closo-$[CrPb_9(CO)_3]^{4-}$: a 100 Year History of the Nonaplumbide Tetra-anion

Bryan W. Eichhorn and Robert C. Haushalter*

Exxon Research and Engineering Co., Annandale, NJ 08801, USA

The $[CrPb_9(CO)_3]^{4-}$ anion, which has a bicapped square antiprismatic geometry, is the first structurally characterized example of a Pb_9 cluster and is the first transition metal-plumbide cluster.

Not long after Seely reported that sodium would dissolve in liquid ammonia without reaction,[1] Joannis published two papers around 1890 on the interaction of an ammonia solution of sodium with metallic lead to give solid sodium plumbides.[2] Subsequently Kraus' work[3] showed that these plumbides were dissociated in $NH_3(l)$ like salts and suggested that the species present were Na^+ and Pb_2^-. In 1917 Smyth demonstrated that a lead cathode would dissolve in liquid ammonia under electrolysis conditions[4] and that 2.14—2.19 mol of Pb dissolved per Faraday of current passed. This result was confirmed and refined by Zintl and co-workers[5] who found a value of 2.25 and formulated the anion present as Pb_9^{4-}. This

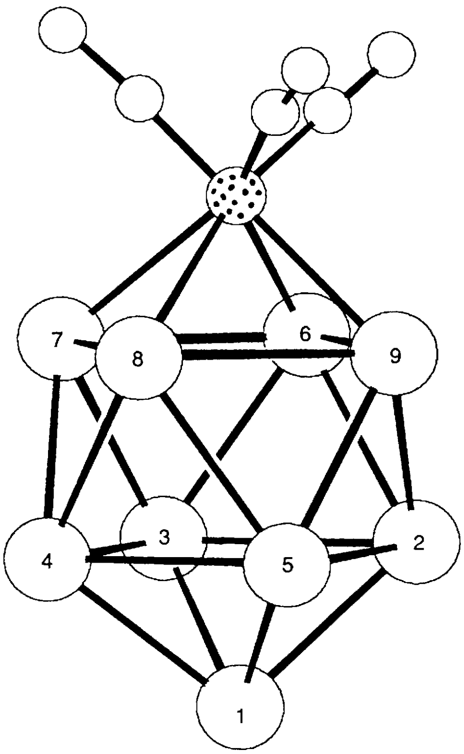

Figure 1. Structure of the $[CrPb_9(CO)_3]^{4-}$ anion (see text for selected distances). Numbered atoms are lead; dotted atom is chromium.

species has never been isolated although Pb NMR spectra of ethylenediamine solutions of M_4Pb_9 (M = alkali metal) indicate the presence of a single species;[6] the structure could not be determined owing to the apparently fluxional nature of the species which prevented the observation of any spin–spin couplings. Although Sn_9^{4-} has been isolated,[7] the only structurally characterized homopolyatomic plumbide cluster is Pb_5^{2-}.[8] While we and others have recently determined the structures of several mixed d-block/p-block clusters like the tellurides $[K_2Au_4Te_4]^{2-}\cdot 4$ solv,[9] $[Hg_4Te_{12}]^{4-}$,[10] $[Mo_4Te_{16}]^{2-}$,[11] $[NbTe_{10}]^{3-}$,[12] the arsenides $[RbNbAs_8]^{2-}$,[13] and $[CrAs_7(CO_3)]^{3-}$,[14] and the stannide $[cryptK]_4[CrSn_9(CO_3)]$ (crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazatricyclo[8.8.8]hexacosane),[15] no mixed plumbide clusters have been previously reported. We describe here the structural characterization and properties of the nonaplumbide 4− anion as its chromium tricarbonyl adduct $[cryptK]_4[CrPb_9(CO)_3]$ (**1**).

When an ethylenediamine (en) solution of K_4Pb_9 is treated with a toluene solution of $[Cr(CO)_3(1,3,5\text{-}Me_3C_6H_3)]$ under the same anaerobic conditions used to prepare $[cryptK]_4[CrSn_9(CO)_3]$,[15] air-sensitive black crystals of (**1**), which were identified by elemental analysis,† IR spectroscopy, and a single crystal *X*-ray diffraction study,‡ can be isolated after 24 hours in *ca.* 50% yield.

Compound (**1**) contains the $[CrPb_9(CO)_3]^{4-}$ anion (**2**) (Figure 1), which can be described as a bicapped square antiprism, isostructural and isoelectronic with $B_{10}H_{10}^{2-}$, with the Cr atom and Pb(1) in capping positions. The main structural features of (**1**) are similar to those in $[cryptK]_4[CrSn_9(CO)_3]$.[15] The Cr bond distances to the four Pb atoms of the square face of the Pb_9 cluster are slightly asymmetric with Cr–Pb contacts of 2.89(1), 2.88(1), 2.99(1), and 2.98(1) Å. This type of asymmetry was not present in either of the two crystallographically independent anions of $[CrSn_9(CO)_3]^{4-}$. All the Pb–Pb contacts in (**1**) (range 3.03—3.40 Å) are shorter than the Pb–Pb bonds in lead metal.[16] The shortest Pb–Pb bonds are the ones from the apical Pb(1) to the plane defined by Pb(2,3,4,5), Plane A, which average 3.06 Å while the longest bonds are among the Pb atoms defining Plane A (average 3.32 Å). The contacts among the Pb atoms of Plane B, Pb(6,7,8,9), and the contacts between Plane A and Plane B, are of intermediate length with average bond distances of 3.18 and 3.13 Å, respectively. All the Cr–C and C–O distances and the Cr–C–O angles are similar to those found in the analogous $[cryptK]_4[CrSn_9(CO)_3]$.[15]

The carbonyl region of the IR spectrum of (**1**) shows the familiar red-shifted CO bands typical of these $[M_xCr(CO)_3]^{n-}$ species (where M = As,[14] $n = 3$ and $x = 7$; M = Sn[15] or Pb, $n = 4$ and $x = 9$). To our knowledge, the frequencies of the bands in (**1**) (1791, 1695, and 1681 cm^{-1}; KI pellet§) are the lowest for stretching bands of any terminal CO ligand.

Since both the Pb_9^{4-} starting material (*nido*, 22e⁻ for nine vertices) and the product $CrPb_9^{4-}$ cluster (*closo*, 22e⁻ for ten vertices) obey Wade's rules,[17] it would be interesting to see if a d-block vertex with a different electron count would lead to a structure in accord with Wade's rules.

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† Found: C, 24.6; H, 4.0; N, 3.1, Pb, 50.9. $C_{75}H_{144}CrK_4N_8O_{27}Pb_9$ requires C, 24.9, H, 4.0, N, 3.55; Pb, 50.1%.

‡ *Crystal data* for (**1**): monoclinic, space group $P2_1/n$, $a = 16.951(7)$, $b = 27.73(2)$, $c = 25.751(8)$ Å, $\beta = 91.87(3)°$, $U = 12\,099(9)$ Å^3 at −160 °C. For 4197 reflections with $I > 3\sigma(I)$, $R(R_w) = 0.064(0.070)$. For Mo-K_α radiation, $\mu = 128.54$ cm^{-1} and an empirical absorption correction was applied. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ A fourth band at 1733 cm^{-1} is observed for (**1**) but its intensity increases relative to the other three upon exposure to the air and therefore probably corresponds to a decomposition product of the extremely air-sensitive compound.