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Heteroatomic Polyanions of the Post Transition Metals. The Synthesis and Structure of a Compound Containing Thallium Nonastannide(3–) (TlSn$_9$$^{3-}$) and Thallium Octastannide(3–) (TlSn$_8$$^{3-}$) with a Novel Structural Disorder

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Abstract: The deep red-brown (2,2,2-crypt-K$^+$)$_3$(TlSn$_9$$^{3-}$TlSn$_8$$^{3-}$)$_{1/2}$·en is obtained from the reaction of the alloy compositions with KTlSn with 2,2,2-crypt in ethylenediamine (en) at room temperature. The composition and structure of the material were established by a single-crystal X-ray diffraction study employing 7433 observed reflections ($I > 3\sigma(I)$) collected on an automated diffractometer at room temperature with monochromatized Mo Kα radiation. The compound is triclinic, space group $P\bar{1}$, with a = 15.141 (4) Å, b = 22.195 (5) Å, c = 14.113 (3) Å, α = 98.72 (2)°, β = 101.04 (2)°, γ = 89.44 (2)°, V = 4600 (2) Å^3, and Z = 2. Direct methods and Fourier syntheses led to final residuals of R = 0.082 and R_w = 0.100 when positional and thermal parameters of the 97 nonhydrogen atoms were refined by full-matrix least squares. An inferior result (R = 0.106) is obtained when a single anion species is refined with variable thallium occupancy. The two anions TlSn$_9$$^{3-}$ and TlSn$_8$$^{3-}$ exhibit an unusual 50:50 occupational disorder in a single anionic site, with seven atoms coincident in both species. The assigned charges are the only plausible possibilities considering the electron counts and anion configurations. The TlSn$_9$$^{3-}$ anion has a bicapped square-antiprismatic geometry, while TlSn$_8$$^{3-}$ has a tricapped trigonal-prismatic configuration, with thallium in a capping position in each case. Bond distances, interbond angles, and particularly dihedral angles which are relevant to both structures and to their distortions are discussed. The thallium substitution position is unusual in view of both the charge distributions predicted by SCF-MO-CNDO calculations for the homostannide analogues and the empiricisms developed for heteroatom placement in boranes. A minimum of about 2.2 and a maximum of 3 p electrons per atom are observed to be required for *skeletal* bonding in all homo- and heteropolyatomic clusters of the main-group elements, irrespective of geometry, size, or charge of the species. Any additional valence electrons generate the lone pairs which have a profound effect on the geometry.

About 50 years ago, Zintl and co-workers reported on electrochemical studies on ammonia solutions of sodium alloys of many post-transition elements in conjunction with the results of exhaustive alloy extractions. Numerous homopolyatomic anions such as Sn$_9$$^{4-}$, Pb$_9$$^{4-}$, Sb$_7$$^{3-}$, Bi$_5$$^{3-}$, and Te$_4$$^{2-}$ were so identified.[2-4] However, evaporation of solvent from these solutions generally resulted only in amorphous products or known phases in the binary alloy systems because of the greater stability of the latter through electron delocalization in the solid state.

Recently, the use of 2,2,2-crypt (or related ligands) to complex the alkali-metal counterion and prevent electron transfer back onto the cation has provided a general route to the stabilization and crystallographic characterization of many of these anions, for example, Sn$_9$$^{4-}$,[5] Ge$_9$$^{4-}$ and Ge$_9$$^{2-}$,[6] Pb$_5$$^{2-}$, and Sn$_5$$^{2-}$,[7] and Sb$_7$$^{3-}$[8] from ethylenediamine (en) solutions. More recent use of mixed-metal systems in which an electron-poorer element is combined with an electron-richer one has also allowed more diverse structures with a greater variety of elements to be synthesized, such as Tl$_2$Te$_2$$^{2-}$[9] and HgTe$_2$$^{2-}$.[10] In this paper we report the results of our investigations into the Tl–Sn anion system.

Homo- and heteropolyatomic anions such as Sn$_9$$^{4-}$, Pb$_9$$^{4-}$, Sn$_{9-x}Pb_x$$^{4-}$, and SnTe$_4$$^{4-}$ have also been identified in solution in ethylenediamine and liquid ammonia by Rudolph and co-workers using ^{119}Sn, ^{207}Pb, and ^{125}Te NMR.[11,12] Interestingly, their studies of the Tl–Sn anion system led to the formulation of one species as TlSn$_8$$^{5-}$, in contrast with the TlSn$_8$$^{3-}$ deduced in the present investigation.

