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# Clusters of the Heavier Elements of Main Groups 14–16: A Novel Synthetic Route for Polyanions in Molten Crown Ether<sup>a)</sup>

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**Abstract.** A novel procedure allows the synthesis of homoatomic polyanions directly from the elements E (E = Sn, As, Sb, Te) in molten A/18-crown-6 as reaction medium (A = K, Rb) at temperatures between 40 and 80° [1]. The reactions are carried out by adding E to mixtures of A and 18-crown-6 that proved to form stable melts under these conditions. Further work off using ethylenediamine or DMF as solvent yielded single crystals of the following compounds: [K(18-crown-6)]<sub>4</sub>Sn<sub>9</sub> (1), [K(18-crown-6)]<sub>3</sub>KSn<sub>9</sub>·en (2), [K(18-crown-6)]<sub>3</sub>As<sub>7</sub> (3), [K([2.2.2]crypt)]<sub>2</sub>[K(18-crown-6)]Sb<sub>7</sub>·0.5en (4), [Rb(18-crown-6)]<sub>3</sub>Sb<sub>7</sub> (5), [K(18-crown-6)]<sub>2</sub>Te<sub>4</sub> (6), and [K(18-crown-6)]<sub>2</sub>Te<sub>4</sub>·en (7). In all compounds short contacts between the Zintl ions and A-atoms are observed. The influence of cation-anion interactions on the structure of these anions is discussed.

## Introduction and Background

Synthesis, determination of physical properties, and theoretical investigations on the electronic structures of compounds containing isolated and linked homoatomic main-group element clusters have been a major research field of our group during the last years [2]. Soluble, ligand-free ('naked') homoatomic polyanions of groups 14–16 are commonly called *Zintl ions*; discrete and linked homoatomic units frequently occur in *Zintl phases*, which represent a subgroup of so-called 'salt-like' intermetallic compounds consisting of an electropositive metal and a semimetal. We report here about our latest results considering soluble Zintl ions; an example of a new intermetallic phase, K<sub>5</sub>Pb<sub>24</sub>, with linked Pb clusters as building blocks was described on a second poster [3].

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There exist several experimental routes to soluble homoatomic anions E<sub>n</sub><sup>x-</sup> (E = group 14–16) in solution [4]: a) dissolving element E in alkaline metal/ammonia solutions at low temperatures, b) extraction of binary alloys A<sub>n</sub>E<sub>m</sub> with amines, and c) electrochemical reduction using conducting elements or phases as cathode. For good crystal packing and thus crystalline compounds, larger cluster anions need relatively large counter-ions. This has been achieved successfully by the addition of [2.2.2]Cryptofix [1] (Fig. 1, a) for sequestering the alkali-metal atom in solutions of the binary alloys. In the crystalline products, direct contacts between cations and anions are obviously inhibited, in contrast to Zintl phases, where several small cations can stabilize also higher negatively charged anions. The idea to stabilize larger units of Zintl phases, that means anions together with a shell of next nearest cations, led to the idea to use A-atom-coordinating molecules such as 18-crown-6 [1], which shield the cation from one side only (Fig. 1, b). To our knowledge, no examples of deltahedral Zintl ions with [A-(18-crown-6)]<sup>+</sup> counterions have been reported, and the addition of 18-crown-6 to the

