Main Group Metal Compounds

Synthesis and structure of [K–(12-crown-4)$_2$]$_2$[K–(12-crown-4)]$_2$[Sn$_9$]·4en[†]

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The new compound [K–(12C4)$_2$]$_2$[K–12C4]$_2$[Sn$_9$]·4en (1), where 12C4 is 12-crown-4 polyether, was crystallized from an ethylenediamine solution of an intermetallic precursor with nominal composition K$_4$Li$_2$Sn$_8$. The structure of the compound (orthorhombic, *Cmca*, *a* = 21.763(4), *b* = 16.030(3), *c* = 51.85(1) Å, *Z* = 8) contains isolated deltahedral clusters of [Sn$_9$]$^{4-}$. The clusters are of C_s symmetry and are *nido* according to the number of bonding electrons. The potassium countercations are sequestered by the very small 12C4 ether: half of them are sandwiched between a pair of molecules and the other half are coordinated by a single molecule. The latter potassium cations also bridge edges of the tin clusters, and each cluster has two such coordinated cations. Coordination of potassium cations by such small crown ethers is quite rare. Copyright © 2003 John Wiley & Sons, Ltd.

INTRODUCTION

Deltahedral Zintl anions have fascinated scientists ever since their discovery in the 19th century,[1] and many such species have been synthesized and characterized since then.[2,3] Typically, they are crystallized from ethylenediamine or liquid-ammonia solutions with the help of various cation-sequestering agents such as crypt-2,2,2 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8] hexacosane) or crown ethers. The most stable species seem to be nine-atom clusters with charges of 3− or 4− and shapes that can be considered as variously distorted tricapped trigonal prisms. As in the well-known cage-like boranes, bonding in these clusters is achieved via delocalization of the available electrons, and the numbers of the latter follow Wade's rules.[4] We have shown that upon soft oxidation such germanium clusters can couple in different modes to form various oligomeric species when crystallized with appropriate countercations. The first dimer of deltahedral clusters was stabilized with a combination of non-sequestered cesium and cryptated

potassium cations in Cs$_4$(K–crypt-2,2,2)$_2$[Ge$_9$–Ge$_9$].[5] Later, two trimers and a tetramer of two-bonded clusters were found in (Rb–crypt-2,2,2)$_6$[Ge$_9$=Ge$_9$=Ge$_9$]·2en and (K–18C6)$_6$[Ge$_9$=Ge$_9$=Ge$_9$]·2en and in (Rb–18C6)$_8$[Ge$_9$=Ge$_9$=Ge$_9$=Ge$_9$]·4en respectively, where 18C6 is 18-crown-6 ether.[6,7] Also, a compound, (K–18C6)$_2$[Ge9]·en, with infinite chains of [–(Ge$_9^{2-}$)–]$_\infty$ was synthesized and characterized by Guloy's group.[8]

The sizes and the shapes of the available cations in the solution and the concentration of the precursor are apparently of great importance for the crystallization of different species, as it seems that differently charged clusters coexist in such solutions, i.e. E$_9^{2-}$, E$_9^{3-}$, E$_9^{4-}$, and various oligomers are in equilibria between themselves and free solvated electrons (E = Ge, Sn, Pb). Thus, the availability of only large and bulky cryptated cations (in excess of crypt) leads usually to crystallization of E$_9^{3-}$, apparently because only three large cations can pack with one cluster.[9–11] The presence of both free and sequestered alkali-metal cations leads to either E$_9^{4-}$ or [E$_9$–E$_9$]$^{6-}$, depending on the ratio between the two types of cation.[5,12,13] Flat sequestering agents, such as crown ethers, on the other hand, seem to have different effects depending on the element forming the cluster. Thus, depending on the concentration of the precursor, 18C6 stabilizes either linear oligomers or polymers of germanium, but the same ether stabilizes just the E$_9^{4-}$ cluster for tin in [K–18C6]$_3$K[Sn$_9$], [K–18C6]$_4$[Sn$_9$], and [Rb–18C6]$_2$Rb$_2$[Sn$_9$]·1.5en.[14,15] Guided by these considerations, we have started exploring the sequestering capabilities

