

configuration of the ω_2 position of all other fungal macrolides. Thus either the reductase involved in the production of this chiral center has a different stereospecificity than the corresponding component of fatty acid synthetase, or acetoacetyl-enzyme is first reduced to (3*R*)-3-hydroxybutyryl-enzyme and then converted to the 3*S* enantiomer by an enzyme similar to 3-hydroxybutyryl-CoA racemase.²¹

The information presented in this paper and the preceding one¹ substantiates the supposition that fatty acids and brefeldin A are assembled by enzymes that exhibit similar or identical stereoselectivities in the reactions which they catalyze. It now remains to be seen how these similarities in comparative biochemistry produce the fascinating stereochemical relationships found among the macrolide antibiotics.

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Naked-Metal Clusters in Solution.¹ 4. Indications of the Variety of Cluster Species Obtainable by Extraction of Zintl Phases: Sn_4^{2-} , TiSn_8^{5-} , $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ ($x = 0-9$), and SnTe_4^{4-}

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We recently reported a multinuclear NMR study which gave prima facie evidence for the fluxional nature of naked-metal clusters such as Sn_9^{4-} in solution, established for the first time the existence of heteroatomic naked-metal cluster anions such as $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ ($x = 0-9$),^{2,3} and showed that they can be generated electrochemically.⁴ Here, we present evidence which demonstrates the rich variety of homo- and heteroatomic anions obtainable in solution from Zintl phases.⁵ This report includes a new naked cluster in solution,³ Sn_4^{2-} , the new heteroatomic naked cluster

TiSn_8^{5-} , the $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ ($x = 0-9$) series, and a "conventional" SnTe_4^{4-} which is proposed to be tetrahedral. Parameters which correlate with chemical shift and lead to the assignment of naked-metal clusters are discussed, also.

If alloys of composition Na_{1-x}Sn are maintained in contact with ethylenediamine (en), the resulting red solution gives a signal 665 ppm upfield from Sn_9^{4-} in the ^{119}Sn NMR in both the presence and absence of 2,2,2-crypt. The solution never becomes as intensely colored as those for Sn_9^{4-} , but with prolonged accumulation a triplet with 0.12/1.00/0.12 relative intensities and a ^{119}Sn - ^{117}Sn coupling of 1224 Hz can be observed. Our calculations of relative intensity as a function of cluster size³ suggest that this is a four-atom cluster, since patterns of 0.16/1.00/0.16, 0.12/1.00/0.12, and 0.08/1.00/0.08 are expected for five, four, and three tin atoms, respectively. A rough analysis of Na_2Sn by ^{23}Na and ^{119}Sn NMR indicated a Na_2Sn_4 stoichiometry. Empirical deduction would also suggest a Sn_4^{2-} rather than Sn_4^{4-} , since no known naked clusters in solution bear anything approaching a unit negative charge per Sn atom. Only in a solid phase such as β - Na_2Sn could a Sn_4^{4-} be construed.⁶

If the Allred-Rochow electronegativity scale⁷ ($\chi_{\text{Pb}}/\chi_{\text{Sn}} = 0.910$) is used to assign a charge per Sn atom (Z_{Sn}) in the series of clusters $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ ($x = 0-9$) by maintaining the total charge of the cluster at -4 and the charge is plotted vs. the chemical shift, the equation $\delta(\text{Sn}-119) = [8991(Z_{\text{Sn}}) + 2760]$ ppm is found [where $\delta(\text{Sn}-119)$ is the shift relative to external $\text{Me}_4\text{Sn} = 0$]. This relationship gives calculated chemical shifts of -836 and -1735 ppm for Sn_5^{2-} ($Z_{\text{Sn}} = -0.4$) and Sn_4^{2-} ($Z_{\text{Sn}} = -0.5$), respectively. Since tin chemical shifts have been shown in certain instances to follow electronegativity,⁸ the observed -1895 value corroborates the rough analytical data mentioned above. We have not yet observed a Sn_3^{2-} in solution, although its crystal structure has been reported.⁹ We also find such charge considerations nicely fit the chemical shifts of the previously reported Te_6^{4+} , Te_4^{2+} , $\text{Te}_3\text{Se}_2^{2+}$, $\text{Te}_2\text{Se}_2^{2+}$, TeSe_3^{2+} series,¹⁰ among others. However, such correlations do not appear to be general as indicated by the $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ discussed later.

