The Nonastannide(4−) Anion Sn_9^{4-}, a Novel Capped Antiprismatic Configuration (C_{4v})[1]

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Abstract: Reaction of alloy compositions near $NaSn_{2.25}$ with 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]-hexacosane) in ethylenediamine yields dark red to black rods which have been shown to be $(\text{crypt-Na}^+)_4Sn_9^{4-}$ by x-ray crystallography. The compound crystallizes in the $P\bar{1}$ space group with $Z = 2$ and $a = 16.655$ (3) Å, $b = 21.207$ (10) Å, $c = 15.370$ (7) Å, $\alpha = 107.98$ (5)°, $\beta = 103.43$ (6)°, and $\gamma = 81.70$ (9)° at 5 °C. Diffraction data were measured over four octants at 5 °C using the four-circle automatic diffractometer and monochromatized Mo Kα radiation, and the structure was solved by conventional Patterson and Fourier techniques. The 117 independent (nonhydrogen) atoms in the structure yielded, with anisotropic thermal parameters for tin and sodium, $R = 0.121$ and $R_w = 0.143$ for 4803 independent observed reflections with $0 < 2\theta < 45°$. One of the four cations exhibits the first example of six rather than eight coordination by 2,2,2-crypt with two opposite oxygen atoms displaced from the coordination sphere (3.12 and 3.30 Å from sodium). The novel anion Sn_9^{4-} represents the first example of a unicapped antiprismatic (C_{4v}) configuration, the distinguishing dihedral angles being: square base (vicinal), $\delta = 2.6$ (2)°, opposed (parallel to fourfold), $\delta = 157.7$ (1)°, 158.3 (1)°. The contrast between the C_{4v} symmetry of Sn_9^{4-} and the D_{3h} symmetry known for the isoelectronic Bi_9^{5+} (in the $HfCl_6^{2-}$ salt) is considered in terms of a potential stereochemical nonrigidity. The distorted Bi_9^{5+} found in the "monochloride" salt $Bi_{12}Cl_{14}$ exhibits dihedral angles which indicate a 25% distortion from D_{3h} toward C_{4v} symmetry. Semiempirical SCF-CNDO-MO calculations suggest there is a negligible barrier along the geometric path between these two limits.

About 45 years ago Zintl and co-workers[2,3] published the results of extensive electrochemical studies on the unusual solutions of sodium intermetallic phases of many of the heavier posttransition elements that can be obtained directly or indirectly in liquid ammonia. Solutes such as Sn_9^{4-}, Pb_9^{4-}, Bi_5^{3-}, and Te_4^{2-} were among the numerous species identified by means of potentiometric titrations or exhaustive alloy extraction followed by analyses. In general evaporation of these solutions yields only amorphous products or known phases in the binary alloy systems. Prevention of electron transfer from the new anions back onto the cation component would appear to be necessary to prevent formation of the generally more stable intermetallic phases.

For a long period of time nothing more was published about these remarkable solutions. In 1970 a note by Kummer and Diehl[4] revealed that the phases $Na_4Sn_9 \cdot x\text{en}$ ($x = 8, 6, 4$; en = ethylenediamine) could be precipitated from solutions of the appropriate alloy in en, although the magnitudes of the en dissociation pressures for the higher solvates suggest that their stabilities are not very large. The availability of the polycyclic ligand 2,2,2-crypt[5] to provide very strong complexing of the alkali metal counterion has now provided a general route to thermodynamically stable polyanions of many elements, e.g., Sb_7^{3-},[6,7] Pb_5^{2-} and Sn_5^{2-},[8,9] Te_3^{2-},[10] and, as reported in a preliminary communication,[8] Sn_9^{4-} in a novel C_{4v} configuration. Since then partial reports[11] on an incomplete crystal structure study of the $Na_4Sn_9 \cdot 7\text{en}$ compound indicate that the compound contains Sn_9^{4-} as a distorted tricapped trigonal prism. The present article describes the synthesis and structural characterization of the compound $(\text{crypt-Na}^+)_4Sn_9^{4-}$ together with some considerations of the contrasting D_{3h} symmetry shown by the isoelectronic cation Bi_9^{5+} [12,13] and of the possibility that these species may be stereochemically nonrigid.

Experimental Section

Synthesis. The 2,2,2-crypt (Merck) was used as received from EM Laboratories and was handled only in the drybox. The alloys were prepared as before[14] by fusion of the appropriate amounts of the elements in a welded tantalum tube followed by quenching and annealing. Alloys with compositions near $NaSn_{2.25}$ dissolve appreciably in ethylenediamine (en) alone to yield the typical orange-red solutions of Sn_9^{4-}, but the process is considerably enhanced both in speed and in quantity by the addition of crypt. An excess of crypt was generally utilized in order to avoid the production of a mixture of the en and crypt complexes. The reaction vessel was equipped with Teflon needle valves (Fischer-Porter) in place of stopcocks, and the en was vacuum distilled from Molecular Sieve. Satisfactory crystals grow best on very slow evaporation of the solvent, even to the point of allowing appreciable digestion of the first crystals in the mother liquor. Large black rods of approximately square cross section were cut to 0.2 × 0.2 × 0.4 mm chunks in the drybox and mounted in 0.2 mm diameter thin-wall capillaries, using silicone grease to hold their position. Because of the cost of the ligand the product analysis was accomplished by x-ray crystallography.