Experimental Section

Materials and Synthesis. Thallium (99.999%, American Smelting and Refining Co.), tin (Baker Analyzed), and potassium (J. T. Baker Chemical Co., Purified) were used directly as obtained. Freshly cut sections of thallium and potassium were prepared and handled only in a drybox. The ternary alloy composition KTlSn was prepared by allowing stoichiometric quantities of the elements to react at 950 °C in a sealed tantalum tube for 12 h. The 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Merck) was also used as received and handled only in the drybox. Ethylenediamine (en, Fisher Scientific Co.) was dried over molecular sieves (Davison, 4A) and CaH$_2$ and then vacuum distilled onto and stored over CaH$_2$, from which it was distilled immediately prior to use. Typical reaction vessels have been described previously.[8]

The alloy KTlSn reacts fairly quickly with en containing a stoichiometric quantity of crypt to give a dark red solution which on standing for ca. 1 week changes to a red-brown color. Decantation of the solution from the insoluble material followed by slow removal of the solvent over a period of 1–2 weeks produces dark red-brown crystals. These were washed with dry ethylamine to remove any unreacted crypt, and the final traces of volatiles were removed under vacuum.

An analysis of a bulk sample of the crystals by atomic absorption gave Sn/Tl (atomic) = 8.4 (ca. 4% max error), while analysis of individual crystals by electron microprobe gave Sn/Tl ≈ 6.5 and K/Tl ≈ 2.7 using KBr and the metals as standards. A known interference between tin and potassium together with probable matrix effects presumably led to the low Sn/Tl and K/Tl ratios from the latter method.

After transfer of the product to a drybox, crystals were mounted in 0.3- or 0.5-mm capillaries. Preliminary oscillation and Weissenberg

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(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Material Sciences Division.

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

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

(4) Zintl, E.; Dullenkopf, W. *Z. Phys. Chem., Abt. B* **1932**, *16*, 183.

(5) Corbett, J. D.; Edwards, P. *J. Am. Chem. Soc.* **1977**, *99*, 3313.

(6) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163.

(7) Edwards, P.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903.

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

(9) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627.

(10) Burns, R. C.; Corbett, J. D. *Inorg. Chem.* **1981**, *20*, 4433.

(11) Rudolph, R.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4269.

(12) Rudolph, R. W.; Wilson, W. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 2480.

0002-7863/82/1504-2804$01.25/0

photographs indicated a rather large cell with triclinic symmetry, and this was verified by investigation on an automated diffractometer.

Data Collection. Diffraction data were collected from a block-shaped crystal of dimensions 0.40 × 0.28 × 0.18 mm. The initial orientation procedure gave a triclinic cell with cell dimensions consistent with those from the photographic examination. Data were collected on this cell on a four-circle automated diffractometer using Mo Kα radiation monochromatized with graphite ($\lambda = 0.71034$ Å) at a takeoff angle of 4.5° over the four octants HKL, $\bar{H}K\bar{L}$, $\bar{H}\bar{K}L$, and $H\bar{K}\bar{L}$ at ambient temperature (ca. 23 °C). As is frequently observed with such crypt compounds, the integrated intensities of the three standard reflections ($29.0° < 2\theta < 30.6°$) which lay approximately along each of the three reciprocal axes were observed to decay over the data collection period, decreasing ca. 38% for the standard out a^*, 48% in b^*, and 45% along c^*. Data were collected in two shells; first, for 9874 reflections with $2\theta \leq 40°$ and, second, for 2157 reflections with $40° < 2\theta \leq 43°$. These were corrected for decay according to the sum of the integrated intensities of the three standards by a third-order polynomial in reflection number and for Lorentz and polarization effects. After the composition of the crystal had been established, the raw data were corrected for absorption ($\mu = 42.19$ cm^{-1}) by using data from a ϕ scan ($\phi = 0 \rightarrow 350°$, $\Delta\phi = 10°$) at $\theta = 5.36°$ together with a program written by Karcher and Jacobson.[13] The transmission coefficients ranged from 0.73 to 0.99. The final data set consisted of 7433 reflections with $I > 3\sigma(I)$ and $F > 3\sigma(F)$ after averaging in $P\bar{1}$. (A value of $R(I) = 0.040$ for averaging 1037 duplicate reflections, with only 14 reflections eliminated by $|F_o - F_i| > 6\sigma(F)$, supported the validity of the decay correction.)

Precise unit-cell dimensions were obtained from the same crystal by a least-squares fit to the average 2θ values of 18 reflections in the range $25° < 2\theta < 32°$ which had been tuned on both Friedel-related peaks to avoid instrument and centering errors. The final unit-cell data are a = 15.141 (4) Å, b = 22.195 (5) Å, c = 14.113 (3) Å, α = 98.72 (2)°, β = 101.04 (2)°, γ = 89.44 (2)°, V = 4600 (2) Å^3 for Z = 2, d_x = 1.82 g/cm^3, and fw = 2520.1. A Howells–Phillips–Rogers test of the intensity distribution of all of the data was strongly indicative of centricity. As described before,[9] the volume of the unit cell together with an empirical volume of ca. 660 Å^3 for a 2,2,2-crypt-K$^+$ cation provide a good idea of the number of cations present and hence the charge on the anion(s). Although seven cations give better agreement in the present case, this would require the space group to be $P1$. Of course, this calculation assumes that the volume occupied by the anions is negligible relative to that of the cations, as usually appears to be the case, and that solvent molecules are not included in the lattice. In hindsight, the volume of these particular $TlSn_x^{3-}$ anions appear to be significant compared with that of the cations, and two molecules of solvent must also be taken into account.