The intensity of the Sn_4^{2-} NMR signal in solutions over the alloy increases and peaks after about 2 weeks at 298-303 K. After that time new species which include Sn_9^{4-} are apparent by ^{119}Sn NMR spectroscopy; their complete characterization will require additional work with sensitive instrumentation. The solution structure of Sn_4^{2-} has been examined theoretically.¹¹ Subsequent to our discovery of Sn_4^{2-} in solution, it also has been isolated and investigated by X-ray.¹²

Alloys of composition NaSnGe and KSnGe give deep red solutions when treated with en. These solutions give a rich ^{119}Sn NMR spectrum which suggests the existence of a *nido*- $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ ¹³ ($x = 0-9$) series to parallel the well established *nido*- $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ series of fluxional clusters. However, unlike the situation with ^{207}Pb , the signals due to the $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ series show no discernable spin-spin coupling to ^{73}Ge (7.7%, $I = 9/2$) which can be attributed to its quadrupolar nature and rapid relaxation. With the absence of ^{119}Sn - ^{73}Ge coupling the cluster stoichiometry must be inferred by analogy to the $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ series. Still, a series

(6) Muller, W.; Volk, K. *Z Naturforsch. B* 1977 32B, 709.

(7) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* 1958, 5, 264.

(8) "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978.

(9) Edwards, P. A.; Corbett, J. D. *Inorg. Chem.* 1977, 16, 903. Our inability to observe Sn_3^{2-} in solution may be due to one or a combination of the following: (1) low solubility, (2) a long T_1 value, and (3) a dispersion of intensity over the many lines of a complex spectrum due to the isotopomers of a nonfluxional cluster.

(10) Lassigne, C. R.; Wells, E. J. *J. Chem. Soc., Chem. Commun.* 1978, 956. Schrobilgen, G. J.; Burns, R. C.; Granger, P. *Ibid.* 1978, 957.

(11) Rothman, M. J.; Bartell, L. S.; Lohr, L. L. *J. Am. Chem. Soc.*, following paper in this issue. In solution a compressed tetrahedron minimum energy is predicted for a fluxional Sn_4^{2-} .

(12) Corbett, J. D., private communication. X-ray crystallography gives distorted tetrahedra for Sn_4^{2-} and Ge_4^{2-} . We thank J.D.C. for communication of these results prior to publication.

(13) The terms *nido* and *closo* are "borrowed" from polyhedral heteroborane nomenclature and connote a correlation between polyhedral structure and electron count. See: Rudolph, R. W. *Acc. Chem. Res.* 1976, 9, 446 for these correlations and the placement of heteroatoms in the polyhedron.

(1) The first three papers of this series are listed as ref 2-4.
(2) Rudolph, R. W.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* 1978, 100, 4629.

(3) Rudolph, R. W.; Taylor, R. C.; Young, D. C. "Fundamental Research in Homogeneous Catalysis", Tsutsui, M., Ed.; Plenum: New York, 1979; pp 997-1005; this paper also mentions a preliminary report of the Sn_4^{2-} described here in detail.

(4) Pons, B. S.; Santure, D. J.; Taylor, R. C.; Rudolph, R. W. *Electrochim. Acta* 1981, 26, 365.

(5) Zintl phases are salt-like alloys typically formed by fusion of an alkali metal with a main-group metal. See: Schäfer, H.; Eisenmann, B.; Müller, W. *Angew. Chem.* 1973, 9, 694.