Data Collection and Reduction. Crystals of the compound are indefinitely stable at room temperature and for a short time in the air but they lose an appreciable fraction of their diffracting ability in about a day at room temperature once they have been exposed to x-rays, even the amount necessary to take a preliminary oscillation photograph. Therefore a satisfactory crystal once located was kept in a freezer until used and was then cooled to about 5 °C during data collection. The preliminary orientation search[15] showed that the compound occurred in the triclinic system, with $Z = 2$ based on density estimates from related compounds.[7,9] Integrated diffraction intensities were collected via an Ω step-scan (0.01° step, 0.5 s count, 1° scan) in the four octants HKL, $HK\bar{L}$, $H\bar{K}L$, and $H\overline{KL}$ using molybdenum radiation monochromatized with a graphite crystal (λ 0.709 54 Å). A limit of $2\theta = 50°$ for data collection was used for the first 1710 reflections checked after which this was reduced to 45°; 71 data on this high angle group were retained as observed (vide infra). A reduction of about 40% in the sum of the intensities of three standard reflections was observed during measurement of the first two octants (8002 reflections); therefore the 6234 additional reflections accessible in the third and fourth octants were measured on a second crystal of similar size. These sets were separately corrected for Lorentz and polarization effects and for absorption ($\mu = 23$ cm^{-1}, transmission coefficients from 0.61 to 0.68) and for the decay in diffraction intensities with time based on that of the standards. The two data sets were then scaled on the basis of 23 moderate-to-strong common reflections and merged. A total of 5763 reflections with $I > 3\sigma_I$ and $F > 3\sigma_F$ were kept as observed, the errors being defined as before.[16] However, a complete block of 960 reflections in the second octant which were measured toward the end of data collection on the first crystal was eliminated toward the completion of the structural solution when it became obvious that the diffractometer had been partially missing many weak reflections in that region because of decomposition or, more likely, crystal misalignment. This was signaled by the fact that the observed background counts at that point had been rather unequal, that 85% of the larger differences between F_o and F_c were then localized in this portion of the data set, and that within the group of 175 worst re-

Table I. Final Atomic Positional and Temperature Factor Parameters for $(2,2,2\text{-cryptNa}^+)_4Sn_9^{4-}$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn(1)	0.3189 (2)	0.3101 (1)	0.4383 (2)	5.3 (2)	4.2 (1)	5.0 (2)	−1.4 (1)	−0.3 (2)	1.5 (1)
Sn(2)	0.3170 (2)	0.1632 (1)	0.3754 (2)	6.5 (2)	3.9 (1)	5.8 (2)	−0.1 (1)	1.6 (2)	2.6 (1)
Sn(3)	0.3672 (2)	0.2180 (1)	0.2444 (2)	4.0 (1)	4.2 (1)	6.0 (2)	−0.9 (1)	1.3 (2)	2.0 (1)
Sn(4)	0.1393 (2)	0.3489 (1)	0.3315 (2)	4.4 (1)	3.3 (1)	6.7 (2)	−0.4 (1)	0.8 (2)	1.4 (1)
Sn(5)	0.0846 (2)	0.2123 (1)	0.2298 (2)	4.6 (1)	3.8 (1)	6.4 (2)	−1.4 (1)	1.1 (2)	1.3 (1)
Sn(6)	0.1867 (2)	0.2560 (1)	0.1314 (2)	5.6 (2)	3.5 (1)	5.0 (1)	−0.9 (1)	0.0 (1)	1.9 (1)
Sn(7)	0.1668 (2)	0.2446 (2)	0.4298 (2)	4.7 (2)	4.9 (1)	6.4 (2)	−0.7 (1)	1.1 (2)	2.9 (1)
Sn(8)	0.2315 (2)	0.1278 (1)	0.1764 (2)	4.8 (1)	3.1 (1)	6.6 (2)	−0.6 (1)	0.2 (2)	1.4 (1)
Sn(9)	0.2923 (2)	0.3555 (1)	0.2689 (2)	5.7 (2)	3.7 (1)	6.9 (2)	−1.4 (1)	1.0 (2)	1.9 (1)
Na(1)	0.7073 (10)	0.3168 (8)	0.3758 (14)	4.0 (8)	4.3 (6)	14.8 (16)	0.0 (6)	2.1 (12)	2.8 (8)
Na(2)	0.9535 (10)	0.1088 (7)	0.7250 (10)	5.6 (8)	3.6 (5)	6.9 (9)	0.5 (6)	0.4 (9)	0.8 (6)
Na(3)	0.4776 (9)	0.1440 (8)	0.8003 (10)	3.8 (7)	4.3 (5)	6.1 (8)	−0.6 (6)	1.3 (8)	1.5 (6)
Na(4)	0.1736 (11)	0.4885 (8)	0.8685 (10)	6.4 (9)	3.9 (5)	5.3 (8)	−0.6 (6)	1.3 (9)	2.0 (6)