Structure Solution. Solution of the structure was achieved by direct methods using "MULTAN 80"[14] and diffraction data out to $2\theta = 40°$. The solution with the second highest figure of merit from the Fourier step of "MULTAN 80" gave a plausible geometry, nine large peaks in the shape of a capped square-antiprism and a tenth peak of lower intensity corresponding to a cap for the open square face. The distances in the nine-atom cluster were all about 3.0 Å while those to the latter atom were 3.1–3.2 Å. Three more atoms of lower atomic number which were well separated from the other atoms and from each other were taken to be potassium. All ten atoms in the anion were initially assumed to be tin (since the analytical results indicated only ca. 12% Tl was present). A few cycles of block-diagonal refinement of positional parameters of all thirteen atoms (with $B = 7.7$ Å^2 according to a Wilson plot) gave a reliability index R ($=\sum||F_o| - |F_o||/|F_o|$) of 0.43. A subsequent Fourier map revealed many peaks attributable to the light atoms in the cations. Several successive refinements of these positions and isotropic temperature factors alternating with Fourier syntheses revealed all of the atoms in the cations and gave $R = 0.179$. Introduction of anisotropic temperature factors (of the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$) for the 13 heavy atoms dropped R to 0.116 after several cycles of refinement.

Models. The result just cited for Sn_{10} as a beginning model was clearly unsatisfactory because of very disparate thermal ellipsoids, the reasons for which will be apparent shortly. Therefore the anion was assumed to be $TlSn_9^{3-}$, in better agreement with analyses, with approximate C_{4v} symmetry. Estimation of the approximate integrated electron density at each atom site in the cluster by summing the peak heights in the three planes defining each thermal ellipsoid in a properly scaled map suggested that the thallium atom was not localized in any one site. Assuming that the smallest result was that of a tin atom and normalizing the sum to the electron density for $TlSn_9^{3-}$ gave about 85% Sn in one cap (the remainder Tl), 88% Sn (12% Tl) for four atoms in the adjacent plane and two opposed atoms in the other plane, 94% Sn (6% Tl) for the remaining two opposed atoms in this other plane, and the presumed 100% Sn in the remaining cap. Continuation of the refinement using this atom distribution and anisotropic temperature factors for the heavy atoms led to $R = 0.109$. An en molecule was also located from a subsequent Fourier map. Further refinement by full-matrix least squares, after introduction of anisotropic temperature factors for nitrogen and oxygen and a recalculation of the distribution of the tin and thallium atoms when close to convergence (with essentially no change in the occupancies), yielded $R = 0.106$ and R_w ($=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) = 0.143 where $w = \sigma(F)^{-2}$.

Although the residuals in this model were not at all unreasonable when compared with those achieved with other structures containing homo- or heteropolyatomic anions and 2,2,2-crypt-K$^+$ (or Na$^+$) cations, the results had a number of unsatisfactory features, as will be discussed later.

A second model was suggested by a separate, full-matrix refinement with only tin atoms in the cluster which converged to $R = 0.169$ when the positional parameters, isotropic temperature factors, and occupancies of the cluster atoms were allowed to vary. This refinement gave 1.20 Sn for the first cap, 1.00 ± 0.06 Sn for the eight atoms in the square antiprism, and 0.84 Sn for the second cap, which in total suggested that the composition of the anion was close to $TlSn_{8.5}^{3-}$ (as analyzed) rather than to $TlSn_9^{3-}$. Reflection on this distribution led to a hypothesis that the anionic site was instead occupied by about equal proportions of $TlSn_9^{x-}$ and $TlSn_8^{x-6}$ with the thallium atoms localized in the two capping positions on the pseudo fourfold axis, one overlapping with a tin atom in the other cluster ($\simeq$1.31 Sn) and the other not and at 50% occupancy ($\simeq$0.81 Sn). This model assumes very good overlap for six of the eight tin atoms in the pseudo square antiprism in each of the clusters, while the two remaining atoms which exhibited elongated thermal ellipsoids in the first model (see below) resolve into two pairs, each with 50% occupancy. Refinement with anisotropic temperature factors for all but the carbon atoms eventually converged to $R = 0.082$ and $R_w = 0.100$ after a reweight of the diffraction data sorted by F_o into 50 groups to allow for a slight dependence of $\sum w(|F_o| - |F_c|)^2$ on F_o. The result is statistically better than the $TlSn_9^{3-}$ model with disordered Tl described above at well above the 99.5% significance level. In the final cycle of refinement the largest shift was 0.01σ for the heavy atoms, 0.08σ in the crypt atoms, and 0.01σ in the en atoms. A difference Fourier map was flat to ±0.6 e Å^{-3} except for four peaks and troughs associated with the anions, the largest of each being 1.5 e Å^{-3} at (0.156, 0.188, 0.656) and −0.9 e Å^{-3} at (0.375, 0.359, 0.813). All of these occur around the periphery of the cluster between atom sites.

