

K_6Pb_8Cd : A Zintl Phase with Oligomers of Pb_4 Tetrahedra Interconnected by Cd Atoms**

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Until recently, large deltahedral clusters were known in the solid state only for the boron group.^[1] For Group 14, such clusters with more than four atoms were characterized only in solution or in compounds crystallized from such solutions with the aid of cryptated alkali metal counteranions.^[2] The recently reported phases A_4E_9 and $A_{12}E_{17}$ ($A = K, Rb, Cs$; $E = Si, Ge, Sn, Pb$) contain isolated E_9^{4-} deltahedra and extend the range of existence of large clusters of this group to the solid state.^[3] According to Wade's rules for counting electrons,^[4] the charge on a deltahedral cluster of a Group 14 element is independent of its nuclearity, and therefore large clusters carry relatively small negative charges. Hence, only a few cations are needed to balance the charge, and they may not adequately shield and separate the larger clusters. In solutions and in crystals grown therefrom the clusters are separated by large organic cations, cryptated alkali metal cations, and/or solvent molecules. In "neat" solids,^[5] however, the available cations are of limited dimensions, and alternative ways to resolve the problem must be found. One such method is to increase the charge on the cluster and therefore the number of required counteranions by substitution with an atom of an electron-poorer element. This approach was used in an attempt to substitute a germanium atom of Ge_9^{4-} by zinc and led to the synthesis of Cs_6Ge_8Zn .^[6] In this compound two eclipsed germanium tetrahedra are interconnected by the zinc atom, which caps a face of each tetrahedron and is thus surrounded by six germanium atoms in a trigonal prismatic arrangement. The analogous attempt to replace a lead atom in Pb_9^{4-} by cadmium led to the synthesis of the title compound K_6Pb_8Cd , which contains oligomers of cadmium-linked Pb_4 tetrahedra.

Isolated Pb_9^{4-} clusters have been structurally characterized in K_4Pb_9 and Cs_4Pb_9 .^[3b, c] Since substitution of one lead atom by a cadmium atom would result in a cluster charge of $6-$, a reaction designed to produce $K_6[Pb_8Cd]$ was carried out.^[7] The formula of the resulting compound corresponds to the reaction stoichiometry, but its structure is entirely different from that intended.^[8] The compound does not contain nine-atom deltahedral clusters. Instead, it contains isolated lead tetrahedra and isolated oligomers of four lead tetrahedra interconnected by cadmium atoms. In the solid state, isolated tetrahedral anions are found in many compounds.^[9] All binary compounds of the alkali metals with Group 14 elements A_4E_4 (except for C), $BaSi_2$,^[9] Na_2In and Na_2Tl ,^[10] and the mixed-cation ternary phases K_3LiSi_4 , $Cs_2Na_2Ge_4$, K_7LiSi_8 , Rb_7NaGe_8 , and K_7NaGe_8 ,^[11] contain such tetrahedra. More recently,

one-dimensional polymers of tetrahedra linked by gold atoms were characterized in $A_3[M_4Au]$ ($M = Sn$ or Pb ; $A = K, Rb, Cs$) and $K_4[(TlSn_3)Au]$.^[12] Each tetrahedron in these infinite chains is bound to two gold atoms by two *trans* edges, and each gold atom is bonded to two tetrahedra (to two orthogonal edges).

K_6Pb_8Cd contains both isolated tetrahedra, like those in K_4Pb_4 as well as parts of chains (Figure 1). The latter consist of four lead tetrahedra that are linked by three bridging cadmium atoms (Figure 2). The oligomer

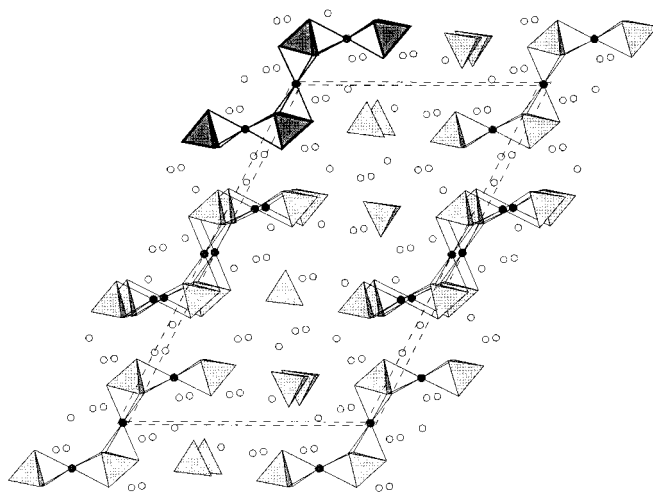


Figure 1. A polyhedral representation of the structure of K_6Pb_8Cd along the b axis (c is horizontal) of the C-centered monoclinic unit cell (outlined). The isolated Pb_4 tetrahedra and the oligomers of $(Pb_4)_4Cd_3$ are clearly visible. Filled and open circles represent Cd and K, respectively. The Cd–Pb bonds are indicated by solid lines. One oligomer (see Figure 2) is emphasized.