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

of other, less conventional, crypts and crown ethers and their capability to stabilize different cluster species for different elements. Here, we present a nine-atom tin cluster, Sn_9^{4-}, crystallized with potassium countercations that are sequestered by the very small 12-crown-4 ether (12C4). Apparently, the small size of the crown ether and its inability to coordinate spherically around the larger potassium stabilize the cluster with a charge of 4− instead of 3− observed with crypt-2,2,2 as a sequestering agent.[9–11]

EXPERIMENTAL

Synthesis

All operations were carried out in inert atmosphere or under vacuum. Ethylenediamine (Aldrich, >99.5%, redistilled, packaged under nitrogen), 12-crown-4 (Acros, 97%), and tin (Alfa, rod, 99.999%) were used as received. The surfaces of potassium (Alfa, sticks, 98% metal basis, packaged in mineral oil) and lithium (Aldrich, rods, 99.9% metal basis, sealed under argon) were cleaned before use.

Preparation of $K_4Li_2Sn_8$

The precursor solid $K_4Li_2Sn_8$ was made from the elements. The mixture was enclosed in a niobium container and the latter was sealed by arc welding. The container was then sealed in an evacuated fused-silica ampoule. This assembly was heated at 400 °C for 20 days.

Preparation of $[K–(12C4)_2]_2[K–12C4]_2[Sn_9]\cdot4en$ (1)

Inside a glove box, 71 mg (∼6×10^{-5} mol) of precursor were placed in a test tube and were covered with 1 ml ethylenediamine. A brown solution was obtained. A large excess of 12C4 (∼300 mg; 1.7×10^{-3} mol) was added, the solution was heated to 45–50 °C, and was stirred at that temperature for about 40 min. The color of the solution changed to red–brown. Some remaining solid was filtered out and the solution was cooled to room temperature and left standing for about 20 h. Red plate-like crystals with sizes suitable for X-ray diffraction studies were formed on the walls and the bottom of the test tube.

Structure determination

Several crystals of **1** were placed on a micro slide and were covered with oil (Paratone–N) inside the glove box. The slide was taken out and, under a microscope, crystals were picked with thin glass fiber. X-ray diffraction data were collected of the best one at 100 K using a Bruker APEX diffractometer with a CCD area detector and graphite-monochromated Mo Kα radiation. The structure was solved by direct methods in *Cmca* and was refined on F^2 (full matrix, absorption correction with XABS) using the SHELXTL V5.1 package. Details of the data collection and refinement are given in Table 1.

Table 1. Selected data collection and refinement parameters for $[K–(12C4)_2]_2[K–12C4]_2[Sn_9]\cdot4en$

Empirical formula	$C_{56}H_{128}O_{24}N_8K_4Sn_9$
Formula weight (g mol^{-1})	2522.27
Measurement temperature (K)	100
Wavelength (Å)	0.710 73
Crystal system	Orthorhombic
Space group, Z	*Cmca*, 8
Unit cell dimensions	
a (Å)	21.763(4)
b (Å)	16.030(3)
c (Å)	51.85(1)
V (Å^3)	18089(5)
Density (g cm^3)	1.852
Absorption coefficient (mm^{-1})	2.691
Crystal size (mm^3)	$0.25 \times 0.25 \times 0.02$
Crystal color/shape	red/plate
2θ range (deg)	3.96–46.64
Collected/independent reflections	53 642
Parameters/data ($I \geq 2\sigma_I$)	459/5227
$R_1/wR_2(I \geq 2\sigma_I)$ (%)	8.8/17.27
R_1/wR_2 (all data) (%)	11.03/18.00