	x	y	z	B		x	y	z	B
N(101)[b]	0.687 (2)	0.437 (2)	0.529 (2)	5.6 (7)	N(301)	0.428 (3)	0.267 (2)	0.764 (3)	8.8 (11)
C(102)	0.641 (3)	0.481 (2)	0.484 (3)	6.5 (10)	C(302)	0.496 (5)	0.286 (3)	0.730 (5)	12.4 (19)
C(103)	0.570 (3)	0.456 (2)	0.406 (3)	8.2 (11)	C(303)	0.573 (4)	0.242 (3)	0.700 (4)	10.5 (16)
O(104)	0.594 (2)	0.399 (1)	0.338 (2)	6.9 (6)	O(304)	0.590 (4)	0.196 (3)	0.754 (4)	16.8 (17)
C(105)	0.519 (3)	0.384 (2)	0.264 (3)	6.6 (10)	C(305)	0.676 (8)	0.189 (5)	0.776 (8)	22.9 (41)
C(106)	0.542 (3)	0.317 (2)	0.204 (3)	7.9 (12)	C(306)	0.685 (4)	0.150 (3)	0.866 (4)	10.5 (17)
O(107)	0.612 (2)	0.306 (2)	0.173 (2)	7.9 (8)	O(307)	0.631 (2)	0.122 (2)	0.889 (2)	7.7 (8)
C(108)	0.622 (4)	0.246 (3)	0.107 (4)	10.3 (15)	C(308)	0.660 (4)	0.060 (3)	0.890 (3)	8.6 (12)
C(109)	0.639 (3)	0.185 (2)	0.138 (3)	5.9 (9)	C(309)	0.592 (3)	0.029 (2)	0.905 (3)	8.3 (12)
N(110)	0.703 (2)	0.195 (2)	0.224 (2)	5.8 (7)	N(310)	0.512 (2)	0.024 (2)	0.830 (2)	6.9 (8)
C(111)	0.778 (3)	0.180 (2)	0.188 (3)	7.3 (11)	C(311)	0.466 (3)	0.027 (2)	0.257 (3)	8.7 (13)
C(112)	0.857 (4)	0.209 (3)	0.272 (4)	10.0 (15)	C(312)	0.518 (4)	0.014 (3)	0.354 (4)	11.8 (18)
O(113)	0.836 (2)	0.272 (2)	0.314 (2)	7.9 (7)	O(313)	0.482 (2)	0.054 (2)	0.649 (2)	7.9 (7)
C(114)	0.908 (3)	0.306 (3)	0.380 (4)	9.2 (14)	C(314)	0.418 (3)	0.058 (2)	0.577 (3)	8.2 (12)
C(115)	0.892 (4)	0.375 (3)	0.409 (4)	8.9 (13)	C(315)	0.345 (2)	0.094 (2)	0.599 (2)	4.6 (7)
O(116)	0.831 (2)	0.386 (2)	0.464 (2)	8.0 (8)	O(316)	0.349 (2)	0.147 (1)	0.681 (2)	5.9 (6)
C(117)	0.818 (3)	0.446 (2)	0.534 (3)	6.2 (10)	C(317)	0.315 (4)	0.206 (3)	0.670 (4)	9.0 (13)
C(118)	0.767 (3)	0.454 (2)	0.587 (3)	7.7 (12)	C(318)	0.358 (4)	0.260 (3)	0.704 (5)	12.0 (18)
C(119)	0.634 (3)	0.436 (2)	0.596 (3)	6.6 (10)	C(319)	0.412 (5)	0.317 (3)	0.855 (5)	14.4 (22)
C(120)	0.656 (3)	0.376 (2)	0.637 (3)	6.0 (9)	C(320)	0.448 (3)	0.309 (2)	0.931 (3)	7.1 (11)
O(121)	0.654 (2)	0.313 (1)	0.567 (2)	7.2 (7)	O(321)	0.441 (2)	0.244 (2)	0.939 (2)	8.0 (8)
C(122)	0.570 (3)	0.303 (2)	0.507 (3)	6.2 (10)	C(322)	0.378 (4)	0.229 (2)	0.972 (3)	8.2 (12)
C(123)	0.581 (3)	0.232 (2)	0.446 (3)	7.8 (12)	C(323)	0.377 (3)	0.164 (2)	0.989 (3)	7.1 (10)
O(124)	0.639 (2)	0.221 (1)	0.390 (2)	6.3 (6)	O(324)	0.391 (2)	0.120 (2)	0.899 (2)	7.9 (7)
C(125)	0.633 (4)	0.151 (3)	0.324 (4)	10.9 (16)	C(325)	0.399 (4)	0.053 (3)	0.917 (4)	12.0 (18)
C(126)	0.703 (3)	0.145 (2)	0.271 (3)	6.9 (10)	C(326)	0.442 (4)	0.006 (3)	0.853 (4)	9.6 (14)
N(201)	0.863 (2)	0.154 (2)	0.576 (3)	7.3 (9)	N(401)	0.692 (3)	0.431 (2)	0.016 (3)	9.0 (10)
C(202)	0.862 (4)	0.221 (3)	0.603 (4)	9.5 (13)	C(402)	0.618 (4)	0.463 (3)	0.034 (4)	11.8 (18)
C(203)	0.853 (3)	0.266 (2)	0.695 (3)	9.1 (13)	C(403)	0.618 (3)	0.484 (2)	0.136 (4)	8.5 (13)
O(204)	0.906 (2)	0.2303 (2)	0.765 (2)	8.5 (8)	O(404)	0.309 (2)	0.477 (1)	0.811 (2)	7.2 (7)
C(205)	0.886 (4)	0.263 (2)	0.862 (4)	9.2 (14)	C(405)	0.300 (3)	0.468 (2)	0.710 (3)	7.4 (11)
C(206)	0.941 (2)	0.223 (2)	0.916 (3)	6.6 (10)	C(406)	0.224 (3)	0.436 (2)	0.662 (3)	7.9 (11)
O(207)	0.912 (2)	0.156 (1)	0.887 (2)	7.6 (7)	O(407)	0.156 (2)	0.479 (1)	0.694 (2)	6.2 (6)
C(208)	0.933 (4)	0.118 (2)	0.951 (3)	8.6 (13)	C(408)	0.076 (3)	0.462 (2)	0.636 (3)	6.9 (10)
C(209)	0.026 (3)	0.095 (2)	0.956 (2)	6.1 (9)	C(409)	0.056 (3)	0.400 (2)	0.648 (3)	7.5 (11)
N(210)	0.046 (2)	0.053 (2)	0.870 (3)	7.6 (9)	N(410)	0.039 (2)	0.407 (2)	0.752 (2)	6.5 (8)
C(211)	0.973 (3)	0.020 (2)	0.155 (3)	6.9 (10)	C(411)	0.970 (3)	0.453 (2)	0.766 (3)	7.7 (11)
C(212)	0.985 (3)	0.049 (2)	0.260 (3)	8.1 (12)	C(412)	0.975 (3)	0.490 (2)	0.869 (3)	7.2 (11)
O(213)	0.058 (2)	0.012 (1)	0.305 (2)	7.1 (7)	O(413)	0.966 (2)	0.466 (1)	0.105 (2)	6.0 (6)
C(214)	0.137 (3)	0.029 (2)	0.306 (4)	8.0 (12)	C(414)	0.991 (3)	0.398 (2)	0.114 (2)	8.0 (12)
C(215)	0.797 (6)	0.992 (4)	0.646 (5)	16.2 (26)	C(415)	0.925 (3)	0.373 (2)	0.137 (3)	6.4 (10)
O(216)	0.805 (2)	0.064 (2)	0.658 (2)	8.8 (9)	O(416)	0.854 (2)	0.381 (2)	0.075 (2)	8.1 (8)
C(217)	0.774 (4)	0.070 (3)	0.567 (4)	9.3 (14)	C(417)	0.782 (4)	0.351 (3)	0.099 (4)	9.8 (14)
C(218)	0.776 (4)	0.138 (3)	0.563 (4)	9.3 (13)	C(418)	0.711 (4)	0.364 (3)	0.020 (4)	9.4 (14)
C(219)	0.898 (4)	0.117 (3)	0.497 (4)	11.7 (17)	C(419)	0.697 (4)	0.432 (3)	0.921 (4)	8.5 (13)
C(220)	0.988 (5)	0.125 (3)	0.513 (5)	12.0 (19)	C(420)	0.732 (6)	0.480 (4)	0.898 (6)	16.9 (28)
O(221)	0.027 (2)	0.099 (2)	0.603 (2)	9.2 (8)	O(421)	0.208 (2)	0.476 (2)	0.033 (2)	9.5 (9)
C(222)	0.115 (4)	0.123 (3)	0.613 (4)	10.6 (17)	C(422)	0.238 (4)	0.417 (3)	0.031 (4)	8.9 (14)
C(223)	0.159 (4)	0.087 (3)	0.711 (4)	9.8 (14)	C(423)	0.178 (4)	0.373 (3)	0.964 (4)	9.8 (14)
O(224)	0.113 (2)	0.132 (2)	0.773 (2)	8.1 (8)	O(424)	0.187 (2)	0.365 (2)	0.873 (2)	8.5 (8)
C(225)	0.153 (3)	0.121 (2)	0.873 (3)	7.6 (11)	C(425)	0.141 (3)	0.322 (2)	0.792 (3)	8.7 (13)
C(226)	0.136 (3)	0.059 (2)	0.873 (3)	7.6 (11)	C(426)	0.052 (3)	0.347 (2)	0.775 (3)	8.2 (12)