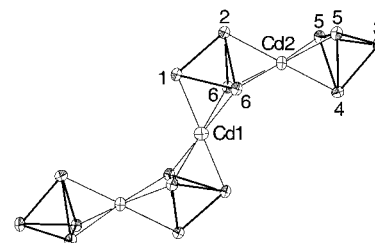


Figure 2. An ORTEP plot of the $(Pb_4)_4Cd_3$ oligomer (90% probability thermal ellipsoids). The numbers correspond to the lead atoms. Selected distances [Å]: Cd1–Pb1 3.086(2), Cd1–Pb6 3.127(2), Cd2–Pb2 3.129(4), Cd2–Pb6 3.157(3), Cd2–Pb4 3.101(4), Cd2–Pb5 3.064(3), Pb1–Pb2 3.025(3), Pb1–Pb6 3.200(2), Pb6–Pb2 3.153(2), Pb6–Pb6 3.344(3), Pb4–Pb3 3.024(3), Pb4–Pb5 3.249(2), Pb5–Pb3 3.020(2), Pb5–Pb5 3.273(3).

$Pb_4CdPb_4CdPb_4CdPb_4$ differs from the gold-containing chains in that the Pb_4 tetrahedra are coordinated to the cadmium atoms through faces as η^3 ligands. The connectivity is similar to that in the zinc-connected dimers of Ge_4 tetrahedra in Cs_6Ge_8Zn with the difference that the germanium tetrahedra are eclipsed while the lead tetrahedra are staggered.^[6] This results in trigonal-antiprismatic (octahedral) geometry at the cadmium center as opposed to the trigonal-prismatic coordination geometry of the zinc atom. The oligomer has an inversion center at the central cadmium atom, Cd1, and pseudo-inversion centers at the other two cadmium atoms, Cd2. The faces that are coordinated to cadmium are larger

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than the other faces of the tetrahedra. The average Pb–Pb distances are 3.228(3) Å for the former, and 3.022(3) Å for the latter. The same effect is observed in Cs₆Ge₈Zn and indicates relatively strong covalent bonding between the tetrahedra and the interconnecting atoms (see below). The average Cd–Pb distances are virtually identical for Cd1 and Cd2 (3.113(2) and 3.112(2) Å, respectively) and compare well with the Pauling single-bond length of 2.884 Å.^[13] The oligomers are stacked along the *b* axis, and Pb5 and Pb6 form “chains” along this axis (Figure 2). The interatomic distances within these chains alternate, shorter within the oligomers and longer between them. The openness of the capped faces results in relatively short interoligomer distances (Pb6–Pb6 3.568(3), Pb5–Pb5 3.639(3) Å). These are comparable with the corresponding intraoligomer distances of 3.344(3) and 3.273(3) Å for the same pairs of atoms. The result is a significant interaction between the oligomers, which leads to essentially metallic behavior (see below).

Another way to look at these unique oligomers is to regard them as coordination compounds of cadmium with two η³ ligands. The tetrahedra act as mono- or bidentate ligands by using one or two of their four faces, respectively. This suggests that branched structures in which three or even four faces are used might be also possible. Similarly, polydentate tetrahedra coordinated through edges to more than two transition metals can be envisioned as well.

The electronic structure of K₆Pb₈Cd was studied by extended Hückel calculations (potassium excluded).^[14] The average bond overlap population (BOP) of 0.192 for the Cd–Pb bonds compares well with that of the Pb–Pb bonds in the capped faces (0.146) and indicates significant covalency. This is in agreement with calculations on Ge₈Zn, which showed highly covalent Zn–Ge bonds with a BOP of 0.299.^[6] The interactions between the oligomers are quite covalent,

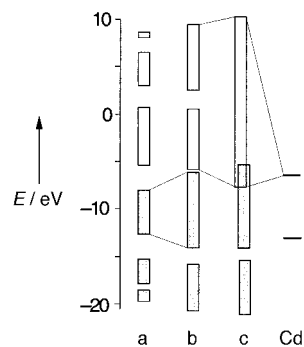
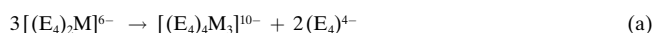


