Stable Homopolyatomic Anions: The Crystal Structures of Salts of the Anions Pentaplumbide(2—) and Enneastannide(4—)

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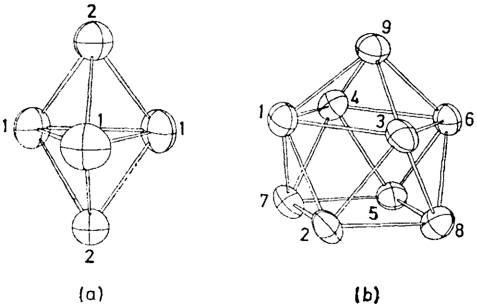
Summary The unique trigonal bipyramidal Pb_5^{2-} and unicapped antiprismatic Sn_9^{4-} anions have been discovered by *X*-ray structural studies on their salts with $Na^+(2,2,2\text{-crypt})$.

ALTHOUGH polyatomic anions of the heavy post-transition metals have long been known, primarily as solutions of alkali metal alloy phases in liquid ammonia,[1] it was only very recently[2] that we discovered a general route to the isolation of stable derivatives of these anions, namely through the use of 2,2,2-crypt[3]† to complex the alkali metal ion and prevent reversion to the alloy phase. We now report the first extensions of that work, the structures of the two red derivatives $[Na(crypt)^+]_2Pb_5^{2-}$ and $[Na(crypt)^+]_4$-Sn_9^{4-}.

X-ray data were obtained from single crystals of the two derivatives with a four-circle automatic diffractometer using Mo-K_α radiation. The lead derivative exhibits hexagonal unit cell parameters, a = 11·615 Å, c = 22·108 Å, and Z = 2, with the extinction condition $h\bar{h}0l$ for l = $2n + 1$. The tin derivative occurs in a triclinic crystal system, a = 16·675 Å, b = 21·243 Å, c = 15·397 Å, α = 107·98°, β = 103·42°, γ = 81·75°, and Z = 2. Heavy atom positions for both structures were inferred from three-dimensional Patterson functions, and light atom positions were successively deduced from least-squares refinement and electron density syntheses. In both structures metal atoms were refined with anisotropic temperature factors and all other temperature factors were varied isotropically. The data set for the lead compound exhibited trigonal rather than hexagonal symmetry and the structure was



(a) (b)

FIGURE. The structures of the ions Pb_5^{2-} (a) and Sn_9^{4-} (b).

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† 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane, $N(C_2H_4OC_2H_4OC_2H_4)_3N$.

refined in the space group $P\bar{3}c1$ by full-matrix least-squares techniques to a conventional discrepancy factor R of 0·118. The 117 independent (nonhydrogen) atoms in the tin structure were likewise refined in the space group $P\bar{1}$ to $R = 0{\cdot}121$.

The most interesting features of the structures are the anions Sn_9^{4-} and Pb_5^{2-} illustrated in the Figure. The Pb_5^{2-} ion has D_{3h} symmetry according to the space group and exhibits axial–equatorial and equatorial–equatorial bond distances of 3·00 and 3·23 Å, respectively, quite reasonable relative to those found in Bi_9^{5+}. The formation of this ion itself is somewhat of a surprise because the green Pb_9^{4-} is so well known in liquid ammonia media[1] and this ion would be isoelectronic with both Bi_9^{5+} and Sn_9^{4-}. But on the other hand the ion found is appropriate for a species isoelectronic with Bi_5^{3+}, a well established ion for which the MO calculations are seemingly unambiguous in predicting D_{3h} configuration[5] but where apparent twinning problems have so far frustrated crystal structure analyses.

Although the anion Sn_9^{4-} is isoelectronic with Bi_9^{5+}, a well behaved tricapped trigonal prism (D_{3h}),[4] the ion found here evidently provides the first clear example of the alternative, an antiprism capped on one square face (C_{4v}). The bottom atoms shown (2, 8, 5, 7 in the Figure) are nearly co-planar with a dihedral angle of 177·4° between planes 2–7–8 and 5–7–8. Nearest neighbour distances throughout the figure, including the capping atom 9, range from 2·93 to 3·02 Å except that distances between atoms 1, 3, 6, and 4 describing the top square face of the parent antiprism before capping are elongated to between 3·20 and 3·31 Å. There appears to be no other example which is at all close to this particular configuration, even for co-ordination polyhedra about metal atoms. The stability of the nine atom clusters with 22 electrons in C_{4v} as well as D_{3h} symmetry can be inferred by inspection of the MO's for the probable effect of capping the antiprismatic Bi_8^{2+} with Bi^{3+};[5,6] the same is implied by calculations on the related[5] B_9H_9 polyhedra.[7]

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