[a] $\beta_{ij} \times 10^3$ is listed. The thermal parameter expression is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] The first digit keys on the crypt cation, the second and third on the atoms therein in the order given in Figure 2 and ref 7.

flections $F_o < F_c$ 98% of the time. Precise lattice dimensions were obtained by least-squares fitting of the 2θ values obtained from the second data crystal by tuning with top-bottom, left-right beam splitting on 25 reflections with $20° < 2\theta < 32.8°$, giving constants of $a = 16.655$ (3) Å, $b = 21.207$ (10) Å, $c = 15.370$ (7) Å, $\alpha = 107.98$ (5)°, $\beta = 103.43$ (6)°, and $\gamma = 81.70$ (9)° at 5 °C.

Structure Solution. The number of large peaks in the sharpened Patterson function was consistent only with the $P\bar{1}$ space group, and the tin atoms were located directly from the Harker vectors therein as these were distinctive in intensity and position owing to the presence of well-separated tin clusters. At this point $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.33$ after a few cycles of positional and isotropic thermal parameter refinement. Four sodium atom positions were then readily deduced by electron density synthesis, and the necessary 104 light (nonhydrogen) atoms were located by three successive Fourier syntheses following modest positional refinements. At this point it was possible to discern the connectivity of the four crypt ligands and thus to assign the correct scattering factors.