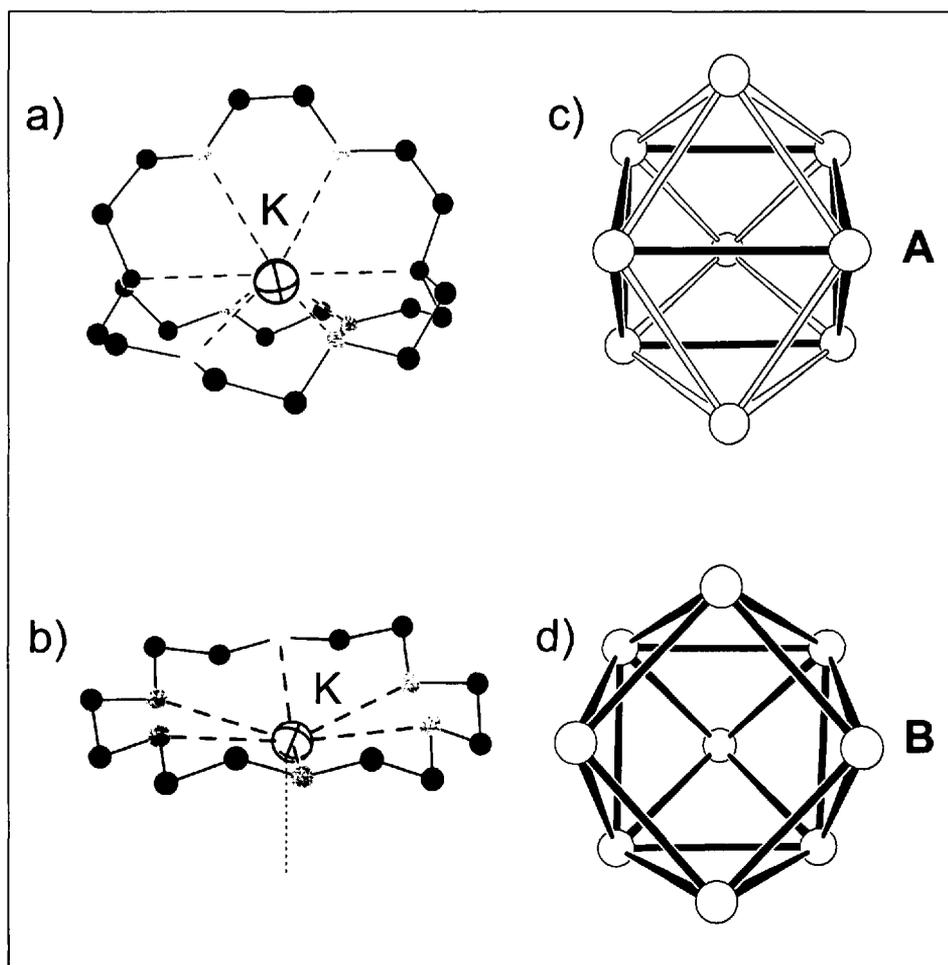


Fig. 1. a) [K([2.2.2]crypt)] unit; b) [K(18-crown-6)] unit with additional coordination site [1]; c) closo-cluster A: tricapped trigonal prism; d) nido-cluster B: monocapped quadratic antiprism

ethylenediamine extracts of alloys did not lead to crystalline compounds. To overcome these problems, we developed a different reaction route. We obtained products which can be seen as 'intermediates' between typical solid-state compounds and 'isolated' molecular units.

### Poster Presentation

The reducing properties of alkali  $A^+$  and  $A^-$  are well documented in solution and in the solid state. Alkaliides are obtained even in crystalline form by disproportionation reactions of alkali metals in ethers and amines in the presence of crown ethers or cryptands [5]. We found recently that the blue melts obtained from alkali metals (K or Rb) and 18-crown-6 at 40–80° are capable of reducing the elements Sn, As, Sb, and Te. The X-ray-amorphous products can be dissolved in ethylenediamine or DMF. From these solutions, several compounds containing polyanions with direct cation-polyanion interactions could be obtained (Fig. 2, a–g).

In the case of Sn, two compounds each containing  $Sn_9^{4-}$  anions could be isolated. From Wade's rules, one would expect a  $C_{4v}$ -symmetric *nido*-structure **B** corresponding to 22 skeletal electrons of  $Sn_9^{4-}$  as shown in Fig. 1, *d. closo*-Clusters **A** (Fig. 1, *c*) are expected for clusters with 20 framework electrons, whereas clusters with 21 electrons adopt structures which lie between the boundary structures **A** and **B**. The appropriate structures of  $Sn_9^{4-}$  and  $Sn_9^{3-}$  are known with [K-crypt] counterions. The use of 18-crown-6 leads to the compounds  $[K(18\text{-crown-6})]_4Sn_9$  (**1**) and  $[K(18\text{-crown-6})]_3KSn_9 \cdot en$  (**2**), in which the  $Sn_9^{4-}$  anions have two and four direct contacts to K-atoms, with distances between 3.535(2) and 4.154(5) Å (Fig. 2, a–c), respectively. Partial charge compensation through the cations might be seen as a reason that the 22-electron clusters in (**1**) and (**2**) adopt structures which are generally found for 21-electron clusters instead of the ideal structure **A**.

Using group-15 elements, we found  $E_7^{3-}$  anions with nortricyclan structure. Our single-crystal structure determinations of  $[K(18\text{-crown-6})]_3As_7$  (**3**),  $[K([2.2.2]\text{-crypt})]_2[K(18\text{-crown-6})]Sb_7 \cdot 0.5en$  (**4**), and  $[Rb(18\text{-crown-6})]_3Sb_7$  (**5**) reveal a gradual change in the binding preference of the alkali-metal cations to the anions. In crystals of (**4**) (Fig. 2, *e*), the cation of the  $[K(18\text{-crown-6})]$  unit coordinates to the two-bonded (2b-E) Sb-atoms (3.686(3) and 3.808(3) Å), which is expected from formal charge allocations. A longer distance

