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Novel synthetic route to soluble polyanions: synthesis and crystal structure of $[K(18\text{-crown-}6)]_4[Pb_9]\cdot en\cdot tol$ †

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$[K(18\text{-crown-}6)]_4[Pb_9]$ was obtained by a novel synthetic procedure, which allows the generation of polyanions by direct reduction of the elements in molten crown ethers at temperatures slightly above 40 °C; the crystal structure refinement shows the coordination of three K atoms to the nonaplumbide anion.

The classical access to soluble homoatomic anions $[E_n]^{x-}$ is the dissolution of an element E in alkali metal–ammonia solutions at low temperatures and traces back to the work of Joannis in 1891.[1] Since then two further important routes were developed: extraction of binary or ternary alloys with amines[2] and electrochemical reduction using conducting elements or phases as the cathode.[3,4] The breakthrough of structural characterization was the introduction of the sequestering agent [2.2.2]crypt,‡,[5] which allowed the structural characterization of several polyanions E_n^{x-}.[6–9] All compounds in the series of homoatomic lead clusters $[Pb_5]^{2-}$,[10] $[Pb_9]^{3-}$,[11] $([Pb_9][Pb_9])^{6-}$ [12] and $[Pb_9]^{4-}$ [13] as well as the organometallic complex $[Cr(CO)_3Pb_9]^{4-}$ [14] have been structurally characterized in the form of their $[K([2.2.2]crypt)]^+$ salts. Attempts to use other counter ions did not lead to crystalline products of nine-atom clusters.[15]

Recently we found that alkali metals K, Rb and Cs dissolve in the crown ether 18-crown-6 above its melting point of 40 °C.[16] The deep blue solutions of alkalides or electrides, which are formed, are capable of reducing Group 14 to Group 16 elements. Further, on addition of a small amount of solvent such as ethylenediamine, DMF or acetonitrile crystalline products containing polyanions are easily available in relatively good yields. Lately, we reported the crystal structures of $K[K(18\text{-crown-}6)]_3[Sn_9]\cdot en$ **1** and $[K(18\text{-crown-}6)]_4[Sn_9]$ **2**, which were synthesized in the described manner.[17] Here we report the synthesis and structural characterization of $[K(18\text{-crown-}6)]_4[Pb_9]\cdot en\cdot tol$ **3**§ that represents the first compound containing the polyanion $[Pb_9]^{4-}$ with a counter ion different to A([2.2.2]crypt) (A = alkali metal).

In crystals of **3** four $[K(18\text{-crown-}6)]^+$ cations are present per one nonaplumbide cluster in addition to one en and a toluene solvent molecule. This clearly indicates a charge allocation of −4 for the polyanion. Three [K(18-crown-6)] units coordinate *via* the K atoms to the cluster (Fig. 1) with K–Pb distances in the range 3.901 to 4.215 Å. The fourth K atom is further away (d(Pb–K) > 6.5 Å) and its coordination sphere is completed by a chelating en molecule. The toluene molecule shows no short contacts to other atoms. The coordination of the [K(18-crown-6)] units to $[Pb_9]^{4-}$ is notable. Two of the three coordinating K-atoms are in contact with a triangular side of the Pb_9 polyhedron, the third binds to the *nido* cluster in a rather symmetrical way *via* the four Pb atoms of the open rectangle of the cluster (Fig. 1). Whereas the first type is more frequent in compounds containing polyanions and alkali metal atoms,[16] the latter η^4 coordination of polyanions to metal atoms is observed for transition metal complexes $[Cr(CO)_3E_9]^{4-}$ (E = Sn,[18] Pb[14]).