After a limited number of block least-squares refinements on 100 atoms the complete structure was refined in parts by full-matrix least-squares utilizing a locally expanded version of ORFLS. In order to reduce the computation time and cost, refinement of the full structure was successively cycled among the heavy atom anion and each of the four crypt-sodium cations, first in positions only and ultimately with anisotropic temperature parameters for tin and sodium and isotropic parameters for the 104 light atoms in the ligands. Along the way the data set was reweighted in ten overlapping groups sorted on F_o when it was observed that $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$, $w = \sigma_F^{-2}$) had an appreciable dependence on the magnitude of F_o. Convergence was obtained with $R = 0.121$, $R_w = 0.143 = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ for 4803 reflections and 515 variables. For comparison 38% of the data set occurs with $2\theta > 33°$, and omission of these from the final calculation would lower the residuals by 0.025 each. In the final cycle the largest shift in the tin parameters was $\leq 0.05\sigma$ while for the light atoms this amounted to $\leq 0.5\sigma$ for a few parameters with $< 0.25\sigma$ for the large majority. The final electron density difference synthesis was flat except for a few areas at ±1 e/Å^3 and a small peak of 2 e/Å^3 near Sn 8; 144 hydrogen atoms have not been located or included in the synthesis. Since the heavy atom moiety of interest was well determined and the crypt-Na$^+$ cations relatively precisely fixed it was not deemed worth the cost or time to include hydrogen atoms or to improve the data set. The neutral atom scattering factors utilized included corrections for the real and imaginary parts of anomalous dispersion; the sources of these and the standard computing programs were as referenced before.[7,17]

Results

The final positional and thermal parameters for the nonhydrogen atoms in (crypt-Na$^+$)$_4$Sn$_9{}^{4-}$ are listed in Table I. The most interesting feature of the structure, the Sn$_9{}^{4-}$ ion, is illustrated in Figure 1, and bond distances and angles therein are given in Table II. The supplementary material contains bond distance and angle data for the crypt-sodium cations, a listing of the shorter interionic distances in the structure, and a tabulation of calculated and observed structure factor amplitudes.

Structures of three of the four sodium-crypt cations in the polytin salt are quite similar to those determined previously,[7,9] including an appreciable variability in the sodium-nitrogen and sodium-oxygen distances and often larger thermal parameters for carbon atoms β to the bridgehead. However, the crypt-Na$^+$(1) ion is the first reported example of a reduction in the coordination number of 2,2,2-crypt from 8 to 6. The result is illustrated in Figure 2 in a view into the open face created when Na-O7 and Na-O21 are lengthened to 3.12 (3) and 3.30 (4) Å, respectively, vs. a range of 2.41-2.76 Å for the normal sodium-oxygen bonds in the structure. Presumably strain is responsible for the lower coordination number, the sodium ion being somewhat undersized for the 2,2,2-crypt ligand.[18] This produces a twist of the order of 40-45° between the oxygen planes 7-13-24 and 4-16-21 in the normal octadentate structure, a condition which is virtually eliminated in the new hexadentate version (see the caption to Figure 2). The

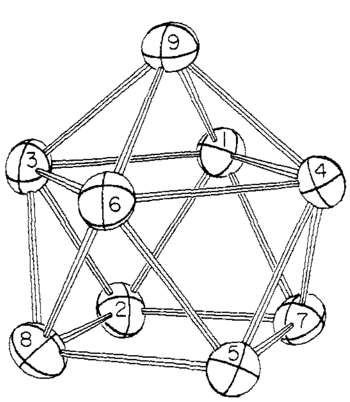

Figure 1. The Sn$_9{}^{4-}$ ion in the compound (2,2,2-cryptNa$^+$)$_4$Sn$_9{}^{4-}$. Thermal ellipsoids are drawn at the 50% probability level.

Table II. Distances and Angles in the Sn$_9{}^{4-}$ Cluster[a]

Tin atoms	d, Å	Tin atoms	d, Å
1-2	2.972 (3)	4-6	3.308 (5)
1-3	3.233 (4)	4-7	2.976 (5)
1-4	3.193 (3)	4-9	2.965 (5)
1-7	3.022 (4)	5-6	2.928 (6)
1-9	2.971 (4)	5-7	2.973 (4)
2-3	2.941 (5)	5-8	2.943 (5)
2-7	2.966 (5)	6-8	2.966 (4)
2-8	2.973 (4)	6-9	2.937 (4)
3-6	3.237 (4)	2-5	4.163 (4)
3-8	2.966 (5)	7-8	4.205 (5)
3-9	2.953 (5)	1-6	4.580 (4)
4-5	2.998 (4)	3-4	4.575 (6)

Tin atoms	Angle, deg	Tin atoms	Angle, deg
3-1-9	56.7 (1)	1-7-4	64.3 (1)
4-1-9	57.4 (1)	2-8-3	59.4 (1)
4-1-7	57.1 (1)	3-8-6	66.1 (1)
2-1-3	56.4 (1)	5-8-6	59.4 (1)
1-2-7	61.2 (1)	1-9-4	65.1 (1)
3-2-8	60.2 (1)	1-9-3	66.1 (1)
1-2-3	66.3 (1)	3-9-6	66.7 (1)
4-5-6	67.8 (1)	4-9-6	68.2 (1)
4-5-7	59.8 (1)	7-2-8	90.4 (1)
6-5-8	60.7 (1)	7-5-8	90.8 (1)
3-6-8	56.9 (1)	2-7-5	89.2 (1)
4-6-5	57.1 (1)	2-8-5	89.6 (1)
4-6-9	56.3 (1)	1-4-6	89.8 (1)
3-6-9	56.9 (1)	4-6-3	88.9 (1)
4-7-5	60.5 (1)	6-3-1	90.3 (1)
1-7-2	59.5 (1)	3-1-4	91.0 (1)

Dihedral Angles between Planes (deg)