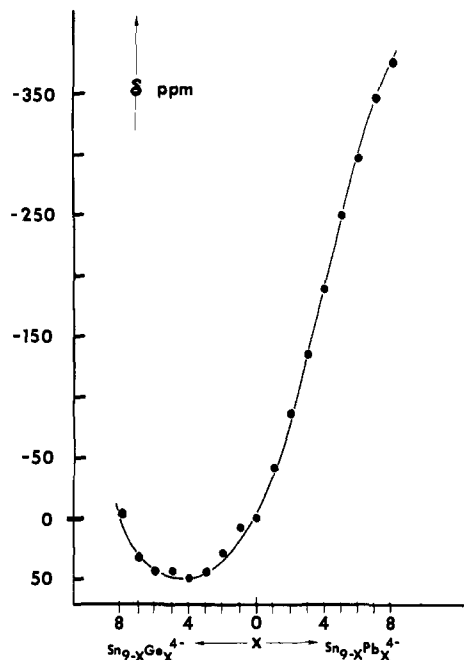


Figure 1. Plot of chemical shift vs. cluster composition for the $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ and the $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ series. The chemical shift of Sn_9^{4-} is set to zero; the value of x increases in opposite directions for Ge and Pb.

of triplets [$J(^{119}\text{Sn}, ^{117}\text{Sn}) = 267\text{--}746$ Hz, regularly with x] can be discerned to the low-field side of Sn_9^{4-} . The relative intensities of the triplet peaks indicate a monotonic decrease in the number of Sn atoms per cluster with each new cluster, *but* unlike the $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ series, the chemical shift progression with x is *not linear* for $\text{Sn}_{9-x}\text{Ge}_x^{4-}$. The shift is downfield as x increases from 1–4, but for $x = 5\text{--}7$ the signals fold back upfield toward Sn_9^{4-} , and for $x = 8$ (SnGe_8^{4-}) the singlet is actually 3 ppm upfield of Sn_9^{4-} . A plot of the observed shift vs. x is roughly parabolic and spans a range of about 55 ppm (Figure 1). We discount the possibility that some of the signals are due to members of a *closo*- $\text{Sn}_{9-x}\text{Ge}_x^{2-}$ series.¹³ Although the *closo*- Ge_9^{2-} is known, the charge per Sn atom would be much lower here and expected at much lower field. For the present, we suspect that the marked difference in plots of δ vs. x for the $\text{Sn}_{9-x}\text{Pb}_x^{4-}$ and $\text{Sn}_{9-x}\text{Ge}_x^{4-}$ series (linear vs. parabolic, respectively, with x and in opposite directions) is due to the dominance of the diamagnetic term⁸ for the former and paramagnetic term⁸ for the latter series. Since Sn and Pb are more similar in size than Sn and Ge, the electron "asymmetry" about Sn should not change much with x for substitution of Sn by Pb, i.e., the diamagnetic term dominates and δ depends on inductive effects (electronegativity) primarily. By contrast, since Ge is substantially smaller than Sn or Pb, the electron "asymmetry"¹⁴ about Sn should increase until the number of each element is about equal ($x = 4\text{--}5$), and then with increased Ge ($x = 5\text{--}8$) electronic "asymmetry" should decrease regularly. Since the paramagnetic term is opposite in sign to the diamagnetic term and increases in magnitude with greater electronic asymmetry,⁸ it would explain the observed parabolic trend of δ vs. x very nicely. Asymmetry effects about Sn would be minimized for SnGe_8^{4-} . The observation of SnGe_8^{4-} at a slightly higher field than Sn_9^{4-} suggests that the relative electronegativities are $\text{Ge} \sim \text{Sn} > \text{Pb}$ for the negative oxidation states.

