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Ge$_9^{3-}$ and Pb$_9^{3-}$: Two Novel, Naked, Homopolyatomic Zintl Ions with Paramagnetic Properties

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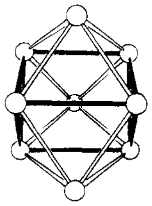
Homopolyatomic anions formed by heavier elements of main group 14−16, appearing in solid state[1] and solution,[2−4] show a large variety of intriguing structures. The growing efforts in isolation of large transition metal clusters, which show extraordinary properties,[5] rises also the interest in the synthesis of larger main group element clusters.[6] One of the remarkable features of the anions built up by elements of group 14 (E) is their distinct tendency of polyhedral cluster formation and their stability in solution. Nevertheless, only a small number of compounds containing isolated anions of the type E_x^{n-} (Zintl ions) have been synthesized and structurally characterized. Up to now, the structures of only four "larger" anions are known Ge$_9^{4-}$, Ge$_9^{2-}$,[7] Sn$_9^{4-}$ [8] and Sn$_9^{3-}$.[9] Remarkable is the absence of a compound containing Pb$_9^{4-}$ anions, even this molecule represents one of the first polyanions proved by Zintl and coworkers using titration methods.[2] However Sn$_9^{4-}$ [10] as well as Pb$_9^{4-}$,[11] could be isolated with the stabilizating help of Cr(CO)$_3$. Besides these soluble nine-atom representatives, there exist also two homoatomic clusters with trigonal bipyramidal structure (E$_5^{2-}$, E = Sn, Pb).[12] The only cluster with an octahedral main group element skeleton is found in the coordinatively stabilized [Sn$_6${Cr(CO)$_5$}$_6$]$^{2-}$.[13]

Except Sn$_9^{3-}$ and the clusters reported here, all homoatomic anions E_x^{n-} are diamagnetic. According to Wade's rules[14] a E$_9^{2-}$ cluster with 20 skeletal electrons forms a tricapped trigonal prism (closo cluster **A**), and E$_9^{4-}$ with 22 skeletal electrons a monocapped quadratic antiprism (nido cluster **B**). Therefore, E$_9^{3-}$ having 21 skeletal electrons should adopt distorted variants of the two cluster isomers **A** and **B**.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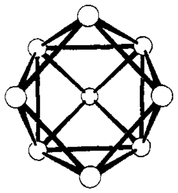
B

A systematic synthesis of the Zintl ions E$_9^{3-}$ (E = Ge, Sn and Pb) was found by a variation of the reaction conditions used by Corbett et al. for the synthesis of Sn$_9^{3-}$.[9] Crystalline compounds of the composition [K-crypt]$_3$E$_9$[15] (E = Ge, **1**; Sn, **2**; Pb, **3**) are obtained by extracting a nominal melt of KE$_{2.25}$ with ethylenediamine (en) and addition of (2,2,2)cryptand[15] and toluene. The salts are isolated as red needles (Ge), dark brown (Sn), and black (Pb) crystals in good yields.[16]

In order to determine the structure of the novel compounds, we carried out single crystal structure analyses for **1** and **3**.[17] There are isolated cluster ions E$_9$ (E = Ge, Pb) and well separated (K-crypt) units. The stoichiometries of **1**, **2**, and **3** reveal that there are three K-crypt units per E$_9$ cluster, resulting in a 3- charge and therefore an odd electron number for the cluster anions (39 valence electrons for E$_9^{3-}$). ESR spectra of the bulk solids confirm the expected paramagnetic character.[18] ESR and magnetic measurements show a strong temperature dependence which are under study now.[19] To our knowledge, compound **3** is the first example of an isolated ligand-free cluster formed by nine lead atoms. It represents the oxidized form of Pb$_9^{4-}$, which was found in solution already seventy years ago.[2]

Figure 1 displays two ORTEP plots of the anion Pb$_9^{3-}$. Ge$_9^{3-}$ shows in principle the same cluster type and is not shown here. The two structures, Ge$_9^{3-}$ and Pb$_9^{3-}$, are best described as

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(15) crypt = (2,2,2)cryptand = 4,7,13,16,21,24-hexaoxa-1.10-diazobicyclo-(8.8.8)hexacosane