(1-2-3)	(4-5-6)	157.7 (1)
(3-6-8)	(1-4-7)	158.3 (1)
(2-3-8)	(4-5-7)	143.1 (1)
(5-6-8)	(7-2-1)	143.5 (1)
(1-2-3)	(1-3-9)	30.3 (1)
(3-6-8)	(3-6-9)	28.9 (2)
(1-4-7)	(1-4-9)	31.9 (1)
(4-5-6)	(4-6-9)	28.9 (1)
(7-8-5)	(7-8-2)	2.6 (2)[b]
(1-7-2)	(1-7-4)	52.3 (1)
(3-8-2)	(3-6-8)	53.4 (1)
(1-2-3)	(2-3-8)	52.8 (1)
(1-2-3)	(1-2-7)	52.8 (1)
(5-6-8)	(3-6-8)	54.1 (1)
(1-4-7)	(4-5-7)	54.7 (1)
(1-3-9)	(3-6-9)	64.1 (1)
(1-4-9)	(6-4-9)	64.4 (1)

[a] Uncertainties include those of cell dimensions. [b] Atoms 7 and 8 are 0.023 Å below best basal plane.

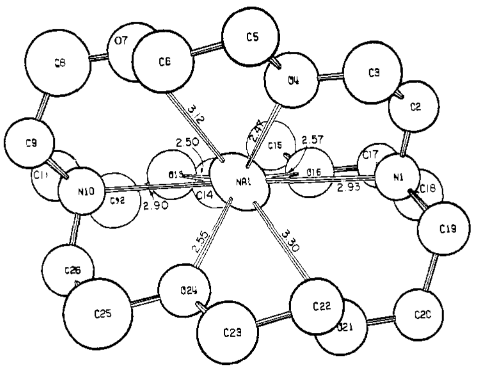

Figure 2. The crypt-Na (1) cation in $(\text{cryptNa}^+)_4\text{Sn}_9{}^{4-}$ looking into the open face generated by long bonds Na-O7 and Na-O21. Pairs of opposed oxygen or nitrogen atoms lie nearly parallel to the plane of the paper; these are, at levels relative to the depth of the ion shown: O4-O24 (0.80), O7-O21 (0.76), N1-N10 (0.58), O13-O16 (0.20). (The first digit identifying the cation in Table I has been dropped in the figure.)

packing considerations necessary to capture this particular configuration in the present compound must be very subtle. There is no evidence whatsoever to suggest that the coordination number reduction has come about because of bonding interactions with the anion, the nearest tin atom (3) being 6.01 Å from Na 1. Although this is 0.44 Å shorter than the next nearest distance between these metals (Sn 4-Na 4), at these large distances the shortening to crypt-sodium 1 must be a result and not a cause of the open face in the cation.

The novel anion $\text{Sn}_9{}^{4-}$ is all the more remarkable because of its close approach to the uncommon C_{4v} symmetry of a unicapped square antiprism, representing as far as is known the first example which clearly has this configuration. With Sn_9 as the apex (Figure 1) the capped square 1-3-6-4 is planar to within experimental error and contains the larger Sn-Sn nearest neighbor distances, 3.19-3.31 Å. All other nearest neighbor distances in the anion fall in the range of 2.93-3.02 Å. The best least-squares plane through the bottom four atoms (2-8-5-7) is 0.023 Å from all atoms (Sn 7 and Sn 8 below the plane) or, in other words, the bottom "square" shows a fold of just 2.6° about the diagonal. Angles in both squares in the antiprism are in the range of 90 ± 0.8° (Table II).

Discussion

The C_{4v} symmetry of $\text{Sn}_9{}^{4-}$ was completely unexpected since the ion is isoelectronic in valence electrons with $\text{Bi}_9{}^{5+}$, and the latter in the salt $\text{Bi}^+\text{Bi}_9{}^{5+}(\text{HfCl}_6{}^{2-})_3$ is rigorously C_{3h} and within 4σ of the D_{3h} symmetry of a tricapped trigonal prism.[13] Another version of the same bismuth ion which has been described as basically a capped trigonal prism showing a moderate distortion to C_{2v} (vide infra) occurs in the salt $(\text{Bi}_9{}^{5+})_2(\text{BiCl}_5{}^{2-})_4(\text{Bi}_2\text{Cl}_8{}^{2-})$.[12,19] (The more closely related $\text{Pb}_9{}^{4-}$ is evidently stable only in liquid ammonia solution as it cannot be isolated through the use of 2,2,2-crypt.[9]) The only other noncentered nine-atom cluster which is structurally well defined is $\text{B}_9\text{H}_9{}^{2-}$,[20] also D_{3h} in symmetry, and for which a bonding relationship to $\text{Bi}_9{}^{5+}$ has been noted, the latter differing principally in the addition of a pair of electrons to a nonbonding orbital.[21]

Although the contrasting symmetries of $\text{Sn}_9{}^{4-}$ and the isoelectronic $\text{Bi}_9{}^{5+}$ do seem unusual they are actually closely related geometrically, and the possible existence of intermediates and interconversions between these two configurations has been well recognized, especially among the centered polyhedra of complex ions ML_9.[22,23] The geometric (and most likely dynamic) route for interconversion of these two configurations in noncentered polyhedra is shown in Figure 3, scaled for the polyatomic ions under present consideration and as an aid to subsequent consideration of possible distorted intermediates. When viewed down the fourfold axis (left) the C_{4v} to D_{3h} conversion is accomplished principally by a compression of the front square along 7-8 together with an elongation of the capped square along 1-3 and 4-6, proceeding through a C_{2v} intermediate to a capped trigonal prism (Figure 3, right) with the threefold axis vertical. (A perfectly acceptable alternate is to generate a horizontal prism axis by opposing faces 123, 456 becoming parallel in D_{3h} symmetry.)

