

Stable Homopolyatomic Anions: The Tetrastannide(2-) and Tetragermanide(2-) Anions, Sn_4^{2-} and Ge_4^{2-} X-Ray Crystal Structure of $[\text{K}^+(\text{crypt})]_2\text{Sn}_4^{2-}$ ethylenediamine

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Summary The salts $(\text{K}-2,2,2\text{-crypt})_2\text{Sn}_4\text{-en}$ (en = ethylenediamine) and $(\text{Na}-2,2,2\text{-crypt})_2\text{Ge}_4$ have been synthesized and shown by single crystal X-ray diffraction to contain the 18-electron, tetrahedral cluster anions Sn_4^{2-} and Ge_4^{2-} .

EARLY electrochemical work by Zintl and co-workers¹ identified many polyatomic anions of the heavy post-transition elements in solutions of their alkali metal alloys in liquid ammonia. Recently, the use of 2,2,2-crypt² as a complexing agent for the alkali metal cation has made possible the isolation of such polyatomic anions as stable salts. Earlier studies of the sodium-tin and potassium-germanium alloy systems led to the characterization of the anions Sn_5^{2-} ,³ Sn_9^{4-} ,⁴ Ge_9^{4-} , and Ge_9^{2-} .⁵ We now report the isolation and X-ray crystal analysis of the new phases $[\text{K}^+(\text{crypt})]_2\text{Sn}_4^{2-}\text{-en}$ and $[\text{Na}^+(\text{crypt})]_2\text{Ge}_4^{2-}$ which contain the unusual 18-electron Sn_4^{2-} and Ge_4^{2-} anions.

Black, plate-shaped crystals of the former salt were one of several products from a reaction of KSn_2 , K_3Bi_2 , and 2,2,2-crypt in ethylenediamine (en). (The intention had been to form a heteropolyatomic tin-bismuth anion

analogous to $\text{Pb}_x\text{Sn}_{9-x}^{4-}$ clusters identified in solution by n.m.r. spectroscopy.⁶)

Crystal data: $\text{C}_{36}\text{H}_{72}\text{O}_{12}\text{N}_4\text{K}_2\text{Sn}_4\text{-C}_2\text{H}_8\text{N}_2$, monoclinic, space group $P2_1$, $a = 12.640(3)$, $b = 20.943(5)$, $c = 12.353(3)$ Å, $\beta = 118.97(2)^\circ$, $Z = 2$. Data were collected on a four-circle automated diffractometer (Mo- K_α radiation) and corrected for Lorentz polarization, a 16% decay of the standard reflections, and a relatively large absorption ($\mu = 19.3 \text{ cm}^{-1}$, transmission coefficients ranged from 0.98 to 0.17). This yielded 2650 independent reflections with $I > 3\sigma(I)$. The structure was solved by Patterson and Fourier techniques and refined (full matrix least-squares), with anisotropic thermal parameters for the Sn and K atoms and isotropic for the other 56 non-hydrogen atoms, to $R = 0.093$ and $R_w = 0.114$.†

The Sn_4^{2-} anion is the surprising feature of the structure. Rudolph and co-workers have predicted the existence of a Sn_4^{2-} anion of uncertain geometry based on the identification of an n.m.r. resonance in solutions of Na-Sn alloys in en,⁷ but the present work provides the first conclusive structural evidence for an 18-electron *tetrahedral* cluster. It is interesting to note that Sn_4^{2-} is isoelectronic with the

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for the communication.

hypothetical tetrahedral $B_4H_4^{2-}$. Of course Sn_4^{2-} with T_d symmetry would have two unpaired electrons in the highest e-orbital and be first-order Jahn-Teller unstable, so the anion should distort to remove the degeneracy. A study of Sn_4^{2-} (g) by Rothman, Bartell, and Lohr⁸ using effective potential calculations predicts a minimum in total valence energy for a compressed tetrahedron (D_{2d}), and also predicts fluxional behaviour, related to a second-order Jahn-Teller effect, through three compressed and three elongated tetrahedra (D_{2d}).

