Deltahedral Clusters in Neat Solids: Synthesis and Structure of the Zintl Phase Cs_4Pb_9 with Discrete $Pb_9{}^{4-}$ Clusters

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Introduction

There is a growing interest toward synthesis and possible use of small semiconducting and metallic particles (nanocrystallites, quantum dots). The boundary conditions of the electronic wave functions in such small formations result in electronic and optical properties quite different from those of the corresponding bulk materials and are of potential use in a variety of applications due to that uniqueness. For the elements of group 14, the tetrels (Tt), the classical methods for preparation of such particles and small clusters have been etching, selective epitaxy, and pulsed laser techniques.[1] Reduction of tetrel chlorides with solvated electrons or alkali-metal anions (electrides and alkalides) has been also attempted. Recently, another method for the synthesis of Si and Ge nanoparticles was reported. It utilizes metathesis reactions in liquid medium between suspensions of the Zintl phases KSi and NaGe with silicon and germanium tetrachlorides, respectively.[2,3] Another approach toward nanoparticles with narrow size distribution would be to use solutions of the Zintl cluster anions $Tt_9{}^{4-}$ instead of suspensions of insoluble solids. It has been shown that upon controlled oxidation such solutions produce island structures on a variety of surfaces such as polymers and metals.[4] We have been interested in the characterization of the precursors to such solutions, solidified melts of an alkali-metal and a tetrel. These precursors have been always regarded as featureless alloys with no cluster formations.[5] We have already shown that Zintl cluster anions of the same type, geometry, and charge as those found in solutions also exist in the corresponding precursors, the compounds Cs_4Ge_9, Rb_4Ge_9, and K_4Pb_9.[6,7] Therefore, it is possible that new precursors containing novel clusters, including heteroatomic, might provide different clusters in solution. Along this direction of research two such potential candidates have been discovered, $Rb_{12}Si_{17}$ and $Cs_6(Ge_8Zn)$ containing discrete clusters of $Si_9{}^{4-}$ and Ge_8Zn^{6-}, respectively.[8,9] In addition, recent Raman measurements suggest that nine-atom clusters of germanium, tin, and lead may exist in other binary compounds in the systems alkali metal−tetrel.[10] Here we report on the synthesis, structure, and properties of Cs_4Pb_9, another Zintl phase with discrete nine-atom deltahedral clusters of lead.

Table 1. Crystallographic Data for Cs_4Pb_9

chem formula	Cs_4Pb_9
fw	2396.35
space group, *Z*	$P2_1/n$ (No.14), 4
unit cell params	$a = 10.042(5)$ Å
	$b = 14.781(8)$ Å
	$c = 15.863(8)$ Å
	$\beta = 100.17(4)°$
	$V = 2317(2)$ Å^3
temp	20 °C
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)
d(calcd)	6.868 g cm^{-3}
abs coeff (μ)	712.84 cm^{-1}
R indices ($I > 2\sigma_I$)[a]	$R1 = 9.89\%$, $wR1 = 21.45\%$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/(\sigma^2F_o^2 + 0.1P^2)$, $P = (F_o^2 + 2F_c^2)/3$.

Experimental Section

The title compound was initially made by a reaction loaded in a molar ratio Cs:Pb = 4:8.5 and carried out in a flux of mercury (Cs:Hg = 1:3). The mixture of the elements (Cs from Acros, Pb from Alfa-Aesar after scraping the surface, Hg from Aldrich) was heated at 650 °C for 12 h and cooled to room temperature at a rate of 5°/h. (Details on handling and containers can be found elsewhere.[11]) Later, a nearly 100% yield of the compound was achieved from a stoichiometric mixture of Cs and Pb after heating it at 650 °C for 2 days and cooling it slowly to room temperature with a rate of 4°/h. A few more reactions with stoichiometric mixtures were carried out at different temperature regimes, but all products had traces of lead according to the X-ray powder patterns. The reaction in flux produced larger crystals of the compound, and a few of them were sealed in capillaries and checked for singularity on a single-crystal diffractometer. Data sets of two of them were collected and refined to quite similar final parameters. The data from the better of the two in terms of standard deviations and remaining positive and negative peaks in the difference Fourier map are reported here.[12] Important parameters of the data collection and refinement are summarized in Table 1, while Tables 2 and 3 list the final atomic parameters and important Pb−Pb distances, respectively. Qualitative microprobe analysis was performed on the same crystal, and it showed the presence of Cs and Pb only.