RESULTS AND DISCUSSION

The specific precursor with nominal composition $K_4Li_2Sn_8$ that was used for the preparation of **1** was chosen because a compound with this stoichiometry was characterized recently.[16] This compound and the isostructural $Rb_4Li_2Sn_8$ contain isolated *arachno*-clusters of Sn_8^{6-}, square antiprisms where the square faces are capped by lithium atoms forming $[Li_2Sn_8]^{4-}$ *closo*-species. The relatively small 12-crown-4 ether was intended to 'exo-cap' the lithium and eventually extract the whole cluster as $[(Li–12C4)_2Sn_8]^{4-}$ in solution. However, the ether sequestered the potassium cations instead. It should be mentioned that the precursor made by this particular synthesis (above) contained more than one phase: $K_4Li_2Sn_8$,[16] $K_{12}Sn_{17}$,[17] and one or more phases that could not be identified. $K_{12}Sn_{17}$ is isostructural with the known $Rb_{12}Si_{17}$ and contains isolated tetrahedra of Sn_4^{4-} and nine-atom clusters of Sn_9^{4-}.[17] This compound is known to dissolve readily in ethylenediamine, even without the help of sequestering agents. The solubility of $K_4Li_2Sn_8$, on the other hand, is not known; therefore, it is not clear whether the solution of the precursor had both phases dissolved or only $K_{12}Sn_{17}$.

The structure of compound **1** is made of isolated deltahedral clusters of Sn_9^{4-} (Fig. 1) that are separated by sequestered potassium cations (Figs. 1 and 2) and some solvent molecules. As with many nine-atom clusters of the carbon group, the clusters of this compound can be described as distorted tricapped trigonal prisms. This particular cluster has C_s symmetry with the mirror plane containing atoms 1, 4, and 6 (Fig. 1). The capping atoms are 1, 5, 5 and the two triangular bases of the prism are 2, 2, 4 and 3, 3, 6.
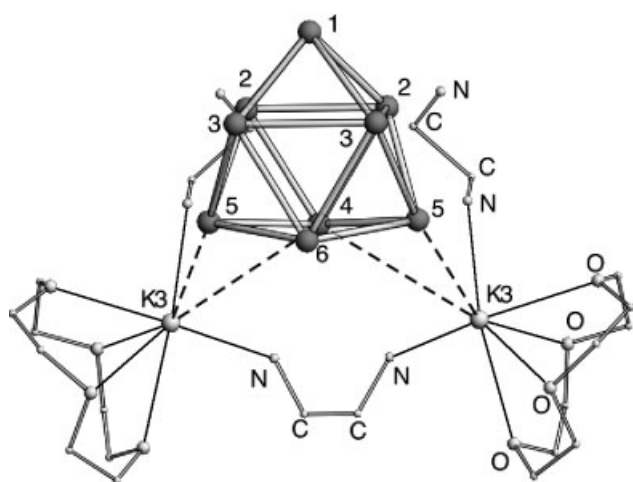
Figure 1. The deltahedral cluster Sn_9^{4-} in **1** together with the two [K–(12C4)] countercations coordinated to two of its edges (edges 4–5). Distances (Å): Sn1–Sn2 2.929(2), Sn1–Sn3 2.937(2), Sn2–Sn2 3.056(2), Sn2–Sn3 3.419(2), Sn2–Sn4 2.977(2), Sn2–Sn5 2.958(2), Sn3–Sn3 3.059(3), Sn3–Sn5 2.962(2), Sn3–Sn6 2.973(2), Sn4–Sn5 2.943(2), Sn5–Sn6 2.964(2).
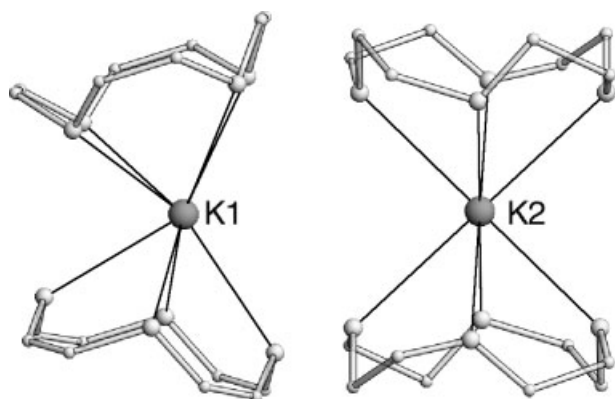

