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Synthesis and Structure of the Zintl-Phase K_4Pb_9 Containing Isolated Pb_9^{4-} Clusters of Two Different Geometries

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The first nine-atom deltahedral clusters of lead in the solid state are found in the Zintl-phase K_4Pb_9. The compound crystallizes in the monoclinic space group $P2_1/m$, $Z = 4$, with $a = 9.648(3)$ Å, $b = 13.243(5)$ Å, $c = 15.909(8)$ Å, and $\beta = 103.24(4)°$. The isolated Pb_9^{4-} clusters are of two different geometries, a monocapped square antiprism and an elongated tricapped trigonal prism.

Introduction

Until recently homoatomic deltahedral clusters in the solid state (larger than four atoms) were known only for the heavier analogues of the boron group and the "anomalous" Bi_9^{5+} of the pnictogens.[1,2] Our attempts to synthesize heteroatomic clusters involving elements of the carbon group have resulted in the discovery of the first large deltahedral cluster of that group in the solid state, Ge_9^{4-}, with the shape of a monocapped square antiprism,[3] and the unique heteroatomic Ge_8Zn^{6-}, a dimer of vertex-fused trigonal bipyramids.[4] Recent measurements by Raman spectroscopy of binary compounds of germanium or tin with different alkali metals have indicated that similar nine-atom clusters of tin may exist as well.[5] Nine-atom clusters of the heavier members of the carbon group were known only in solutions[6] or in compounds crystallized from such solutions, usually with cryptated alkali metal.[1] The current theory on the formation of these clusters infers that they assemble during the dissolution of the precursor in the solvent, usually ethylenediamine or liquid ammonia, and that they do not exist in the precursor,[1] a binary A_xE_y compound (A = alkali metal, E = group 14 element) usually referred to as a "melt" or an "alloy". We have already shown that Ge_9^{4-} exists in the precursor Cs_4Ge_9, and here we report on similar clusters of lead. In K_4Pb_9 we have characterized the first clusters of this element in the solid state. The clusters Pb_9^{4-} found in this compound are of two different geometries, a monocapped square antiprism and a tricapped trigonal prism. The latter is the only other example besides Bi_9^{5+} of a tricapped trigonal prism with $2n + 4$ skeletal electrons instead of the usual $2n + 2$.

Table 1. Selected Data Collection and Refinement Parameters for K_4Pb_9

empirical formula	K_4Pb_9
fw	2021.11
unit cell params[a]	$a = 9.648(3)$ Å
	$b = 13.243(5)$ Å
	$c = 15.909(8)$ Å
	$\beta = 103.24(4)°$
	$V = 1978.6(14)$ Å^3
space group, Z	$P2_1/m$ (No. 11), 4
radiation, λ	Mo Kα, 0.710 73 Å
μ	770.83 cm^{-1}
temp	293 K
density (calcd)	6.785 g·cm^{-3}
R indices ($I > 2\sigma_I$)[b]	R1 = 7.00%, wR2 = 13.70%

[a] Room temperature Guinier data with Si as an internal standard ($\lambda = 1.540\ 562$ Å). [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2F_0^2 + (0.0610P)^2 + 9.4728P]$, $P = (F_o^2 + 2F_c^2)/3$.

Experimental Section

K_4Pb_9 was made in high yield by fusion of a stoichiometric mixture of K and Pb (Alfa-Aesar) at 900 °C for 1 h, followed by slow cooling at a rate of 5°/h. The surfaces of the elements were scraped before use. Containers and handling are described in more detail elsewhere.[7]

A single crystal of the dark gray, brittle compound was studied by X-ray diffraction. Data were collected on a Siemens SMART system with Mo Kα radiation ($2\theta_{max} = 50°$, crystal size 0.20 × 0.17 × 0.08 mm) at 25 °C and corrected for absorption by semiempirical methods. The structure was solved by direct methods in the monoclinic space group $P2_1/m$ ($Z = 4$) and refined with the use of the SHELXTL-V5.0 package. The lattice parameters of the compound, $a = 9.648(3)$ Å, $b = 13.243(5)$ Å, $c = 15.909(8)$ Å, and $\beta = 103.24(4)°$, were determined from the corresponding X-ray powder pattern (Enraf-Nonius Guinier camera, Cu Kα radiation) by least-squares refinement of the mesured 2θ values together with those of the internal standard silicon. Details of the data collection and refinement and of important Pb−Pb distances are listed in Tables 1 and 2, respectively. The compound diffracted extremely weakly.