(16) All experiments were carried out in a dried argon atmosphere using freshly distilled solvents. The elements K/Ge (K/Sn or K/Pb) were mixed in the molar ratio 1:2.25 and hold in welded niobium (steel) tubes at 740 °C (600 °C) for five hours. 1620 mg (Ge), 2320 mg (Sn), and 4050 mg (Pb), respectively, of the solidified melts (E = Ge, Sn and. Pb) were dissolved in 20.0 mL of dried ethylenediamine. The green brown (Ge), deep red (Sn), and brown (Pb) solutions were filtered. To 2.0 mL of each filtrate (containing roughly 0.2 mmol E$_9$) 301 mg of (2,2,2)cryptand (0.8 mmol) and 1.2 mL of toluene were added. Storage at room temperature produced crystals of **1** after one day, **2** and **3** after seven days, respectively. Yields referring to Ge, Sn, and Pb: **1**, 172 mg (44%); **2**, 254 mg (55%); **3**, 529 mg (84%). Anal. Calcd (found) for **1**·0.5en, C$_{54}$H$_{108}$Ge$_9$K$_3$N$_6$O$_{18}$·0.5C$_2$H$_8$N$_2$ (*M* = 1930.32 g mol^{-1}): C, 34.22 (33.55); H 5.85 (5.68); N, 5.08 (5.20); K, 6.08 (6.13); Ge, 33.85 (34.29). Calcd (found) for **2**, C$_{54}$H$_{108}$Sn$_9$K$_3$N$_6$O$_{18}$ (*M* = 2315.17 g mol^{-1}): C, 28.02 (27.98); H, 4.70 (4.70); N, 3.63 (4.32); K, 5.07 (4.73); Sn, 46.15 (45.68); Calcd (found) for **3**·0.5en, C$_{54}$H$_{108}$Pb$_9$K$_3$N$_6$O$_{18}$·0.5C$_2$H$_8$N$_2$ (*M* = 3141.63 g mol^{-1}): C, 21.03 (20.69); H, 3.59 (3.31); N, 3.12 (2.92); K, 3.73 (3.57); Pb 59.36 (59.78).

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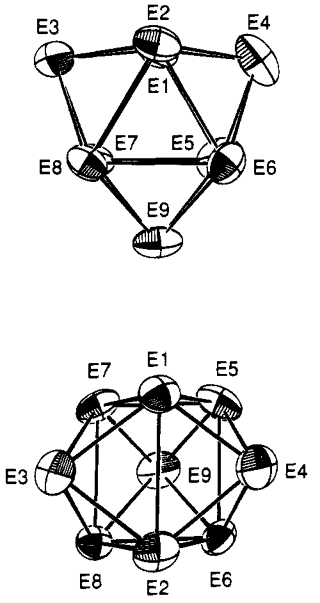

Figure 1. Two representations of the crystal structure of the anion Pb_9^{3-} (ORTEP plot, thermal ellipsoids at 50% probability level). Selected distances (pm), E = Pb: E1−E5 321.4(4), E1−E7 321.9(2), E5−E7 325.9(4), E2−E6 319.3(4), E2−E8 316.5(2), E6−E8 322.0(4). Mean distances μ^4- capping atoms to next neighbors: *d*(E3) = 307.9, *d*(E4) = 307.1, *d*(E9) = 308.0. Corresponding distances for the anion Ge_9^{3-} (same order, E = Ge: 256.2(7), 268.787), 269.5(7), 258.9(6), 271.3(7), 269.7(7), *d*(E3) = 255.1, *d*(E4) = 256.7, *d*(E9) = 255.4. Further distances see text and Table 1.

Table 1. Relative Distances[a] for E_9^{n-} (See Figure 1 and Text)

	Ge_9^{2-} [7]	Ge_9^{3-}	Sn_9^{3-} [9]	Pb_9^{3-}
E1−E2	1.13	1.18	1.01	1.06
E5−E6	1.02	1.12	1.01	1.00
E7−E8	1	1.02	1	1
mean dist in the triangles E1−E5−E7 and E2−E6−E8	0.95	0.93	0.94	0.95
mean dist of μ^4-capping atoms to next neighbors	0.91	0.89	0.90	0.91

[a] The shortest height of each trigonal prism is set to 1. In the case of the two Ge_9 clusters, Ge_9^{2-} is chosen as the reference.

distorted variants of tricapped trigonal prisms. The distances along the height of the trigonal prisms (E1−E2, E5−E6, E7−E8, Ge_9^{3-}: 332.4(8), 315.4(7), 286.8(6) pm, Pb_9^{3-}: 359.9(3), 340.6(3), 339.5(3) pm) are found to be elongated compared to all other intramolecular E−E distances (extreme values of *d*(E−E): Ge_9^{3-} 249.4(7) − 271.3(7) pm, Pb_9^{3-} 302.2(4) − 325.9(4) pm). In order to compare the distortions in various clusters of different elements, all distances are scaled to the shortest height of each trigonal prism (Table 1).