In order to estimate the occupancies of the two anionic clusters, positional parameters, anisotropic temperature factors, and occupancies of the two capping atoms (one 50% Sn and 50% Tl, the other 100% Tl but with 50% occupancy) were allowed to vary independently for two additional cycles. This produced no significant change in the observed occupancy (θ) ratio for these sites, the resulting value of 2.007 (17) for $(\phi_{Sn} + \phi_{Tl})/\phi_{Tl2}$ being indistinguishable from the expected value of 2.000.

Finally, an attempt was made to refine the structure in the acentric space group $P1$ starting with the two separate and slightly displaced $TlSn_8$ and $TlSn_9$ units. The refinement (in separate blocks to minimize coupling effects) was unsatisfactory as R did not drop below 0.123 and pairs of previously resolved tin atoms tended to move to the intermediate positions that they had occupied in the first model. The tenth atom also appeared in the nine-atom cluster in a Fourier synthesis, also supporting the presence of centricity.

The final residuals for this structure are generally better than those achieved with other structures of this type, as are the standard deviations in the fractional coordinates, bond distances, and interbond angles.[5-10,15,16] Those parameters involving the atoms with only partial occupancy are, as expected, somewhat greater but are in themselves quite satisfactory. This also attests to the correctness of the final model. It should be noted that the hydrogen atom positions have not been determined, leaving 9.5% of the total electron density unassigned. Also, no attempt was made to correct for the observed anisotropic decay in the intensities of the reflections. Although a better solution might be expected from data obtained at low temperatures, this was not judged worthwhile in view of the actual result and size of that task.

Sources of all programs and procedures were as previously referenced,[8,9] as were the atomic scattering data for the neutral atoms, which included corrections for the real and imaginary parts of anomalous dispersion.

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(13) Karcher, B. A.; Jacobson, R. A., personal communication, 1980.

(14) Main, P. "MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures for X-Ray Diffraction Data", University of York Printing Unit, York, United Kingdom, 1980.

(15) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 632.

(16) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2482.

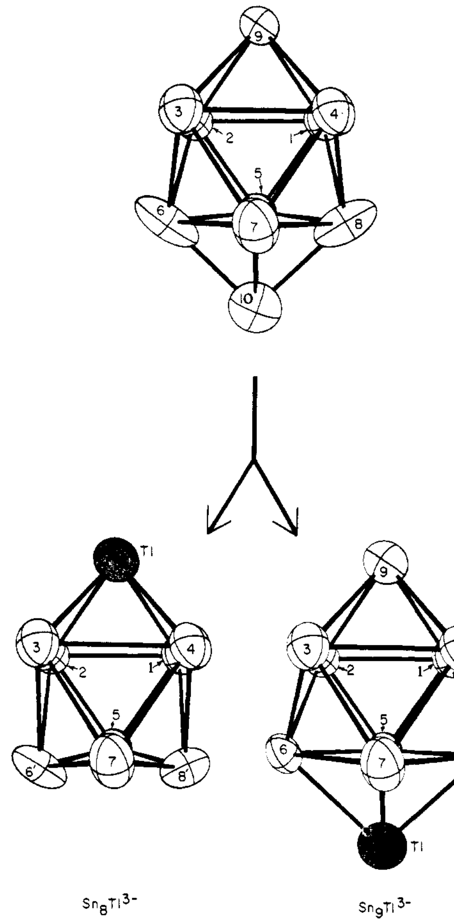

Figure 1. The refinement result for $\mathrm{TlSn_9}^{3-}$, model one, with a disordered thallium atom (R = 0.106) (top) and the $\mathrm{TlSn_8}^{3-}$ and $\mathrm{TlSn_9}^{3-}$ polyhedra resolved therefrom (bottom). Atoms 1–5, 7, and 9 have identical coordinates in both polyhedra. (Projections made with same scale, viewing distance and 50% probability thermal ellipsoids.)

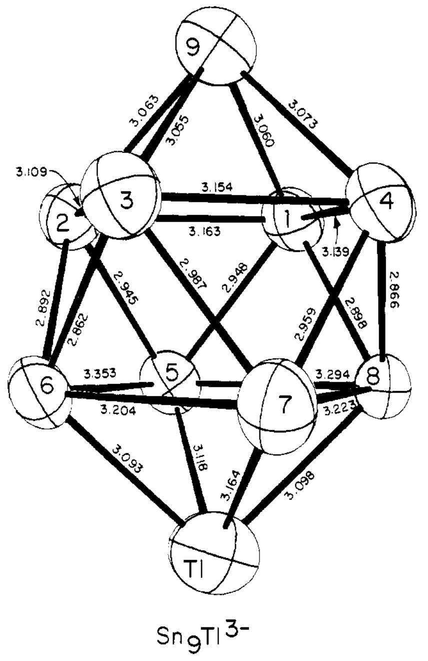

Figure 2. The $\mathrm{TlSn_9}^{3-}$ anion in (2,2,2-crypt-K$^+$)$_3$($\mathrm{TlSn_9}^{3-}$-$\mathrm{TlSn_8}^{3-}$)$_{1/2}$·en, with distances in Å.