Figure 3. Schematic representation of the results from extended Hückel calculations on well-separated oligomers without Cd atoms (a), the oligomers at the real distances without Cd (b), and the real oligomers with inclusion of the Cd atoms (c). The interactions between the oligomers cause broadening of the valence band (a→b), while the Cd–Pb interactions lead to broadening of the conduction band and its overlap with the filled states (b→c). The energy levels of cadmium are shown on the right.

with an average BOP of 0.171 for the interoligomer Pb6–Pb6 and Pb5–Pb5 bonds. Due to the specific position of the Pb5 and Pb6 atoms, the bond overlap population is larger than that of the intraoligomer bonds even though the interatomic distances are longer. The interactions between the oligomers and between cadmium and the tetrahedra lead to a density of states with no gap at the Fermi level. Both calculations on the Pb sublattice only (all tetrahedra included) and on the real structure but with larger interoligomer separations show well-defined gaps between the valence and conduction bands (Figure 3). Additionally, the calculations show that the interac-

tions between the oligomers lead to broadening mainly of the valence band (Figure 3 a, b), while the introduction of cadmium–lead interactions results in broadening of the conduction band (Figure 3 c). Consequently the compound is expected to be metallic (and appears to be so^[15]) not due to a partially filled band, but because of overlap between bands.^[16]

Finally, an interesting comparison can be made between the title compound and Cs₆Ge₈Zn. Both compounds have the same stoichiometry but one consists exclusively of bridged dimers only, while the other is composed of bridged tetramers and isolated tetrahedra. This reminds one of a disproportionation reaction of the type (a).



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- [7] All manipulations were performed under an inert atmosphere or under vacuum. A stoichiometric mixture of the elements (Alfa-Aesar) was melted in a welded niobium ampule (sealed in a fused silica jacket) at 700 °C and then was slowly cooled (5 K h⁻¹) to room temperature. The product usually contains traces of lead metal.
- [8] Single crystals were selected, mounted in glass capillaries, and checked for singularity on a CAD4 single-crystal diffractometer. Data from one of them (barlike, 0.22 × 0.08 × 0.06 mm) were collected with monochromated MoK_α radiation at 21 °C (ω/2θ scans, 2θ_{max} = 50°, a hemisphere). The data were corrected for Lorentzian and polarization effects and for absorption (ψ scans). The structure was solved by direct methods in the space group C2/m and refined on F² (SHELXTL 5.0). The lattice parameters were refined from a Guinier powder pattern with Si as an internal standard. Crystal data: *a* = 28.80(1), *b* = 6.912(2), *c* = 18.576(8) Å, β = 117.05(3)°, *Z* = 6; ρ_{calcd} = 6.065 g cm⁻³; μ = 631.64 cm⁻¹; residual electron density +4.56/–4.16 e Å⁻³ at 0.67/1.15 Å from Pb2/Pb1, respectively. The refinement of all atoms with anisotropic thermal parameters converged to *R*1 = 0.0631, *wR*2 = 0.1524 (*I* > 2σ(*I*)) for 1977 observed reflections and 128 variables. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-410552.
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- [14] Calculations were carried out with a variety of available sets of H_{ii} values for Cd and Pb (four relativistic sets, four nonrelativistic sets, one charge-iterated set, and one set from DFT calculations,) and qualitatively similar results were obtained in each case.
- [15] The crystals have metallic luster and appearance, and two-probe conductivity measurements showed virtually only contact resistance, that is, the same resistance as when the probes are short-circuited.
- [16] While the manuscript was being reviewed, we synthesized and characterized the isostructural Rb_6Pb_8Cd ($a = 29.398(7)$, $b = 7.142(1)$, $c = 19.052(9)$ Å, $\beta = 116.18(2)^\circ$). Although the tetramers are better separated by the larger Rb cations, this compound is also predicted to be metallic. The extent of the broadening of the valence band due to interoligomer interactions is smaller, but since the Cd–Pb interactions are virtually the same as in K_6Pb_8Cd the conduction band is wide enough to overlap with the lower bands.