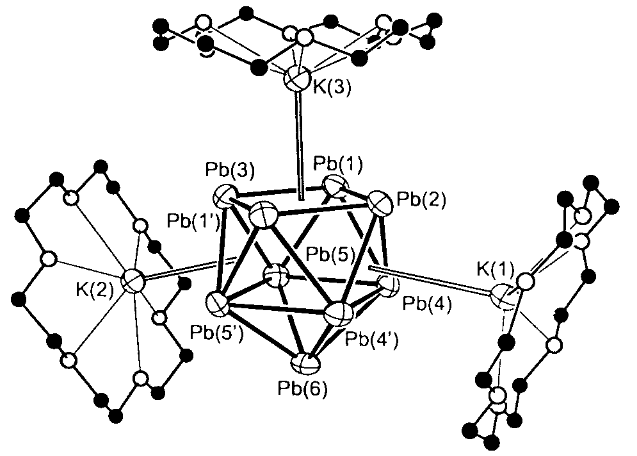
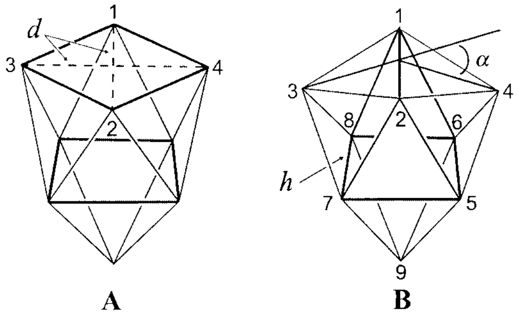


Fig. 1 Details of the crystal structure of **3**. The displacement parameters of the Pb and K atoms are shown with 50% probability ellipsoids. For reasons of clarity crown ether molecules are shown as stick-and-ball models. Important distances (Å): Pb(1)–Pb(2) 3.175(1), Pb(1)–Pb(3) 3.127(1), Pb(1)–Pb(1′) 4.427(1), Pb(1)–Pb(4) 3.114(1), Pb(1)–Pb(5) 3.080(1), Pb(2)–Pb(4) 3.104(1), Pb(3)–Pb(5) 3.122(1), Pb(4)–Pb(4′) 3.324(1), Pb(4)–Pb(5) 3.367(2), Pb(4)–Pb(6) 3.081(1), Pb(5)–Pb(5′) 3.475(1), Pb(5)–Pb(6) 3.070(1).

From Wade's rules, one would expect a C_{4v} symmetric *nido* structure **A** corresponding to the 22 skeletal electrons of $[Pb_9]^{4-}$. *Closo* clusters with D_{3h} point symmetry **B** are expected for clusters with 20 framework electrons, whereas clusters with 21 electrons, as found in $[Pb_9]^{3-}$, adopt structures which lie between these boundary structures. The classification of the structure to the polyhedra **A** and **B** can be accomplished according to the criteria in Scheme 1 and Table 1. An ideal threefold capped trigonal prism **B** has equal prism heights h and three equal dihedral angles α, whereas in an undistorted monocapped square antiprism **B** one angle α equals zero and the non-capped face possesses two diagonals of same length d.



Scheme 1 Two possible structures, **A** and **B**, of nine-atom clusters: a threefold capped trigonal prism **B** arises from a singly capped square antiprism **A** when the atom sites 1 and 2 of **A** approach each other. The parameters prism height h, dihedral angle α, and the diagonal lengths d in **A** characterize the two boundary structures.

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3339/

Table 1 Structural parameters of nine-atom lead clusters (see Scheme 1)

Compound[a]	h^1	h^2	h^3 [b]	a[c]/°			d[d]/Å	
$[K([2.2.2]crypt)]_3Pb_9$ [11]	1.08	1.01	1.01	14	20	21	3.599	4.892
$[K([2.2.2]crypt)]_6Pb_9Pb_9$ [12]	1.07	1.02	1	16	18	23	3.580	4.938
	1.15	0.98	0.98	12	30	21	3.626	4.687
	1.08	1.02	0.99	18	19	20	3.634	5.112
$[K([2.2.2]crypt)]_4Pb_9$ [13]	1.30	1.03	1.00	1	29	31	4.334	4.376
$[K(18\text{-crown-}6)]_4Pb_9$ **3**	1.32	1.04	0.99	0	28	30	4.427	4.433
K_4Pb_9 [19]	1.31	1.06	1.02	0	32	33	4.388	4.388
	1.16	1.16	1.03	17	17	28	3.452	5.075
Cs_4Pb_9 [20]	1.29	1.06	1.01	5	23	27	4.307	4.480