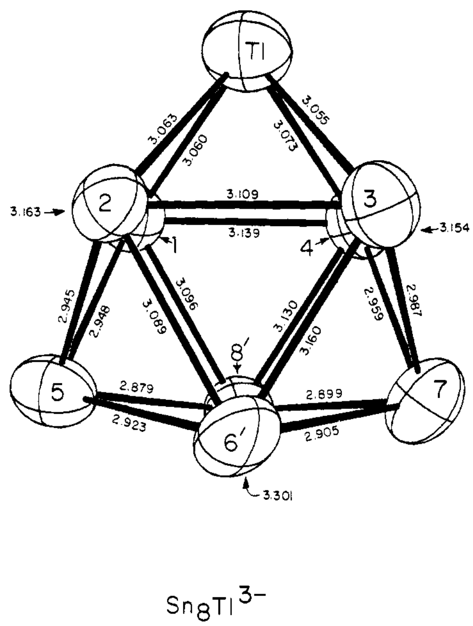

Figure 3. The $\mathrm{TlSn_8}^{3-}$ anion in (2,2,2-crypt-K$^+$)$_3$($\mathrm{TlSn_9}^{3-}$-$\mathrm{TlSn_8}^{3-}$)$_{1/2}$·en viewed along the best pseudo three-fold axis of the trigonal prism (distances in Å).

Results and Discussion

Refinement of the structure according to a model with nine tin atoms and one disordered thallium atom in a single polyhedron gave the result pictured at the top of Figure 1. The solution appeared generally satisfactory in terms of the residuals (R = 0.106), bond lengths, and interbond angles and their errors, especially when compared with results for related structures. Nonetheless, the solution is wrong. A number of relatively small features collectively caused questions to be raised about the model: (a) a relatively poor agreement with the bulk analysis for the anion ($\mathrm{TlSn_{8.4}}^{3-}$), (b) lack of a reasonable mechanism whereby 6–15% thallium would be distributed over nine of ten positions rather than localized at just one site, (c) the presence of a residual electron density (ca. 3.0 e Å^{-3}) at the top capping atom (85% Sn, 15% Tl), and a "hole" (ca. −2.5 e Å^{-3}) at the other (100% Sn) in a final difference map, (d) the extreme (1.9:1.0 root mean square) thermal ellipsoids for opposed atoms 6 and 8 in one face of the square-antiprism (see Figure 1, top), and (e) troughs (ca. −1.0 e Å^{-3}) at the refined positions of these two atoms in the difference map with slight peaks (ca. 2.0 and 1.5 e Å^{-3}) diametrically opposed around the sites, suggestive of positional disorder.

The structure was subsequently successfully (and correctly) refined with not one but two different anions, $\mathrm{TlSn_9}^{3-}$ and $\mathrm{TlSn_8}^{3-}$, well superimposed at the anionic site, each with 50% occupancy and with the thallium atoms opposed in direction. The bottom of Figure 1 shows the two deconvoluted anions and depicts their relationship to the refined result of the first model with fixed viewing direction, perspective, and scale. This second model accurately accounts for the observed electron distribution at the anionic site and is much more realistic and chemically sensible than the thallium distribution artificially imposed in the first model. Seven of the atoms (1–5, 7, and 9) from the two clusters overlap so well that they can not be distinguished from single atoms and are therefore represented with single positional coordinates in both clusters. That the cavity defined by 2,2,2-crypt-K$^+$ cations can be so specific in maintaining this relationship is very remarkable. On the other hand, the fact that the two anions did exhibit some distinct geometric differences between the capping atoms in each (see below) led to the exclusion of the $\mathrm{Sn_9}^{2-}$ and $\mathrm{TlSn_8}^{4-}$ pair from consideration as these should be more symmetric than observed.

The final positional and thermal parameters for the 97 nonhydrogen atoms in the compound (2,2,2-crypt-K$^+$)$_3$($\mathrm{TlSn_9}^{3-}$-$\mathrm{TlSn_8}^{3-}$)$_{1/2}$·en are listed in Table I. Important bond distances and dihedral angles in the ten- and nine-atom clusters are given in Tables II and III, respectively. Views of $\mathrm{TlSn_9}^{3-}$ and $\mathrm{TlSn_8}^{3-}$ which are more appropriate for geometric analysis are shown in

