_4Sn_9 (K_4Ge_9) was prepared from a

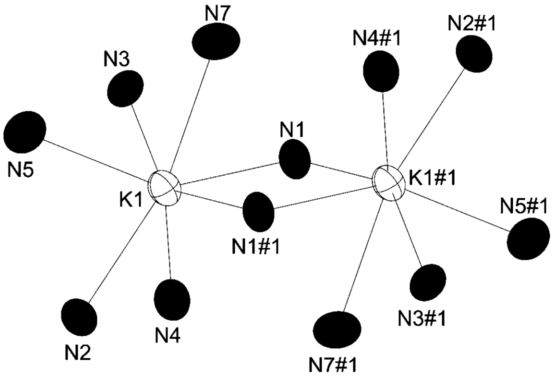

Fig. 7. *$[K_2(NH_3)_{12}]^{2+}$ Cation in $[K_2(NH_3)_{12}]Sn_6Ph_{12} \cdot 4\,NH_3$.* Selected distances [Å]: K1−N1 = 3.087(2), K1−N2 = 2.933(2), K1−N3 = 2.9463(2), K1−N4 = 2.998(2), K1−N5 = 2.938(2), K1−N7 = 2.969(3). Symmetry operations for the generation of equivalent atoms: #1: $-1-x$, $-y$, $-z$.

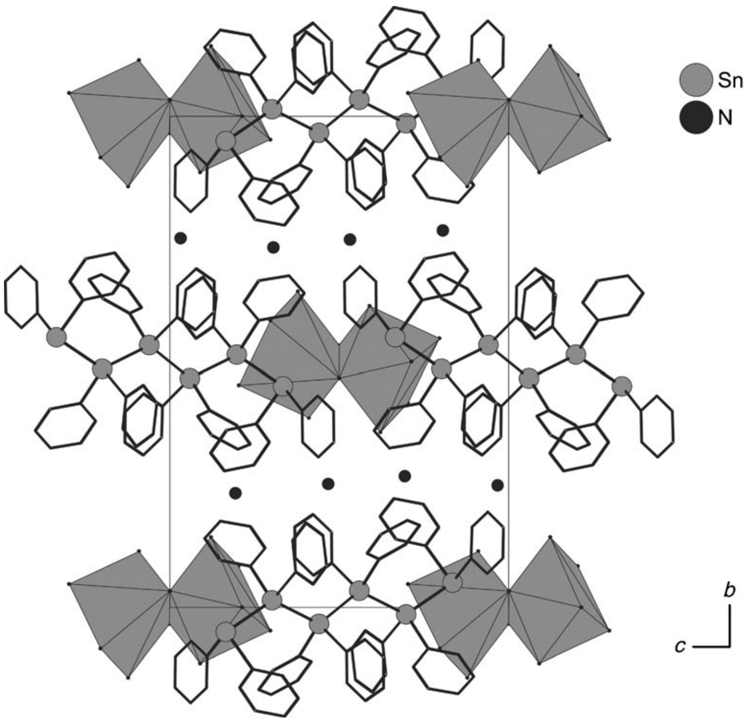

Fig. 8. *Unit cell of $[K_2(NH_3)_{12}]Sn_6Ph_{12} \cdot 4\,NH_3$; projection on the* ac-*plane.* $[K_2(NH_3)_{12}]^{2+}$ Complexes shown as polyhedra.

stoichiometric mixture of the elements in a sealed *Duran* glass ampoule (silica ampoule) by heated at 330° for 72 h (650° for 96 h). All ammoniate crystals are extremely unstable at temp. above −20° or in air.

[K(18-crown-6)(NH$_3$)$_2$]$_2$Sn$_2$Ph$_4$ (**1**). K_4Sn_9 (260 mg, 0.212 mmol), Ph_2SnCl_2 (168 mg, 0.489 mmol; *Aldrich*, 96%), elemental Li (11 mg, 1.58 mmol), and 18-crown-6 (260 mg, 0.983 mmol) were placed into a *Schlenk*-type reaction tube. About 30 ml of dried NH_3 were condensed into the mixture, resulting in a brown soln. After storage of the soln. for five weeks at −38°, red crystals precipitated, which proved to be suitable for X-ray crystallography.

Cs$_6$[Sn$_4$Ph$_4$](NH$_2$)$_2$·8 NH$_3$ (**2**). After Ph_2SnCl_2 (920 mg, 2.68 mmol; *Aldrich*, 96%) and a fivefold surplus of Cs (1.786 g, 13.44 mmol) were placed into a *Schlenk*-type reaction tube, *ca.* 30 ml of NH_3 were condensed into this mixture of starting materials. Within a day, the color of the resulting mixture turned from blue to red. After about one week, it was possible to isolate small brown needles for X-ray crystallography.