A powder sample was measured for unpaired electrons on a VARIAN EPR spectrometer at room temperature.

Extended Hückel calculations were carried out on the Pb_9^{4-} clusters with the following parameters for Pb: $H_{ii} = -12.49$ and -6.53 eV for s and p, respectively, and $\zeta = 2.386$ and 1.880 for s and p, respectively.[8]

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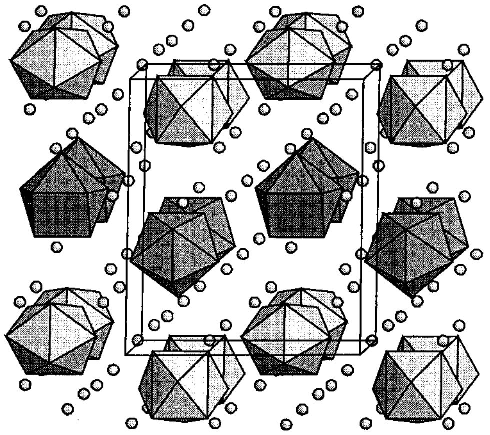

Figure 1. A general view along *b* of the structure of K_4Pb_9 (monoclinic) showing the two types of nine-atom clusters: the A-types are darker than the B-types. The potassium cations are shown as isolated spheres, and the unit cell is outlined.

Table 2. Important Pb−Pb Distances [Å] in K_4Pb_9

Pb1 −	Pb1	3.096(4)	Pb7 −	2 Pb8	3.132(2)
	Pb2	3.234(3)		Pb9	3.080(3)
	Pb3	3.895(3)		Pb10	3.077(3)
	Pb5	3.147(2)	Pb8 −	Pb7	3.132(2)
	Pb6	3.082(3)		Pb9	3.419(2)
Pb2 −	2 Pb1	3.234(3)		Pb10	3.544(3)
	Pb4	3.452(3)		Pb11	3.166(3)
	2 Pb5	3.188(2)		Pb12	3.103(2)
Pb3 −	Pb1	3.895(3)	Pb9 −	Pb7	3.080(3)
	Pb3	3.136(4)		2 Pb8	3.419(2)
	Pb4	3.340(3)		2 Pb11	3.159(2)
	Pb5	3.113(3)	Pb10 −	Pb7	3.077(3)
	Pb6	3.127(3)		2 Pb8	3.544(3)
Pb4 −	Pb2	3.452(3)		2 Pb12	3.137(3)
	2 Pb3	3.340(3)	Pb11 −	Pb8	3.166(3)
	2 Pb5	3.083(2)		Pb9	3.159(2)
Pb5 −	Pb1	3.147(2)		Pb11	3.119(4)
	Pb2	3.188(2)		Pb12	3.076(3)
	Pb3	3.113(3)	Pb12 −	Pb8	3.103(2)
	Pb4	3.083(2)		Pb10	3.137(3)
Pb6 −	2 Pb1	3.082(3)		Pb11	3.076(3)
	2 Pb3	3.127(3)		Pb12	3.139(4)

Results and Discussion

The structure of the title compound can be described as built of isolated nine-atom clusters of lead surrounded by potassium cations (Figure 1). The clusters are of two different geometries (Figure 2) but with the same formal charge of 4−. Type A clusters (atoms Pb7−Pb12) are nido species, monocapped square antiprisms expected for that charge (Figure 2a). Type B clusters, on the other hand (atoms Pb1−Pb6), have the shape of elongated tricapped trigonal prisms (Figure 2b) with two very long vertical edges of 3.895(3) Å and a shorter third one of 3.452(3) Å. Such a geometry for a cluster of nine atoms and 22 skeletal electrons (corresponding to a charge of 4−) is quite unusual, and the only other example is Bi_9^{5+} found in $BiBi_9(HfCl_6)_3$ and $Bi_9(Bi_3Cl_{14})$.[9,10]