Table I. Positional and Thermal Parameters for $(2,2,2\text{-crypt-K}^+)_3(\text{TlSn}_9{}^{3-}\ \text{TlSn}_8{}^{3-})_{1/2}\cdot\text{en}$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tl–Sn[a]	0.3447 (1)	0.37676 (6)	0.8647 (1)	7.96 (7)	9.05 (8)	10.14 (9)	−0.37 (6)	0.79 (6)	1.13 (7)
Tl[b]	0.0975 (2)	0.13000 (13)	0.6902 (2)	9.70 (15)	10.23 (16)	16.39 (23)	−0.61 (13)	1.47 (15)	0.68 (15)
Sn1	0.3605 (1)	0.26560 (7)	0.7120 (1)	5.31 (7)	7.66 (9)	6.95 (8)	−0.12 (6)	1.49 (6)	1.71 (7)
Sn2	0.1838 (1)	0.34354 (7)	0.6970 (1)	6.54 (8)	6.38 (8)	6.87 (8)	0.26 (6)	0.75 (6)	2.44 (6)
Sn3	0.1710 (1)	0.32935 (7)	0.9098 (1)	7.10 (8)	8.26 (9)	6.70 (8)	1.03 (7)	1.89 (7)	0.63 (7)
Sn4	0.3452 (1)	0.24955 (7)	0.9255 (1)	5.97 (7)	8.55 (9)	5.72 (7)	0.74 (7)	−0.12 (6)	1.00 (6)
Sn5	0.1883 (1)	0.22008 (8)	0.5869 (1)	6.51 (8)	7.68 (9)	9.25 (10)	0.26 (7)	−0.41 (7)	0.94 (8)
Sn6[c]	0.0516 (2)	0.26548 (14)	0.7438 (2)	4.51 (13)	7.54 (17)	6.96 (16)	0.33 (12)	0.14 (11)	2.02 (13)
Sn6′[c]	0.0707 (2)	0.23632 (20)	0.7304 (3)	6.41 (17)	13.23 (28)	9.10 (21)	−3.61 (18)	−0.49 (15)	4.52 (20)
Sn7	0.1643 (1)	0.19471 (8)	0.9077 (1)	6.67 (8)	9.26 (10)	9.93 (11)	1.21 (8)	2.66 (8)	4.06 (9)
Sn8[c]	0.3024 (2)	0.15293 (13)	0.7636 (2)	5.40 (4)	5.55 (14)	7.70 (16)	0.98 (11)	0.29 (12)	1.09 (12)
Sn8′[c]	0.2550 (3)	0.15473 (15)	0.7465 (2)	11.30 (24)	6.28 (17)	7.69 (18)	−0.59 (16)	1.56 (17)	1.04 (4)
K1	0.6835 (3)	0.0175 (2)	0.7335 (4)	7.5 (3)	6.0 (2)	8.6 (3)	−0.3 (2)	1.7 (2)	1.4 (2)
K2	0.2946 (3)	0.4867 (2)	0.3367 (3)	6.5 (2)	6.0 (2)	5.3 (2)	−0.5 (2)	0.8 (2)	0.9 (2)
K3	0.8287 (3)	0.3063 (2)	0.2106 (2)	4.9 (2)	6.5 (2)	5.7 (2)	0.4 (2)	0.5 (2)	0.5 (2)
N11[d]	0.650 (1)	−0.1089 (8)	0.777 (2)	10 (1)	7 (1)	11 (1)	0.3 (9)	−0.7 (10)	−0.2 (9)
N12	0.706 (2)	0.1476 (12)	0.697 (2)	16 (2)	13 (2)	16 (2)	−5.7 (15)	5.1 (16)	3.6 (15)
N21	0.260 (1)	0.3507 (9)	0.286 (1)	12 (1)	9 (1)	8 (1)	0.9 (11)	2.5 (10)	1.7 (10)
N22	0.329 (1)	0.6228 (7)	0.392 (1)	10 (1)	6 (1)	8 (1)	0.1 (8)	1.4 (8)	1.6 (8)
N31	0.907 (1)	0.2274 (8)	0.357 (1)	6 (1)	9 (1)	8 (1)	0.8 (8)	0.9 (7)	2.5 (8)
N32	0.748 (1)	0.3869 (8)	0.062 (1)	6 (1)	9 (1)	8 (1)	0.2 (8)	−0.7 (8)	3.3 (9)
O11	0.560 (1)	−0.0044 (8)	0.858 (1)	9.2 (10)	10.0 (11)	14.4 (14)	−0.1 (8)	3.7 (9)	1.7 (10)
O12	0.575 (1)	0.1117 (7)	0.808 (2)	14.9 (15)	6.7 (9)	16.5 (16)	1.5 (9)	4.1 (12)	2.2 (9)
O13	0.830 (1)	−0.0475 (9)	0.822 (2)	9.0 (10)	11.6 (12)	16.6 (16)	−1.0 (9)	−0.2 (10)	4.5 (11)
O14	0.850 (1)	0.0777 (9)	0.813 (2)	9.7 (11)	11.3 (12)	20.2 (19)	−1.3 (9)	3.0 (12)	4.9 (12)
O15	0.623 (1)	−0.0765 (9)	0.577 (1)	17.6 (17)	13.3 (14)	8.7 (10)	−2.3 (12)	5.1 (11)	1.2 (9)
O16	0.672 (2)	0.0388 (11)	0.539 (2)	22.7 (23)	15.6 (18)	13.4 (16)	−4.3 (16)	5.3 (16)	3.7 (13)
O21	0.117 (1)	0.4425 (8)	0.254 (1)	8.1 (10)	10.8 (11)	13.9 (13)	−3.1 (8)	1.6 (9)	1.1 (10)
O22	0.159 (1)	0.5707 (8)	0.276 (1)	5.8 (7)	14.2 (13)	10.1 (10)	−0.2 (8)	0.1 (7)	2.9 (9)
O23	0.359 (1)	0.4117 (6)	0.482 (1)	13.9 (12)	6.5 (7)	6.3 (7)	0.5 (7)	2.0 (7)	1.9 (6)
O24	0.348 (1)	0.5381 (6)	0.532 (1)	8.9 (8)	6.7 (7)	6.7 (7)	0.3 (6)	0.6 (6)	0.5 (6)
O25	0.376 (1)	0.4204 (7)	0.195 (1)	11.6 (11)	8.9 (9)	7.8 (8)	−1.2 (8)	4.0 (8)	−0.3 (7)