[K$_2$(NH$_3$)$_{12}$]Sn$_6$Ph$_{12}$·4 NH$_3$ (**3**). To a soln. comprised of Ph_2SnCl_2 (340 mg, 0.989 mmol; *Aldrich*, 96%) and K (0.09 g, 2.3 mmol) in 30 ml of NH_3, K_4Ge_9 was added after *ca.* 2–3 h. Orange-colored crystals

Table. *Crystal Data and Refinement Results of [K(18-crown-6)(NH$_3$)$_2$]$_2$Sn$_2$Ph$_4$* (**1**), *Cs$_6$[Sn$_4$Ph$_4$](NH$_2$)$_2$·8 NH$_3$* (**2**), *and [K$_2$(NH$_3$)$_{12}$]Sn$_6$Ph$_{12}$·4 NH$_3$* (**3**)

	1	**2**	**3**
Empirical formula	$Sn_2K_2N_4C_{48}H_{80}O_{12}$	$Sn_4Cs_6N_{10}C_{24}H_{48}$	$Sn_6K_2N_{16}C_{72}H_{108}$
Formula weight [g/mol]	1220.804	1749.018	1988.228
Crystal size [mm]	0.2 × 0.15 × 0.10	0.17 × 0.13 × 0.10	0.2 × 0.15 × 0.10
Crystal system	triclinic	Orthorhombic	monoclinic
Space group	$P\bar{1}$	*Fdd*2	$P2_1/c$
Cell parameters:			
a [Å]	11.268(2)	28.4074(6)	13.131(1)
b [Å]	11.621(2)	13.4867(5)	22.056(2)
c [Å]	12.500(2)	24.4804(8)	17.539(2)
α [°]	79.41(2)	90	90
β [°]	72.21(2)	90	119.755(8)
γ [°]	74.27(2)	90	90
V [Å^3]	1491.1(4)	9379.0(5)	4409.8(7)
Z	1	8	2
Density [mg/m^3]	1.360	2.477	2.086
T [K]	123(2)		
Absorption correction	DELrefABS	DELrefABS	X-Red/X-Shape
Absorption coefficient [mm^{-1}]	1.032	6.723	3.570
F (000)	630	6336	1980
θ [°]	2.23–26.03	2.20–27.91	2.01–25.90
Reflections collected	6444	19818	61315
Independent reflections	4382	5604	8495
R_{int}	0.0532	0.0498	0.0586
Completeness to θ [%]	74.6	99.7	99.0
Parameter	331	223	470
Restraints	0	1	0
Goodness-of-fit (F^2)	0.733	1.058	1.008
X-Ray	MoK_α	MoK_α	MoK_α
Wavelength [Å]	0.71073	0.71073	0.71073
Monochromator	graphite	graphite	graphite
$R_1(I>2\sigma(I))$	0.0386	0.0420	0.0297
$wR_2(I>2\sigma(I))$	0.0653	0.1014	0.0558
R_1(all data)	0.0787	0.0493	0.0338
wR_2(all data)	0.0733	0.1042	0.0570
Largest diff. Peak/hole [eÅ^{-3}]	0.412/−0.455	2.888/−3.221	0.830/−0.403

of **3** suitable for X-ray analysis were grown by cooling the solution at $-38°$ for two months. The role of K_4Ge_9 in this reaction is not clear; however, no **3** was detected to form if just Ph_2SnCl_2 and K were used as starting materials.

X-Ray Crystallography. The details of the crystal structure determinations and refinements are given in the *Table*. The measurement was performed on an IPDS (Imaging Plate Diffraction System) instrument (*STOE & Cie*) using graphite-monochromated MoK_α radiation (λ 0.71073 Å). For this purpose, the crystals were attached to a glass fiber with perfluoroether, which was cooled under a N_2 stream to 213 K. For structure solving and refinement, the software package SHELX-97 [21][22] was used. The structure was solved by direct methods. All non-H-atoms were refined with anisotropic thermal parameters. Some H-atoms were refined with a riding model and a common isotropic thermal parameter. The position of the remaining H-atoms were taken from difference-*Fourier* analysis.

The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as supplementary publication No. CCDC-299479 (**1**), CCDC-299481 (**2**), and CCDC-299480 (**3**). Copies of the data can be obtained, free of charge, by application to the *CCDC*, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

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