In order to “assign” a particular cluster to one of the above-mentioned geometries, some criteria need to be compared. Traditionally these have been ratios between important distances in the cluster as well as some of its dihedral angles.[1] Listed in Table 3 are the corresponding numbers for a monocapped square antiprism represented by the *nido*-Pb_9^{4-} in (2,2,2-crypt-K)$_3$[KPb_9],[11] a tricapped trigonal prism represented by the paramagnetic *closo*-Pb_9^{3-} in (2,2,2-crypt-K)$_3$$Pb_9$·0.5en,[12] and the unusual elongated tricapped trigonal prism observed for Bi_9^{5+}. We have also calculated these parameters for the two Pb_9^{4-} clusters in the present compound in order to compare them. Clearly the A-type clusters belong to the nido class, while the numbers for the B-type clusters are much closer to those of the tricapped trigonal prism Pb_9^{3-}. Nevertheless, the larger height-to-edge ratio (*h*:*e* in Table 3) for clusters B suggests that they belong rather to the elongated tricapped trigonal prism of the Bi_9^{5+}-type. Electronic similarity with Pb_9^{3-} is ruled out also by the lack of paramagnetic signal in the EPR spectra of K_4Pb_9.

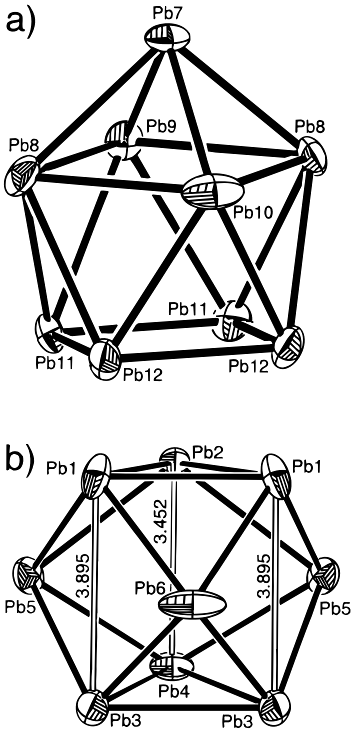

Figure 2. ORTEP drawings of the two types of Pb_9^{4-} clusters in K_4Pb_9: (a) the A-type, a monocapped square antiprism, and (b) the B-type, an elongated tricapped trigonal prism. The thermal ellipsoids are drawn with 50% probability.

Table 3. Selected Edge Ratios and Dihedral Angles in Some Nine-Atom Clusters

		ratios[a]			angles[b]		
cluster	sym	*h*:*e*	h_3:h_1	h_2:h_1	1	2	ref
Pb_9^{4-}	$\sim C_{4v}$	na	1.30	1.02	159	1	11
Pb_9^{4-}(A)	C_{2v}	na	1.28	1.04	160	0	this work
Pb_9^{3-}	$\sim D_{3h}$	1.07	1.06	1.00	176	14	12
Bi_9^{5+}(I)	D_{3h}	1.15	1.00	1.00	180	22	9
Bi_9^{5+}(II)	$\sim D_{3h}$	1.19	1.07	1.00	174	16	10
Pb_9^{4-}(B)	C_{2v}	1.16	1.13	1.13	171	17	this work

[a] *h*:*e*, h_3:h_1, and h_2:h_1 are the ratios of the average height to the average edge of the base, the longest to the shortest height, and the second longest to the shortest height, respectively. [b] Angle 1 is the dihedral angle between the two bases of the trigonal prism or opposed faces in the waist of the square antiprism; Angle 2 is the smallest dihedral angle in the waist of the trigonal prism or the dihedral angle in the base of the square antiprism.

The two types of clusters are in a one-to-one ratio, which means that the formula can be written as $K_8(Pb_9\text{-}A)(Pb_9\text{-}B)$. The

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total charge of 8− for the two clusters and the fact that the A-type clusters are "normal" nido species and therefore bear a charge of 4− mean that the B-type clusters have the same charge. This, in turn, means that the number of skeletal bonding electrons in the cluster is $2n + 4$ and not the $2n + 2$ prescribed by Wade's rules for tricapped trigonal prisms.[13] Extended Hückel calculations on the two clusters show similar HOMO−LUMO gaps, 3.6 and 3.2 eV for the A- and B-types, respectively, at 40 electrons ($2n + 4 = 22$ skeletal electrons plus $2n = 18$ lone pair electrons). Exactly as in Bi_9^{5+}, the extra filled orbital in the B-type clusters is of a_2'' type and is σ-antibonding between the two bases of the trigonal prism, but it is σ- and π-bonding within them. Upon elongation of the prism, that particular orbital is stabilized and eventually becomes the HOMO. For Pb_9^{4-} it is only 0.35 eV above the next filled orbital and below the gap of more than 3 eV.