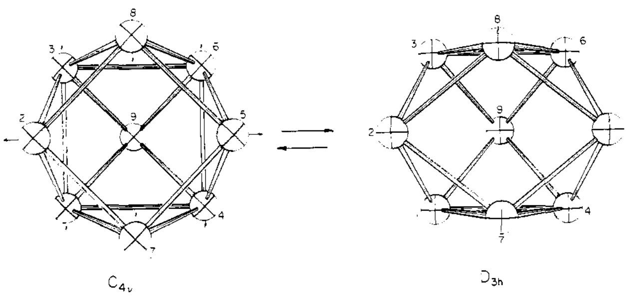

Figure 3. The interconversion of nine atom clusters with unicapped antiprismatic (left) and tricapped trigonal prismatic (right) configurations.

Guggenberger and Muetterties[23] have recently examined all structurally well-defined examples of ML_9 and M_9 species and have concluded that the D_{3h} symmetry is very heavily favored, to the extent that the only examples which even begin to approach C_{4v} probably do so as a result of constraints imposed by the presence of edge or face sharing among the nine atom polyhedra. Of course the usefulness of this generalization to homopolyatomic examples may be seriously limited by the fact that the ligand-ligand interactions in ML_9 species which dictate D_{3h} symmetry are repulsive in character whereas the "ligands" in $\text{Sn}_9{}^{4-}$ are clearly attractive to one another. Nonetheless the precedent afforded by $\text{Bi}_9{}^{5+}$ and $\text{B}_9\text{H}_9{}^{2-}$ were consistent with their conclusion at that time. The same article illustrates well how dihedral angle data provide meaningful quantitative criteria by which one can distinguish between these geometries and define possible distorted intermediates. The most useful dihedral angles (δ) for our purposes are those defined by the two pairs of opposed and equivalent triangular faces in the C_{4v} case which have one atom on the square base, viz., 368, 147 and 123, 456, one pair of which becomes parallel ($\delta = 180°$) to define the trigonal prism. Thus these dihedral angles, 158 ± 0.3° in $\text{Sn}_9{}^{4-}$, diverge to yield the faces of the trigonal prism ($\delta = 180°$) and a pair of triangles at opposing caps which are parallel to the threefold axis (123, 456, $\delta = 142°$ in $\text{Bi}_9{}^{5+}$).

These systematics in terms of dihedral angles reveal that the distortions observed in the first characterized $\text{Bi}_9{}^{5+}$ ion (in $(\text{Bi}_9{}^{5+})_2(\text{BiCl}_5{}^{2-})_4(\text{Bi}_2\text{Cl}_8{}^{2-})$)[12] are in fact toward C_{4v} though not in a completely concerted manner, thus giving rational interpretation to deviations from the tricapped trigonal prism which were interpreted before in terms of "packing interactions". In reference to Figure 3 (right), Bi 7-Bi 8 therein was found to be elongated by 0.28 Å relative to prism edges 1-3 and 4-6 (3.70 Å) while Bi 3-Bi 6 was 0.09 Å longer than any other edge. The more quantitative description of this particular configuration relative to the higher symmetry extremes in terms of dihedral angles which is given in Table III shows that the distortions are very plausible in this view and are of the order of 25% toward those expected for C_{4v} polyhedron. This sort of analysis is considerably more informative than distance comparisons alone, which would also be clouded by a change in the elements involved.

In 1970 Kummer and Diehl[4] described a clever synthesis of the phase $\text{Na}_4\text{Sn}_9\cdot8\text{en}$ (and lower solvates) which was speculated to contain the tricapped trigonal prism $\text{Sn}_9{}^{4-}$. The stability of this compound under manipulative conditions ap-

Table III. Some Dihedral Angles in Nine Atom Polyhedra[a]

D_{3h}	Type faces	Trigonal prism (opposed)	Cap to cap (vicinal)		Prism end to cap (vicinal)		
	Example, Figure 3	(368, 147)	(278, 578)		(368, 568)		
	δ, Bi_9^{5+} [b]	180°	22° (x3)		43° (x6)		
~C_{2v}	δ Bi_9^{5+} [c]	174°	14	24 (x2)	41	43	48 (x4)
C_{4v}	δ Sn_9^{4-} [d]	158° (x2)	3	30	29 (x2)	32	52, 53, 54, 55
	Type faces		Base	Cap to antiprism			Belt of antiprism

[a] Vicinal angles around capping atoms 2, 5, 9 are not included. [b] Reference 13. [c] Reference 12. [d] This work.

pears to be limited by the loss of en, however, with a dissociation pressure of 24 Torr being cited at 58 °C. Recent publications[11] give some details on an incomplete structural study of $Na_4Sn_9 \cdot 7en$ (a corrected composition), the investigation being limited by an inability to resolve the evidently disordered en molecules ($R = 0.117$ for data at $2\theta \leq 30°$). The Sn_9^{4-} anion therein exhibits some relatively large and anisotropic thermal ellipsoids of a character to suggest some disorder on one side. The largest two (≥0.7 Å rms deviations) pertain to capping atoms on what is described as a distorted tricapped trigonal prism. However, the principal distortion here is unusual in light of the previous discussion in that *two* prismatic edges (e.g., 1-3 and 6-4, Figure 3, right) are elongated (3.81, 3.71 Å) relative to a more reasonable third, 3.16 Å (δ(opposed) = 167°); that is, *away from* the C_{4v} configuration. A less extreme version of this type has been noted before as a hypothetical example.[23] But the present case likely does not represent a distortion of the free ion in that the two sodium ions which are three rather than four coordinate to nitrogen are approximately centered on the elongated edges of the prism and 3.5-3.6 Å from the four tin atoms involved. In other words the en molecules in this compound are not able to fully sequester the sodium ions from remnant interactions with tin. The advantage of crypt for this purpose is clear.