Alloys of composition $\text{NaSnTl}_{1.5}$ impart a deep red-brown color to en. The ^{119}Sn NMR spectra of these solutions is rather simple and show only a doublet of quintets at 63 ppm downfield from a weak Sn_9^{4-} signal. In en at 30 °C, the couplings are $J(^{119}\text{Sn}, ^{205,203}\text{Tl}) = 800$ Hz and $J(^{119}\text{Sn}, ^{117}\text{Sn}) = 410$; however, these values are temperature and solvent dependent. In en the values

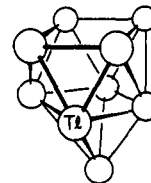


Figure 2. Proposed structure of TlSn_8^{5-} .

range 793–842 Hz and 410–406 Hz as the temperature increases from 30 to 110 °C; in NH_3 (l) from -74 to -34 °C the corresponding values are 927–1001 and 437–400 Hz.

The observed separations within the multiplet are field independent which is a particularly salient demonstration that the doublet feature is due to one Tl in the cluster. Along with the relative intensities of the quintet features, (indicative of eight tin atoms), these NMR data suggest a fluxional TlSn_8^{5-} cluster isoelectronic with Sn_9^{4-} . The 5- charge was established by satisfactory elemental analyses for all elements [$\text{Na}_5(\text{en})_2(\text{TlSn}_8)$]. Formally, a Tl^- replaces a Sn in the Sn_9^{4-} cluster. The TlSn_8^{5-} represents the first well characterized example of a Tl compound in a formal negative oxidation state. However, we doubt that Tl is actually more electron rich than Sn in this case. Several naked-metal clusters have structures reminiscent of heteroboranes. In the heteroboranes, heteroelements electron poor relative to boron are usually found in the polyhedron at the highest-order vertex.¹³ Therefore, we propose an idealized TlSn_8^{5-} structure based on the known uncapped square antiprism (C_{4v}) polyhedron of Sn_9^{4-} in which the Tl substitutes for any Sn atom of the square which is capped [this "lower belt" contains the order 5 vertices; all others are order 4 (Figure 2)].

Red-orange solutions of SnTe_4^{4-} are obtained when Na/Sn/Te alloys are extracted with en. The relative intensities of the multiplet peaks in the ^{119}Sn and ^{125}Te NMR spectra establish a SnTe_4 stoichiometry, and total elemental analysis gives the molecular formula as $\text{Na}_4(\text{en})_4(\text{SnTe}_4)$. The signals appear -598 ppm from Sn_9^{4-} and -604 ppm from Me_2Te in the ^{119}Sn and ^{125}Te regions, respectively; $J(^{119}\text{Sn}, ^{125}\text{Te}) = 2804$ and $J(^{117}\text{Sn}, ^{125}\text{Te}) = 2679$ Hz. The SnTe_4^{4-} anion does not appear to be polyhedral cluster anion but rather a classical, Sn-centered, tetrahedral tellurostannate anion. The proposed structure is based on the high negative charge which would be unprecedentedly high on a charge per metal basis for a polyhedral naked-metal cluster. Moreover, the line width of the NMR signal for SnTe_4^{4-} remains at about $\Delta\nu_{1/2} = 6$ Hz at both 28.2 and 112.9 MHz unlike our observations for naked-metal cluster anions such as TlSn_8^{5-} , Sn_9^{4-} , and Sn_4^{2-} which are broadened appreciably at the higher field. We suggest that chemical-shift anisotropy dominates the relaxation mechanism⁸ in these cases but is not effective for the symmetric tetrahedral field in SnTe_4^{4-} . An analogous SnSe_4^{4-} was recently crystallographically reported.¹⁵ However, to our knowledge, this is the first report of SnTe_4^{4-} and the first example where extraction of a Zintl phase has yielded a classical anion as opposed to a polyhedral naked-metal cluster.

The range of results here for extraction of Zintl phases with en and NH_3 (l) portends a rich chemistry, especially for heteroatomic species. For instance, several other ternary alloys such as Na/Sn/Bi, K/Sn/Bi, K/Sn/Pb, Na/Sn/Se, Na/Sn/Sb, Na/Sn/Ga, and K/Ge/Te show NMR spectra with new species which will be reported on latter.

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(14) Here electronic asymmetry refers to the imbalance of electron density in the valence orbitals of the Sn nucleus. Since these clusters are fluxional, rigorously the imbalance would be for an "average" structure.

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