The different prism heights occurring in Ge_9^{3-} and Pb_9^{3-} result in a only pseudo threefold axes for the prisms. From Table 1, we also see that the distortions from the ideal geometry **A** is most expressed in the case of Ge_9^{3-}. There is, on the other hand, for all clusters a much stronger deviation from structure **B**. This is documented in the distances E1−E2 and E3−E4 (Ge_9^{3-}: 332.4(8) and 382.7(8), and Pb_9^{3-}: 359.9(3) and 489.2(5), respectively), which should be of equal length in the case of the C_{4v} symmetric **B**.[20] The structures have therefore topological similarities with Sn_9^{3-}.[9]

However, Ge_9^{3-} shows some interesting changes in the heights of the trigonal prism if compared to the distorted tripcapped trigonal prism of Ge_9^{2-}, which is found as one cluster component in the mixed valent compound $[K^+\text{-crypt}]_6[Ge_9^{2-}Ge_9^{4-}]$, **4**. Even though the earlier reported crystal structure refinement for **4** was also of poor quality (R_1 = 0.149)[7], it appears that all three prism heights of Ge_9^{3-} are elongated relative to **4** (Table 1). This is consistent with the occupation of an orbital that is σ antibonding along the height of the trigonal prism for a 21 electron cluster.[9]

From the series of E_9^{3-} structures (E = Ge, Sn, Pb) it is obvious that distorted tricapped trigonal prisms are favored over monocapped quadratic antiprisms for 21 skeletal electrons. The well-directed syntheses in good yields offers the possibility to study in more detail physical properties and chemical reactivity of radical element clusters, and might lead even to the preparation of larger main group element clusters.

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Supplementary Material Available: Complete listings of crystallographic data, bond lengths and angles, atomic coordinates, and anistropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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(17) Crystal structure data for **3**·0.5en. Space group $P\bar{1}$, a = 1496.2(5), b = 1633.8(5), c = 2048(1) pm, α = 92.66(3), β = 96.37(3), = γ 112.02(3)°; $V = 4591 \times 10^6$ pm^3, Z = 2, ϱ_{calc} = 2.25 g cm^{-3}. Data collection: STOE IPDS, irradiation Mo Kα, $2\theta_{max}$ = 45.0° (imaging plate to crystal distance 90 mm), T = 293 K, R_1 = 0.065, 3424 reflections with $I > 5\sigma(I)$. wR_2 = 0.168 (on F^2). A second modification was isolated using similar conditions. Space group $P2_1/c$, a = 2835.6(8), b = 23.757(5), c = 27.885(8) pm, β = 94.01(2)°; $V = 18745 \times 10^6$ pm^3 (253 K). Crystal structure data for **1**·0.5 en. Space group $P\bar{1}$, a = 1439.8(7), b = 1524.1(9), c = 2057(2) pm, α = 90.46(2), β = 96.71(6), γ = 114.09(4)°; $V = 4084 \times 10^6$ pm^3, Z = 2, ϱ_{calc} = 1.57 g cm^{-3}. Data collection: STOE IPDS, irradiation Mo Kα, $2\theta_{max}$ = 48.4° (imaging plate to crystal distance 80 mm), T = 193 K, R_1 = 0.102, 3412 reflections with $I > 4\sigma(I)$. wR_2 = 0.240 (on F^2). Crystals of **1** were of poorer quality (larger reflex profiles) than the one of **3**. Structure solution and refinement with SHELXS86- and SHELXL93 (G. M. Sheldrick, Universität Göttingen). The crystal structure of **2** was determined earlier.[9] We found crystals of **2** with a monoclinic cell ($P2_1/c$) a = 2770.3(7), b = 2352.7(3), c = 2804.2(5) pm, β = 93.46(2)°.

(18) Room temperature ESR spectra of powder samples with g values: **1**: 2.04, 1.99, **2**: 2.07, 1.92 (broad), **3**: 1.68 (very broad). **1** and **2** show two signals as expected for axially symmetric species. For **1** and **2** only one phase was obtained. For a powder of **3** a separation of the two modifications[17] was not possible. g Values determination using the program AESR5, Rhode, B.; Heinzer, J.; Roduner, E.; Oth, J. F. M. ETH Zürich 1992.

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