O26	0.421 (1)	0.5434 (6)	0.257 (1)	6.9 (7)	8.7 (9)	8.3 (8)	−0.3 (6)	1.8 (6)	1.7 (7)
O31	0.720 (1)	0.2188 (7)	0.261 (1)	7.4 (8)	9.9 (10)	9.8 (10)	−1.0 (7)	0.3 (7)	3.2 (8)
O32	0.638 (1)	0.3018 (7)	0.138 (1)	7.2 (8)	9.5 (9)	8.0 (8)	−1.1 (7)	−0.3 (6)	2.1 (7)
O33	0.906 (1)	0.3608 (6)	0.404 (1)	8.6 (8)	7.5 (8)	7.2 (8)	−0.6 (7)	−0.5 (6)	0.8 (6)
O34	0.854 (1)	0.4337 (6)	0.256 (1)	9.5 (9)	6.6 (8)	8.6 (9)	0.5 (7)	0.3 (7)	1.7 (6)
O35	0.964 (1)	0.2243 (7)	0.172 (1)	9.7 (9)	9.5 (9)	7.4 (8)	2.5 (8)	2.9 (7)	2.0 (7)
O36	0.871 (1)	0.2857 (7)	0.020 (1)	8.1 (8)	9.6 (9)	8.4 (8)	1.8 (7)	2.8 (7)	2.5 (7)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C11	0.597 (2)	−0.104 (1)	0.857 (2)	11.2 (7)	C212	0.333 (2)	0.640 (1)	0.497 (2)	8.9 (6)
C12	0.524 (2)	−0.065 (1)	0.837 (2)	12.2 (8)	C213	0.293 (2)	0.329 (1)	0.195 (2)	10.1 (7)
C13	0.491 (2)	0.039 (1)	0.857 (2)	11.4 (8)	C214	0.386 (2)	0.355 (1)	0.189 (2)	10.8 (7)
C14	0.534 (2)	0.098 (1)	0.888 (2)	13.3 (9)	C215	0.441 (2)	0.447 (1)	0.161 (2)	9.3 (6)
C15	0.601 (2)	0.174 (2)	0.812 (3)	15.1 (11)	C216	0.423 (1)	0.511 (1)	0.159 (2)	8.3 (5)
C16	0.626 (2)	0.183 (2)	0.724 (3)	14.2 (10)	C217	0.421 (1)	0.610 (1)	0.264 (2)	8.2 (5)
C17	0.740 (2)	−0.134 (2)	0.798 (2)	14.2 (10)	C218	0.412 (2)	0.638 (1)	0.365 (2)	8.5 (5)
C18	0.802 (2)	−0.091 (1)	0.876 (2)	11.5 (8)	C31	0.842 (2)	0.176 (1)	0.357 (2)	9.1 (6)
C19	0.902 (2)	−0.008 (1)	0.879 (2)	12.3 (8)	C32	0.745 (2)	0.198 (1)	0.352 (2)	8.9 (6)
C110	0.927 (2)	0.040 (2)	0.827 (3)	14.7 (10)	C33	0.623 (2)	0.226 (1)	0.233 (2)	10.1 (7)
C111	0.873 (2)	0.127 (2)	0.771 (2)	13.9 (10)	C34	0.602 (2)	0.243 (1)	0.138 (2)	10.0 (7)
C112	0.797 (2)	0.170 (2)	0.767 (3)	14.7 (10)	C35	0.613 (2)	0.324 (1)	0.045 (2)	9.9 (6)
C113	0.606 (2)	−0.144 (1)	0.688 (2)	12.0 (8)	C36	0.649 (1)	0.385 (1)	0.051 (2)	8.2 (5)
C114	0.634 (2)	−0.135 (1)	0.598 (2)	12.9 (9)	C37	0.925 (2)	0.264 (1)	0.456 (2)	8.6 (6)
C115	0.651 (2)	−0.066 (2)	0.494 (3)	15.1 (11)	C38	0.971 (2)	0.325 (1)	0.457 (2)	8.5 (6)
C116	0.623 (2)	−0.007 (2)	0.463 (3)	15.5 (11)	C39	0.939 (2)	0.421 (1)	0.414 (2)	9.1 (6)
C117	0.644 (3)	0.105 (2)	0.529 (3)	17.9 (13)	C310	0.870 (2)	0.457 (1)	0.360 (2)	9.0 (6)
C118	0.730 (3)	0.145 (2)	0.602 (3)	16.2 (12)	C311	0.788 (2)	0.468 (1)	0.194 (2)	11.3 (8)
C21	0.157 (2)	0.342 (1)	0.266 (2)	11.8 (8)	C312	0.788 (2)	0.449 (1)	0.090 (2)	9.3 (6)
C22	0.106 (2)	0.381 (1)	0.207 (2)	12.0 (8)	C313	0.990 (2)	0.201 (1)	0.332 (2)	9.0 (6)
C23	0.068 (2)	0.483 (1)	0.192 (2)	12.3 (8)	C314	0.981 (2)	0.175 (1)	0.224 (2)	9.1 (6)
C24	0.068 (2)	0.543 (1)	0.257 (2)	12.5 (8)	C315	0.955 (2)	0.202 (1)	0.070 (2)	8.8 (6)
C25	0.164 (2)	0.629 (1)	0.344 (2)	9.5 (6)	C316	0.955 (2)	0.255 (1)	0.018 (2)	8.9 (6)
C26	0.254 (2)	0.656 (1)	0.339 (2)	8.8 (6)	C317	0.869 (2)	0.339 (1)	0.975 (2)	9.0 (6)
C27	0.311 (2)	0.322 (1)	0.368 (2)	11.1 (7)	C318	0.772 (2)	0.366 (1)	0.964 (2)	10.0 (7)
C28	0.302 (2)	0.354 (1)	0.469 (2)	13.6 (9)	N(en)1	0.739 (4)	0.075 (3)	0.096 (5)	37 (3)
C29	0.346 (2)	0.440 (1)	0.574 (2)	8.7 (6)	N(en)2	0.757 (3)	0.030 (2)	0.250 (3)	25 (2)
C210	0.399 (2)	0.498 (1)	0.598 (2)	8.6 (6)	C(en)1	0.746 (5)	0.035 (3)	0.129 (5)	31 (3)
C211	0.389 (2)	0.598 (1)	0.558 (2)	9.7 (6)	C(en)2	0.834 (3)	0.006 (2)	0.146 (4)	22 (2)