[a] Formulae minus any associated solvent molecules. [b] Normalized heights[11] of a best trigonal prism **B**. Reference value is the shortest height (3.345 Å) of the non-disordered anion in $[K([2.2.2]crypt)]_6Pb_9Pb_9$. This compound contains two crystallographically independent Pb_9 clusters. One of them shows a rotational disorder, thus the structure was described with three independent clusters. K_4Pb_9 contains two independent clusters. [c] Dihedral angles 3–1–2–4, 3–7–8–9, 4–5–6–9 (Scheme 1). [d] Diagonal lengths 1–2 and 3–4 of the open rectangle in structure type **A**.

The nonaplumbide anion in **3** lies on a crystallographic glide plane and clearly adopts a monocapped square antiprismatic structure with C_{4v} point group symmetry. Similarly all other structurally characterized $[Pb_9]^{4-}$ clusters possess almost perfectly C_{4v} symmetry (Table 1). In contrast $[Sn_9]^{4-}$ clusters in **1** and **2** form distorted tricapped trigonal prisms with approximately C_{2v} symmetry.[17]

The most common route to homoatomic nine-atom clusters is the extraction of more or less well defined precursor alloys. The characterization of alloys containing $[Pb_9]^{4-}$ clusters leads to the view that the extraction of the related alloys is a simple dissolution of an ionic compound.[19] The synthetic route described here *via* the reduction of tin or lead with alkali metals at temperatures below the melting points of the involved elements shows, however, that there is no necessity for preformed clusters.

Acknowledgements

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Notes and references

‡ 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane, en = ethylenediamine, tol = toluene, [2.2.2]crypt = 1,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

§ Synthesis of **3**: 18-Crown-6 (800 mg, 3.0 mmol), K (98 mg, 2.5 mmol) and Pb (725 mg, 3.5 mmol) were mixed in a Schlenk tube (20 mL). The mixture was heated to 40–50 °C, just allowing the crown ether to melt, and stirred at this temperature for 1 h. Alternatively K and 18-crown-6 can be stirred at 40 °C, and Pb added in a second step to the deep blue melt. The color of the originally blue melt changes during the reaction from light gray to dark gray. Ethylenediamine (2 mL) was added to the cooled melt, and the mixture sonicated for not more than 5 min (the solution is unstable at higher temperatures and should be kept below 50 °C). The brown solution was filtered and layered with toluene (4.5 mL). After one week the product was obtained in the form of dark red, nearly black, brick-shaped crystals (yield: 90 mg; 7.2% based on employed Pb and 25% based on Pb undergoing reaction). Elemental analysis: calc. (found) [%]: C 21.19 (21.35), H 3.49 (3.39), K 4.84 (5.28), N 0.87 (0.81), Pb 57.72 (58.80).

Crystal data for **3**: $C_{57}H_{112}K_4N_2O_{24}Pb_9$, 3230.71 g mol^{-1}, monoclinic, $P2_1/m$ (no. 11), $Z = 2$, $a = 14.618(2)$, $b = 14.771(2)$, $c = 21.583(3)$ Å, $\beta = 108.13(3)°$, $V = 4428.8(1)$ Å^3, $T = 223$ K, μ(Mo-Kα) = 17.289 mm^{-1}. Of a total of 39939 reflections measured 9452 were independent ($R_{int} = 0.099$). Final residuals were $R_1 = 0.043$ and $wR = 0.084$ for 5934 reflections with $I > 2\sigma(I)$ and $R_1 = 0.081$ and $wR = 0.097$ for all reflections. The crown ether molecule coordinated to K1 is disordered over two sites and was refined with split positions of equal weights. CCDC reference number 186/1634. See http://www.rsc.org/suppdata/dt/1999/3339/ for crystallographic files in .cif format.

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