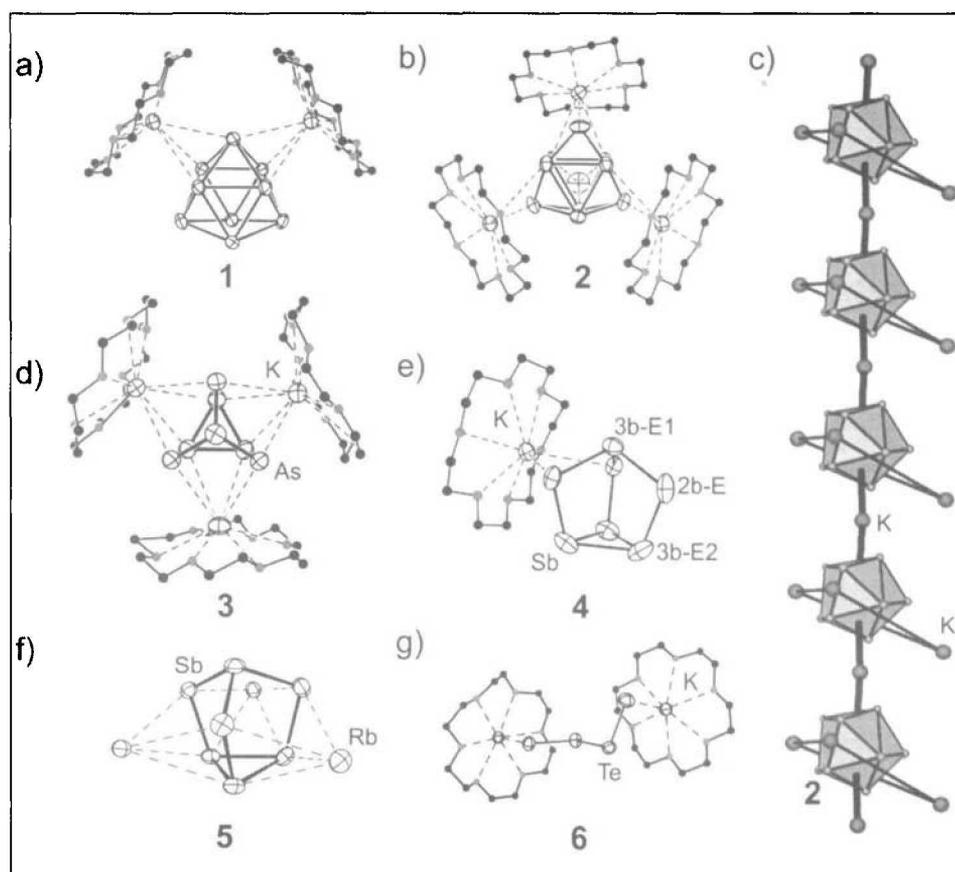


Fig. 2. X-ray single-crystal structures: a)  $[K(18\text{-crown-6})]_4Sn_9$  (**1**); b)  $[K(18\text{-crown-6})]_3KSn_9 \cdot en$  (**2**); c) infinite chain  $[K_4Sn_9]_n$  of **2** (18-crown-6 molecules are omitted); d)  $[K(18\text{-crown-6})]_3As_7$  (**3**); e)  $[K([2.2.2]\text{-crypt})]_2[K(18\text{-crown-6})]Sb_7 \cdot 0.5en$  (**4**); f)  $[Rb(18\text{-crown-6})]_3Sb_7$  (**5**) (for reasons of clarity the 18-crown-6 molecules are omitted); g)  $[K(18\text{-crown-6})]_2Te_4$  (**6**)

(4.382(3) Å) is observed between K and the apical three-bonded Sb-atom (3b-E1), the longest (4.802(3) Å) are the ones to the three-bonded Sb-atoms of the basal plane (3b-E2). In **3**, each K-atom is bound to 2b-As-atoms ( $\emptyset$  3.484 Å) and with significantly different distances to 3b-As2-atoms ( $\emptyset$  3.714 Å). The bonding situation in **5** resembles the one in **3** (Fig. 2, *f*), however, no apparent preference of the coordination of Rb to the 2b-Sb-atoms over the 3b-Sb2-atoms is found (distance range: 3.750(2) to 4.158(2) Å).

Anions of group-16 elements have higher valence-electron concentrations and form chains instead of deltahedral clusters. Our reaction route led to two compounds containing the well-known  $Te_4^{2-}$  anion:  $[K(18\text{-crown-6})]_2Te_4$  (**6**) and  $[K(en)(18\text{-crown-6})][K(18\text{-crown-6})]Te_4$  (**7**). Among the multitude of known salts with tetratelluride anions, compounds with  $[K(18\text{-crown-6})]$  units did not exist. In crystals of **6**, the  $Te_4^{2-}$  anion shows short contacts to both  $[K(18\text{-crown-6})]$  units (3.578(2) and 3.610(2) Å). In **7**, only one K-atom coordinates directly to a Te-atom. The coordination sphere of the second  $[K(18\text{-crown-6})]$  unit is completed by an ethylenediamine molecule.

### Conclusions

The newly developed synthetic route leads to *Zintl* anions from the corresponding elements under 'soft' conditions. Complexation of the counterions with 18-crown-6 opens the possibility to stabilize larger units of *Zintl* phases, as it is shown for the infinite chain  $[K_4Sn_9]_n$  of **2** (Fig. 2, *c*).

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- [1] 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane; [2.2.2]crypt = [2.2.2]Cryptofix = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; en = ethylenediamine; DMF = *N,N'*-dimethylformamide.
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