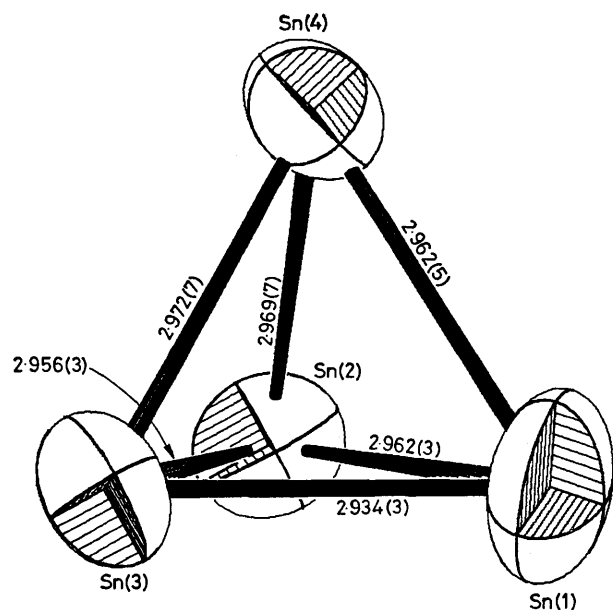


FIGURE. The structure of the Sn_4^{2-} anion. Thermal ellipsoids are drawn at the 50% probability level.

The Sn_4^{2-} cluster actually found in this structure is only slightly distorted from T_d toward C_{2v} symmetry, as shown in the Figure, with only one edge [$2.934(3)$ Å] significantly shorter than the other five. This bears little resemblance to the predicted minimum energy structure, a compressed tetrahedron with four short and two long bond lengths, but the C_1 site symmetry of the cluster in the crystal probably influences the observed geometry to a large extent. If a restricted amount of the fluxional behaviour described by Rothman *et al.* still occurs in this solid the distortions necessary are small enough that they would easily be hidden in the rather typical³⁻⁵ thermal ellipsoids of the tin atoms, for which equivalent isotropic temperature factors range from 7 to 10 Å². E.s.r. measurements on the crystals at 77 and 293 K give no evidence for unpaired spins.

The presence of this anion also confirms our work on the X-ray crystal structure of $(Na-2,2,2-crypt)_2Ge_4$, which clearly contains the analogous tetrahedral Ge_4^{2-} anion. The latter is slightly elongated to C_{3v} symmetry (as required by the space group $P\bar{3}$) with comparatively long Ge-Ge bond lengths of 2.77 and 2.79 Å. Note that distortion only to C_{3v} symmetry is not sufficient to break the degeneracy of the highest e-orbital. Unfortunately the anion is disordered in this structure with two major and several minor components, causing a high R factor and presenting some difficulties in determining the precise cluster configuration.

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¹ E. Zintl, J. Goubeau, and W. Dullenkopf, *Z. Phys. Chem., Abt. A*, 1931, **154**, 1.

² 4,7,13,16,21,24-Hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane, $N(C_2H_4OC_2H_4OC_2H_4)_3N$; B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 1969, 2885.

³ P. A. Edwards and J. D. Corbett, *Inorg. Chem.*, 1977, **16**, 903.

⁴ J. D. Corbett and P. A. Edwards, *J. Am. Chem. Soc.*, 1977, **99**, 3313.

⁵ C. H. E. Belin and J. D. Corbett, *J. Am. Chem. Soc.*, 1977, **99**, 7163.

⁶ R. W. Rudolph, W. L. Wilson, F. Parker, R. C. Taylor, and D. C. Young, *J. Am. Chem. Soc.*, 1978, **100**, 4629.

⁷ R. W. Rudolph, W. L. Wilson, and R. C. Taylor, *J. Am. Chem. Soc.*, 1981, accepted for publication.

⁸ M. J. Rothman, L. S. Bartell, and L. L. Lohr, Jr., *J. Am. Chem. Soc.*, 1980, submitted for publication.