The distances within the clusters range from 3.076 to 3.544 Å for the A-type and from 3.082 to 3.452 Å for the B-type (Table 2). Compared to Cs_4Ge_9, the clusters in K_4Pb_9 are somewhat closer (relative to the intracluster distances), most likely due to the smaller potassium and larger lead.[3] The closest intercluster contacts of 3.669 Å occur between atoms Pb11 and Pb12 of the bases of the A-type clusters (Figure 2a). Nonetheless, despite that seemingly short distance, there are certainly no bonds between the clusters, and the arguments for this are as follows. The interactions are not radial to the clusters as in all compounds with exo-bonded clusters[2] but are rather parallel to the plane of the base. Second, the distances are not shorter than the intracluster distances as in all exo-bonded clusters (indicative of a localized 2-center, 2-electron bond).[2] Finally, the calculated bond overlap population of less than 0.02 confirms the lack of intercluster interactions. For comparison, these numbers for the edges of the capped square in cluster A are 0.11 and 0.20 for Pb8−Pb10 of 3.544 Å and Pb8−Pb9 of 3.419 Å, respectively. Nevertheless, the effect of the short intercluster contacts is clearly visible on the calculated density of states for the compound. The valence p-band is somewhat broader than usual with a width of about 5 eV. The broadening is due almost completely to the A−A intercluster interactions. Since the band is filled, that is, the upper-energy antibonding states are occupied, the net result is nonbonding interactions between the clusters. The broadening of the valence band leads also to a small band gap of only about 0.30 eV.

There have been three reports in the last four years on compounds containing nine-atom clusters of lead.[11,12,14] All of them have been made by dissolving in ethylenediamine solidified "melts" or "alloys" with nominal compositions of $KPb_{2.05}$ or $KPb_{2.25}$ and then crystallizing the corresponding compounds with the aid of 2,2,2-crypt. It is very likely that both compositions contained primarily K_4Pb_9, and therefore the preassembled clusters of Pb_9^{4-}. This is yet another example, besides Cs_4Ge_9 containing Ge_9^{4-}, showing that the nine-atom clusters do not form during the dissolution. The process of their extraction is perhaps a simple dissolution of an ionic compound composed of monatomic cations of K^+ and polyatomic polyanions of Pb_9^{4-}. The three reports mentioned above describe two different types of clusters, $[K(Pb_9^{4-})]$ and Pb_9^{3-}. With the structure of the precursor known we can now try to better rationalize the results from the solution work. First, we should point out that the two types of clusters in K_4Pb_9 differ in total energy (at the extended Hückel level) by only 0.15 eV, which is 0.04%. Upon dissolution, both clusters may end up as monocapped square antiprisms as in $(2,2,2\text{-crypt-K})_3[KPb_9]$,[11] that is, the clusters of type B convert to the C_{4v} geometry and retain the charge. On the other hand, if any oxidizing agent is present in the solution, the conversion may take a different path. The B-type clusters may "shrink" along the 3-fold axis and become "normal" tricapped trigonal prisms. As a result of this, the a_2'' orbital will go up in energy, will become virtually nonbonding, and will lose an electron. This is what most likely happens during the formation of $(2,2,2\text{-crypt-K})_3Pb_9\cdot0.5en$ and $(2,2,2\text{-crypt-K})_6Pb_9Pb_9\cdot1.5en\cdot0.5tol$ with the paramagnetic clusters of Pb_9^{3-}.[12,14] The clusters in the former compound and one of the two types of clusters in the latter compound are indeed very close to the D_{3h} symmetry, that is, the remnants of the B-type clusters. However, the second type of clusters in the second compound can be interpreted as Jahn-Teller distorted monocapped square antiprisms with 21 electrons.[1] This is consistent with a soft oxidation upon dissolution of K_4Pb_9. The A-clusters will end up with three electrons on a doubly degenerate HOMO (for C_{4v}) and will somewhat distort. It is not clear why the elongated prism can exist in the solid but has not been isolated from solutions.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of K_4Pb_9 is available on the Internet only. Access information is given on any current masthead page.

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