The obvious questions as to whether a dynamic interconversion exists between these two limits or some intermediate or whether materially different species along the configurational pathway might be isolated in other compounds cannot be answered at present. The relatively low solubility of the compound coupled with a low natural abundance of useful tin isotopes discourages an NMR investigation. However, some semiempirical energy calculations suggest that the barrier between the two configurational limits represented in Figure 3 is probably negligible and the stability difference, small. For comparison a hypothetical Sn_9^{4-} ion with the D_{3h} configuration was proportioned as is Bi_9^{5+}, using 3.00, 3.62, and 3.14 Å for the prism end, height, and cap distances, respectively. The computed atomization energy of Sn_9^{4-} (SCF-MO-CNDO[24]) was found to vary only from 28.0 eV for the observed C_{4v} symmetry (using distances corrected for thermal motion for independent atoms) to 27.5 eV at both the C_{2v} intermediate and the D_{3h} endpoint, a difference that is probably not meaningful. Moreover, the distances selected for the D_{3h} limit are probably an important consideration in a comparison of even relative energies, since a reduction of only 0.02 Å in the chosen distances reduces the 0.5 eV difference from C_{4v} by half. The implied nonrigidity of Sn_9^{4-} between C_{4v} and D_{3h} configurations, although not yet demonstrated kinetically or by isolation of distinct geometries, is in marked contrast to the behavior of another well known, nine skeletal atom cluster, $B_9H_9^{2-}$. Here 20 rather than 22 electrons in the cage require[20] a degenerate ground state for the capped antiprism, so that the hypothetical $B_9H_9^{4-}$ (C_{4v}) would be qualitatively more similar to Sn_9^{4-} (or Sn_9^{2-} (D_{3h}), to $B_9H_9^{2-}$).

The charge distribution calculated for the Sn_9^{4-} capped antiprism is interesting, −0.55 on each atom in the open face, −0.25 each for the capped square, and −0.75 for the apex. This and the distribution of filled orbitals are consistent with the observation[25] that Sn_9^{4-}-like species can be derived from $B_{10}H_{10}^{2-}$ (D_{4d}) by the removal of an axial BH^{2+} leaving the cage-bonding electrons behind.

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Supplementary Materials Available. Tables of crypt-Na^+ bond distances and angles, interionic distances, and structure factor amplitudes are available (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Work performed for the U.S. Energy Research and Development Administration Division of Physical Research under Contract No. W-7405-eng-82.

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

(3) E. Zintl and A. Harder, *Z. Phys. Chem., Abt. A*, **154**, 47 (1931).

(4) D. Kummer and L. Diehl, *Angew. Chem., Int. Ed. Engl.*, **9**, 895 (1970).

(5) 4,7,13,16,21,24-Hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane, N-$(C_2H_4OC_2H_4OC_2H_4)_3N$; J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975), provide extensive information.

(6) J. D. Corbett, D. G. Adolphson, D. J. Merryman, P. A. Edwards, and F. J. Armatis, *J. Am. Chem. Soc.*, **97**, 6267 (1975).

(7) D. G. Adolphson, J. D. Corbett, and D. J. Merryman, *J. Am. Chem. Soc.*, **98**, 7234 (1976).

(8) J. D. Corbett and P. A. Edwards, *J. Chem. Soc., Chem. Commun.*, 984 (1975).

(9) P. A. Edwards and J. D. Corbett, *Inorg. Chem.*, **16**, 903 (1977).

(10) A. Cisar and J. D. Corbett, *Inorg. Chem.*, **16**, 632 (1977).

(11) L. Diehl, K. Khodadedeh, D. Kummer, and J. Strähle, *Z. Naturforsch. B*, **31**, 522 (1976); *Chem. Ber.*, **109**, 3404 (1976).

(12) A. Hershaft and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).

(13) R. M. Friedman and J. D. Corbett, *Inorg. Chem.*, **12**, 1134 (1973).

(14) M. Okada, R. A. Guidotti, and J. D. Corbett, *Inorg. Chem.*, **7**, 2118 (1968).

(15) R. A. Jacobson, "An Algorithm for Automated Indexing and Bravais Lattice Selection, The Programs BLIND and ALICE", USAEC Report IS-3469, Iowa State University, 1974.

(16) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **7**, 2124 (1968).

(17) D. G. Adolphson and J. D. Corbett, *Inorg. Chem.*, **15**, 1820 (1976).

(18) D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 396 (1973).

(19) R. M. Friedman and J. D. Corbett, *Inorg. Chim. Acta*, **7**, 525 (1973).

(20) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

(21) J. D. Corbett, *Inorg. Chem.*, **7**, 198 (1968).

(22) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 161 (1967).

(23) L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 7221 (1976).

(24) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **11**, 220, 239 (1968).

(25) W. J. Evans, private communication.