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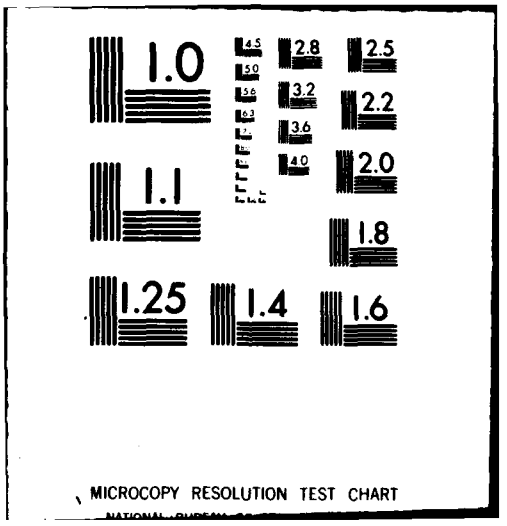
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Electrochemical Generation of the Naked Metal Anionic Clusters, $Sn_{9-x}Pb_x$ (x=0 to 9).

by

B. Stanley Pons, David J. Santure, R. Craig Taylor and Ralph W. Rudolph

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ELECTROCHEMICAL GENERATION OF THE NAKED METAL ANIONIC CLUSTERS, $Sn_{9-x}Pb_x^{4-}$ (x = 0 to 9)

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Recently there has been considerable interest in the structure and chemistry of cluster compounds of the main group elements[1] as well as the corresponding clusters of the transition elements[2]. In our laboratories, we have established the fluxional nature in solution of the naked metal anionic clusters $Sn_{9-x}Pb_x^{4-}$ (x = 0 to 9) by the use of ^{119}Sn and ^{207}Pb nmr[3]. These clusters are formed when alloys of composition Na/Sn/Pb are maintained in contact with anhydrous ethylenediamine (en) for an extended period of time. We now wish to report that these clusters may also be generated by constant current electrolysis.

We have observed that deposition of sodium from an en solution 0.1 M in NaI at either a lead or tin cathode leads to the formation of the Pb_9^{4-} and Sn_9^{4-} clusters, respectively. The lead cluster appears rapidly and quantitatively with current, whereas the dissolution of the tin cluster from the electrode surface is considerably slower. If the electrolytic cell and its contents are allowed to stand after conclusion of current passage, the concentration of the Sn_9^{4-} cluster increases continuously for several days.

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Tin and lead electrodes reduce in the presence of electrodeposited sodium in ethylenediamine to give highly charged naked metal anionic clusters.

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Examination of the catholyte solutions by either ^{207}Pb or ^{119}Sn nmr after removal of an aliquot from the cells at various electrolysis times always reveals the same species, i.e., Pb_9^{4-} or Sn_9^{4-}. Although other cluster species have been observed when Na/Pb or Na/Sn alloys of varying compositions have been extracted with en, notably Sn_4^{2-} [4], Sn_5^{2-} [5] and Pb_5^{2-}[5], the electrolytic method apparently produces the nine atom clusters exclusively regardless of the electrolyte concentration or the current density.

In a typical experiment, a current density of 10 ma/cm^2 (Hi-Tek potentiostat) is passed between a clean tin cathode and a Pt-gauze anode in an all glass H-cell, the two electrode compartments separated by a glass frit. The solution is 0.1 M NaI in en. Aliquots of the catholyte solution examined by ^{119}Sn nmr gave a quintet of intensity ratio 0.045:0.311:1.000: 0.311:0.045 in excellent agreement with that predicted for a fluxional nine atom tin cluster[3]. Furthermore, the chemical shift and ^{119}Sn - ^{117}Sn coupling constants agree within experimental error with those values obtained previously[3]. In a classic paper, Zintl and Kaiser[6] were able to produce Pb_9^{4-} by electrolytic reduction of a lead cathode in $NH_3(\ell)$. Surprisingly, they observed that a tin cathode remained passive to Sn_9^{4-} formation and only plated out metallic sodium which gave the typical blue solution of the active metal. Our present study in en provides a more convenient solvent system which appears to give important new dimensions to electrolytic production of naked metal clusters. In the present situation, tin passivity is obviously diminished. For this reason a variety of other metals as well as alloys are currently under investigation. For instance, it is observed that reduction of Na^+ at a Pb/Sn (1:1 mole ratio) alloy electrode produces all species in the

series $Sn_{9-x}Pb_x^{4-}$ (x = 0 to 9) with the relative intensities in the nmr spectrum indicating predominance of the least entropic species, Sn_9^{4-} and Pb_9^{4-} (Figure). In contrast, when a 1:1:1 mole ratio of Na/Sn/Pb alloy is conventionally extracted with en, the most entropic species, $Sn_5Pb_4^{4-}$ and $Sn_4Pb_5^{4-}$, predominate[3].