Results and Discussion

The structure of Cs_4Pb_9 (Figure 1) consist of isolated nine-atom clusters of lead that are separated by cesium cations. The clusters (Figure 2) are of one type only, a *nido*-deltahedron with the shape of a monocapped square antiprism. This shape “assignment” for the cluster is quite unambiguous (versus tricapped trigonal prism) according to the dihedral angles and edge ratios that are traditionally used for such purposes.[5] Thus, the two squares of the prism are quite planar with deviations from the least-squares planes of 0.007(1) and 0.050(1) Å. They

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(12) Structure solution and refinement were handled with the SHELXTL V5.0 software package. A hemisphere of data was collected on a CAD4 single-crystal diffractometer at room temperature from a crystal with dimensions 0.10 × 0.15 × 0.20 mm. The data were corrected for Lorentz and polarization effects and for absorption with DIFABS (Xabs). Final *R*-factors ($I > 2\sigma_I$) and positive/negative peaks in the difference Fourier map for the second crystal: $R1/wR1 = 9.92/25.73$ and +7.79/−4.57 e/Å^3, respectively.

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for Cs_4Pb_9

	x	y	z	$U_{eq}{}^a$
Pb1	0.2240(3)	−0.0097(2)	0.3966(2)	0.0383(6)
Pb2	−0.0538(2)	0.0772(2)	0.4058(2)	0.0325(6)
Pb3	0.0190(3)	−0.0077(2)	0.2219(2)	0.0363(6)
Pb4	0.3076(2)	0.1010(2)	0.2514(2)	0.0378(7)
Pb5	0.2318(2)	0.1921(2)	0.4434(2)	0.0334(6)
Pb6	−0.1796(2)	0.1547(2)	0.2263(2)	0.0403(7)
Pb7	0.0592(3)	0.1791(2)	0.1306(2)	0.0387(7)
Pb8	0.2166(2)	0.3018(2)	0.2746(2)	0.0341(6)
Pb9	−0.0357(2)	0.2874(2)	0.3650(2)	0.0349(6)
Cs1	−0.1114(4)	0.4326(3)	0.1585(3)	0.046(1)
Cs2	0.4876(5)	0.2724(3)	0.1211(3)	0.045(1)
Cs3	0.2545(5)	0.4625(4)	0.4863(4)	0.060(1)
Cs4	0.6027(4)	0.2278(4)	0.4088(3)	0.059(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Pb−Pb Distances ($d < 3.6$ Å) in Cs_4Pb_9

Pb1	Pb4	3.061(4)	Pb6	Pb7	3.078(3)
	Pb5	3.072(4)		Pb9	3.107(4)
	Pb2	3.099(3)		Pb2	3.122(4)
	Pb3	3.148(5)		Pb3	3.129(4)
Pb2	Pb1	3.099(3)	Pb7	Pb6	3.078(3)
	Pb6	3.122(4)		Pb4	3.089(4)
	Pb9	3.184(4)		Pb8	3.120(4)
	Pb5	3.296(4)		Pb3	3.176(4)
	Pb3	3.373(4)			
Pb3	Pb6	3.129(4)	Pb8	Pb5	3.111(4)
	Pb1	3.148(5)		Pb7	3.120(4)
	Pb7	3.176(4)		Pb9	3.131(3)
	Pb4	3.275(4)		Pb4	3.146(4)
	Pb2	3.373(4)			
Pb4	Pb1	3.061(4)	Pb9	Pb5	3.093(4)
	Pb7	3.089(4)		Pb6	3.107(4)
	Pb8	3.146(4)		Pb8	3.131(3)
	Pb3	3.275(4)		Pb2	3.184(4)
	Pb5	3.533(4)			
Pb5	Pb1	3.072(4)			
	Pb9	3.093(4)			
	Pb2	3.296(4)			
	Pb8	3.111(4)			
	Pb4	3.533(4)			

are also nearly parallel to each other with a dihedral angle of 1.2(1)° between them. The smallest dihedral angle between opposing triangular faces of the waist (possible bases of a trigonal prism) is very big, 18.5(1)°, and typical for such a geometry (compared with the range of 0−10° observed for trigonal prisms). These numbers compare very well with those for one of the two types lead clusters found in K_4Pb_9, the one with the geometry of a monocapped square antiprism.[7] According to the above criteria, the second type of clusters in the latter structure has been defined as an elongated tricapped trigonal prism.

The distances within the cluster range between 3.061(4) and 3.533(4) Å. The longest ones occur within the capped square of the antiprism (all five-bonded atoms) while the shortest ones are from the capping atom and within the open square of the antiprism (all four-bonded atoms). Clearly the capping atom and the bonding associated with it cause the opening of the capped square of the antiprism. It is also clear that the distances within the square will be inversely proportional to the distance between the capping atom and the square. For example, Pb4 and Pb5 (Figure 2) are the closest to the capping atom at distances of 3.061(4) and 3.072(4) Å, respectively, and as a result of this, the distance between them is the longest, 3.533(4) Å.