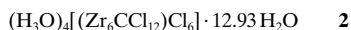
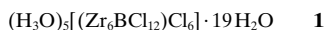
Isolation of Reduced Zirconium Chloride Clusters $[(Zr_6CCl_{12})Cl_6]^{4-}$ and $[(Zr_6BCl_{12})Cl_6]^{5-}$ from Acidic Aqueous Solution**

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Because reduced zirconium compounds are easily oxidized to Zr^{IV} products, no aqueous-solution chemistry of reduced zirconium compounds (oxidation state ≤ 3) is known.^[1, 2] However, a rich solid-state chemistry of centered zirconium halide clusters $[(Zr_6ZX_{12})X_6]^{n-}$ ($Z = H, Be$ to N, Al to P, Mn to Ni ; $X = Cl, Br, I$), in which reduced zirconium forms metal–metal bonds, was developed by Corbett et al. in the 1980s and early 1990s.^[3–7] In a preliminary investigation of the dissolution of these cluster-based phases, it was assumed that, as good reducing agents, all (Zr_6ZX_{12}) -based clusters would undergo oxidation and solvolysis with water, alcohols, and acetone.^[8]

We recently found that solutions of $Rb_5Zr_6Cl_{18}B$ in methanol at room temperature are stable indefinitely^[9] and that an aqueous solution of $Rb_5Zr_6Cl_{18}B$ exhibited the characteristic red color of the $[(Zr_6B)Cl_{12}]^+$ ion for several hours at room temperature. This led us to more closely examine the reactivity of these zirconium chloride clusters in water. Here we report the isolation of the two reduced zirconium compounds **1** and **2** from aqueous media. We also

present preliminary electrochemical and NMR data for $[Zr_6ZCl_{12}]^{m+}$ clusters ($Z = C, m = 2$; $Z = B, m = 1$) in aqueous solution.



The cluster unit of **1**, $[(Zr_6BCl_{12})Cl_6]^{5-}$, is centered on the cell origin and has perfect O_h symmetry, with Zr–Zr and Zr–B distances of 3.2519(8) and 2.2994(5) Å, respectively. These distances are consistent with those previously reported for B-centered clusters with 14 cluster bonding electrons (CBEs).^[9–12] When crystals of **1** are redissolved in deoxygenated water or methanol, the ^{11}B NMR spectra of the solutions show sharp signals, a further indication that the clusters are not oxidized. Hence, the cluster bears a charge of -5 , and a requisite number of counteranions is required for charge balance. A fragment of the crystal structure of **1** is presented in Figure 1 a.

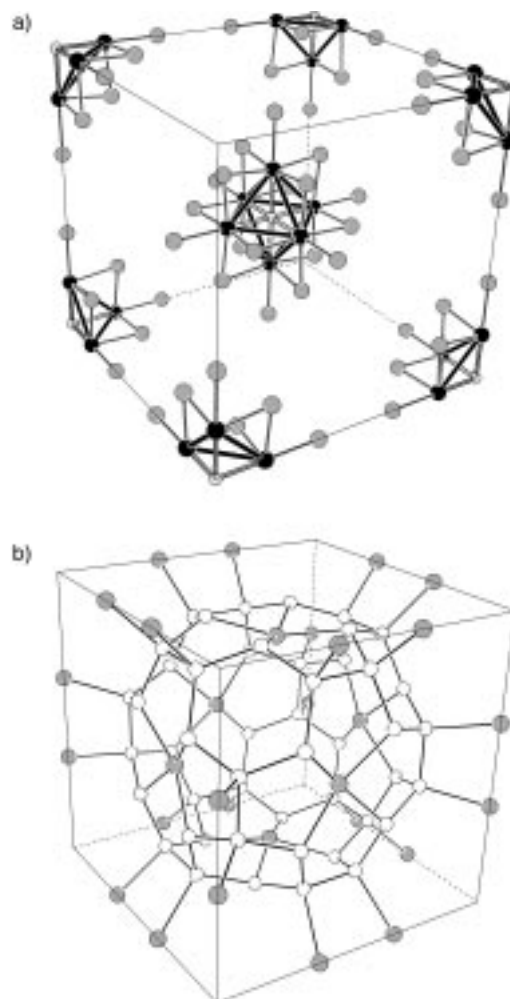


Figure 1. a) $[(Zr_6BCl_{12})Cl_6]^{5-}$ clusters in **1**. Two cluster fragments at the corners of the cube (foreground and background) have been omitted (black circles: Zr, smaller circle: B, shaded circles: Cl). b) The water cage that surrounds the central cluster depicted in a). The shaded circles represent the terminal chloride ligands of the clusters, and the open circles the oxygen atoms of lattice water molecules. Hydrogen bonds are indicated by lines.

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