It is not clear why these results should be dissimilar. Solvent systems, electrode surfaces, and the identification and kinetics of the intermediates of formation are under investigation by several techniques including modulated specular reflectance spectroscopy[7].

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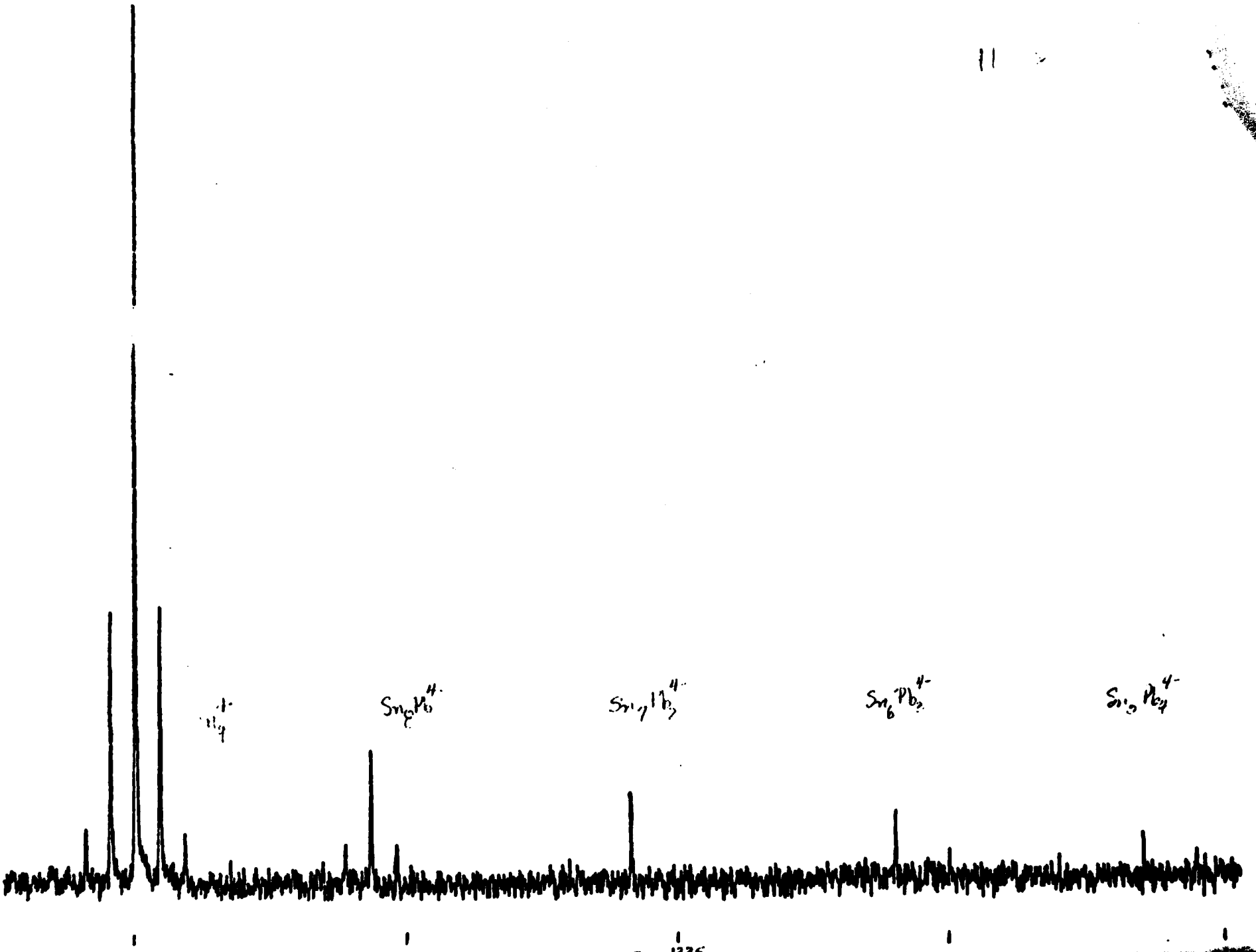
Figure. Tin-119 nmr spectrum of the catholyte solution after constant current electrolysis at a 1:1 Sn/Pb alloy electrode in 0.1 M NaI in en. Species shown are the clusters $Sn_{9-x}Pb_x^{4-}$ (x=0 - 4). Chemical shifts in ppm relative to external $(CH_3)_4Sn$ (δ=0).

The central peak of the Sn_9^{4-} cluster is at 29.625306 MHz; spectral width, 8kHz. Total accumulation time: 30.4 hrs. Data collected on a Varian FT-80 NMR. The species $Sn_{9-x}Pb_x^{4-}$ (x=5 - 9) have been identified by lead-207 nmr (not shown).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$Sn_6Pb_3^{4-}$
$Sn_5Pb_4^{4-}$
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