The clusters form “wavy” close-packed layers perpendicular to the c axis (Figure 1 and the synopsis figure). The layers are stacked in a hexagonal fashion (ABAB) along that axis. The cesium cations are between the layers and between the clusters of the layers with Cs−Pb and Cs−Cs distances in the ranges 3.873(5)−4.585(6) and 4.497(8)−5.083(6) Å, respectively. They cap faces, edges, and vertexes and are shared by three to five clusters. The shortest intercluster distance, 3.765(5) Å, occurs between two Pb2 atoms. It is longer than the shortest intercluster contact in K_4Pb_9, 3.669(3) Å, due to the larger cesium. Despite the short distance in K_4Pb_9 it has been shown that there are no intercluster bonding interactions in that structure.[7] On the basis of the same arguments, this is even more so for the better separated clusters in Cs_4Pb_9.

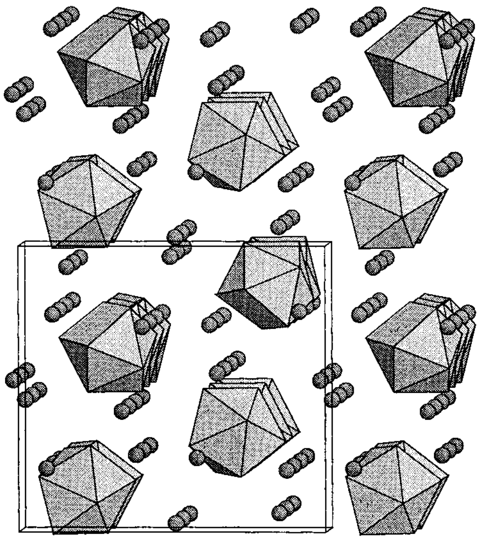

Figure 1. General view of the structure of Cs_4Pb_9 along the a axis (monoclinic, b is vertical). The nine-atom clusters and the cesium cations are shown as polyhedra and isolated spheres, respectively, and the unit cell is outlined.

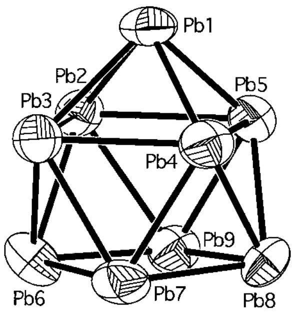

Figure 2. $Pb_9{}^{4-}$ cluster shown with thermal ellipsoids at the 90% probability level. Average distances (Å): to the capping atom, 3.095; in the capped square, 3.369; in the waist, 3.131; in the open square, 3.109. Diagonals of the open square (Å): Pb6−Pb8, 4.480(4); Pb7−Pb9, 4.307(4).

The stoichiometry of the compound can be easily rationalized by the Wade’s rules for counting electrons in deltahedral clusters.[13] The monocapped square antiprism requires $2n + 4$ bonding electrons (*nido*-deltahedron) and $2n$ electrons for lone pairs. This totals 40, and the same number of electrons is available from a formula unit of the compound (4×1 from Cs $+ 9 \times 4$ from Pb). Extended-Hückel band calculations of the structure (clusters only) showed a gap of ca. 0.8 eV at 40 electrons. This gap is more than twice larger and the valence band is quite narrower than those of K_4Pb_9 (band gap of ca.

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(13) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

0.3 eV),[7] and this is most likely due to the longer intercluster distances in Cs_4Pb_9. These considerations clearly suggest that Cs_4Pb_9 is an electronically balanced, closed-shell compound. This was confirmed by the magnetic measurements of the compound which showed diamagnetic behavior. After all corrections were applied, the magnetic susceptibilities of two samples were negative and temperature independent, $-(6.21-6.25) \times 10^{-3}$ and $-(6.74-6.89) \times 10^{-3}$ emu/mol, respectively.[14]

Cs_4Pb_9 belongs to a class of solid-state compounds with general formulas A_4Tt_9 and $A_{12}Tt_{17} = (A_4Tt_4)_2(A_4Tt_9)$ which crystallize in different structures, but all contain isolated clusters of Tt_9^{4-}. The clusters of lead in this compound resemble very closely the nine-atom lead clusters crystallized from solutions with the aid of 2,2,2-crypt.[15,16] Their existence in the precursor and in the corresponding solution show once again that in the case of these compounds the cluster formation does not take place during the dissolution step. The clusters are already preformed in the precursor, and their extraction is a simple dissolution of an ionic compound composed of polyatomic anions and single-atom cations.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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(14) The magnetizations of two samples of Cs_4Pb_9 (26 and 29 mg) were measured at a field of 3 T over the range 10−300 K on a Quantum Design MPMS SQUID magnetometer. Corrections were applied for the holder, the ion-core diamagnetism for 4 Cs^+ and 9 Pb^{4+} ions, and the diamagnetism due to Larmor precession of the delocalized pairs of electrons on cluster orbitals. Details of the sample preparation, holder, and data corrections can be found elsewhere.[11]

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