Figure 2. The two cations K1 and K2 in **1** are each sandwiched by two molecules of 12C4. The latter are staggered and tilted with respect to each other around K1, but are eclipsed and parallel around K2.

Typically, the distortions are elongations of one or more of the trigonal prismatic edges along the threefold axis. A special case among these is an elongation of one prismatic edge to such an extent that a monocapped square antiprism with C_{4v} symmetry is achieved. However, more common are clusters of lower symmetry due to either the degree of elongation or the number of elongated edges. It has been shown that, independent of the type of distortion, all these clusters carry charges of 3– or 4–, but not 2–. The distortion observed for the clusters in **1** is clearly elongation along the three prismatic edges, i.e. along 4–6 and the two edges 2–3. These edges,

3.734(2) Å for 4–6 and 3.419(1) Å for 2–3, are clearly much longer than the rest of the distances in the cluster, which fall in the range 2.927(1)–3.059(2) Å. Extended Hückel calculations carried out for $[Sn_9]^{4-}$ confirmed the *nido*-character of the cluster with a HOMO–LUMO gap of 3.69 eV at 22 bonding electrons (in addition to 18 for lone pairs).

The four potassium countercations in the structure are sequestered in two different modes by the 12C4 ether molecules: K1 and K2 are sandwiched by two ether molecules (Fig. 2), whereas K3 is coordinated by only one such molecule (Fig. 1). The potassium cations are removed quite far from the planes of the cycles. This is quite normal, as a result of the small size of 12C4 ether and in order to achieve normal K–O distances, within 2.68(1)–2.88(2) Å in this particular case. These distances are actually shorter than those observed between potassium and 12C4 in the structure of the alkalide [K⁺–(18C6)(12C4)](Na⁻), 2.815–3.131 Å.[18]

The two sandwiched cations in **1** differ from each other in the way they are coordinated by the crown ethers. The oxygen atoms of the two cycles are staggered around K1 but are eclipsed around K2. Furthermore, the planes of the rings are parallel in the latter but are substantially tilted with respect to each other in the former. One possible reason for the tilt is the presence of additional ligands, such as solvent molecules, coordinated to the open side of this potassium atom. However, no electron density was found in this vicinity; also, there is no room for an ethylenediamine molecule there. A closer look at the surroundings of this sandwich revealed the presence of two [K2–(12C4)₂] cations nearby that have their crown-ether ligands too close to those of K1. Thus, simple space issues seem to be the reason for the somewhat distorted coordination around K1.

K3 is the cation coordinated with only one crown-ether molecule, and, as a result of this, half of its coordination sphere is exposed for other interactions. Thus, it is found to be additionally coordinated by lone pairs of electrons from the tin cluster as well as ethylenediamine molecules captured in the structure. There are two such potassium cations per cluster, each bridging an edge. The two bridged edges are equivalent, between tin atoms 4 and 5, and the two K–Sn distances are 4.193(5) Å and 4.030(6) Å respectively. These distances are similar to those observed in [K–18C6]₃K[Sn₉].[14,15] The two ethylenediamine molecules around K3 complete its coordination sphere with K–N distances of 2.96 and 2.84 Å.

In conclusion, we have found that small crown ethers, such as 12C4, stabilize Sn_9^{4-} by sandwiching some of the countercations but also by capping cations that can interact with the clusters. Only the latter type of coordination is similar to that observed for larger crown ethers, such as 18C6.

Acknowledgements

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