The Structure of the Pb_9^{-4} Ion

Sir:

Zintl, *et al.*,[1] found evidence from potentiometric titrations in liquid ammonia solutions for a number of compounds involving group IV and V elements in unusual oxidation states. The compounds suggested were

		Na_4Pb_7
	Na_4Sn_9	Na_4Pb_9
Na_3As	Na_3Sb	Na_3Bi
Na_3As_3	Na_3Sb_3	Na_3Bi_3
Na_3As_5		Na_3Bi_5
Na_3As_7	Na_3Sb_7	

It was suggested that these could be thought of as the most negative possible ions (*e.g.*, Pb^{-4} or As^{-3}) surrounded by 2, 4, 6, or 8 neutral atoms, but no detailed structural suggestions were put forth. They determined the sodium:heavy element ratio, so that Na_3As_3, for example, is more correctly formulated $(NaAs)_x$. With the trivial exceptions of Na_3As, Na_3Sb, and Na_3Bi, none of the electronic arrangements in these compounds is known. More recently, Marsh and Shoemaker[2] determined the crystal structure of NaPb, a compound not on the above list, and found tetrahedral Pb_4^{-4} groups. They suggested the possibility of two tetrahedra sharing a corner for Pb_7^{-4} and three tetrahedra sharing three corners for Pb_9^{-4}.

Both of the structures suggested for Pb_9^{-4} can be argued against. The eightfold coordination of Pb^0 around Pb^{-4} suggested by Zintl involves two drastically different kinds of lead atoms, which seems unlikely. The Pb_4^{-4} ion found by Marsh and Shoemaker has an electronic arrangement that is more or less normal, similar to that of P_4, while the proposed Pb_9^{-4}, consisting of three tetrahedra cyclically arranged, does not. The lack of a normal bonding arrangement does not make this proposal incorrect but it does say that the proposal does not follow from the Pb_4^{-4} arrangement.

It is suggested here that the structure of the Pb_9^{-4} ion can be assigned by analogy to be the same as that of Bi_9^{+5}. Hershaft and Corbett[3] determined the crystal structure of "bismuth monochloride" (actually $[Bi_9][BiCl_5]_4[Bi_2Cl_8]$, the stoichiometry is Bi_6Cl_7) in which they found Bi_9^{+5} groups of D_{3h} symmetry with all Bi atoms approximately equidistant from the center of the group. The structure is shown in Fig. 1.

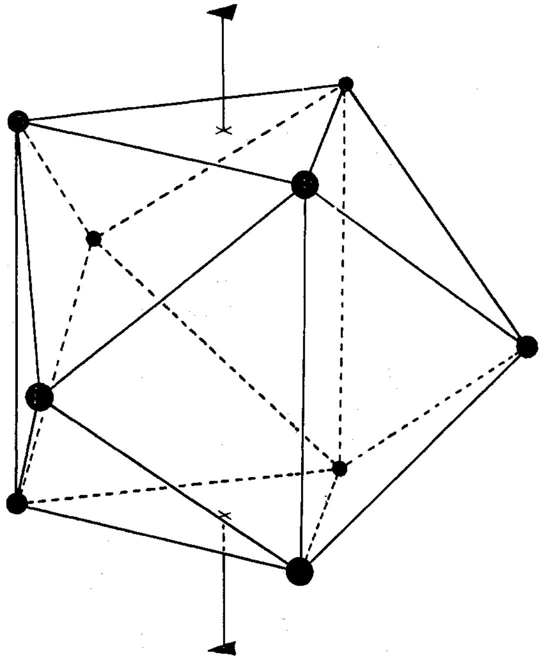

Fig. 1.—Probable shape of the Pb_9^{-4} ion. With the exception of the vertical lines the lines shown connect nearest neighbors. The threefold axis of the figure is shown.

The Bi_9^{+5} group is isoelectronic with the Pb_9^{-4} group, and it seems very likely, therefore, that it is also isostructural. A qualitative one-electron LCAO molecular orbital treatment[4] of the twenty-seven p-orbitals on the nine atoms shows that a reasonable arrangement of eleven pairs can be found. Since no quantitative calculations were made, it does not seem worthwhile to include the details here.

If this structure is correct, it would suggest that structures for the other ions Zintl found might be among the compact spherical arrangements possible[5] for five[6] and seven spheres.

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[1] E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. physik. Chem.*, **A154**, 1 (1931).

[2] R. E. Marsh and D. P. Shoemaker, *Acta Cryst.*, **6**, 197 (1953).

[3] A. Hershaft and J. D. Corbett, *J. Chem. Phys.*, **36**, 551 (1962).

[4] For example, see the treatment of B_{12}^{-2} by W. N. Lipscomb and D. Britton, *ibid.*, **33**, 275 (1960), or J. R. Canon and G. H. Duffey, *ibid.*, **35**, 1657 (1961).

[5] See, for example, R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

[6] For the ions As_5^{-3} and Bi_5^{-3} another more attractive possibility is that these should be As_{10}^{-6} and Bi_{10}^{-6}, in which case the P_4O_6 structure is the obvious answer.

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