[a] Occupancy is 0.50 Tl($\text{TlSn}_8{}^{3-}$) and 0.50 Sn($\text{TlSn}_9{}^{3-}$). [b] 0.50 Tl. [c] 0.50 Sn. [d] The first digit refers to the cation.

Figures 2 and 3, respectively. The supplementary material contains the interbond angles in the two clusters, bond distances and angles for the 2,2,2-crypt-K$^+$ cations and ethylenediamine, and the observed and calculated structure factor amplitudes.

The conformation of the 2,2,2-crypt-K$^+$ cations found in this study are similar to those in other symmetry-unconstrained cations found in the 2,2,2-crypt-K$^+$ salts of $\text{Tl}_2\text{Te}_2{}^{2-}$,[9] $\text{HgTe}_2{}^{2-}$,[10] and $\text{Te}_3{}^{2-}$[15] and as such are quite unremarkable. There is no significant

Table II. Bond Distances (Å) and Dihedral Angles (Deg) in $TlSn_9^{3-}$

atom 1	atom 2	dist	atom 1	atom 2	dist
Tl	5	3.118 (3)	3	7	2.987 (3)
Tl	6	3.093 (4)	4	7	2.959 (2)
Tl	7	3.164 (4)	4	8	2.866 (3)
Tl	8	3.098 (4)	1	8	2.898 (3)
9	1	3.060 (2)	1	2	3.163 (2)
9	2	3.063 (2)	2	3	3.109 (2)
9	3	3.055 (2)	3	4	3.154 (2)
9	4	3.073 (2)	1	4	3.139 (2)
1	5	2.948 (2)	5	6	3.353 (3)
2	5	2.945 (2)	6	7	3.204 (3)
2	6	2.892 (3)	7	8	3.223 (3)
3	6	2.862 (3)	5	8	3.294 (3)
plane 1	plane 2	angle	plane 1	plane 2	angle
(5-6-Tl)	(7-6-Tl)	65.5	(1-2-5)	(2-5-6)	57.2
(6-7-Tl)	(7-8-Tl)	68.4	(2-5-6)	(3-2-6)	52.0
(7-8-Tl)	(8-5-Tl)	64.7	(2-3-6)	(3-6-7)	53.6
(5-8-Tl)	(5-6-Tl)	72.5	(3-6-7)	(3-4-7)	54.6
(5-6-Tl)	(2-5-6)	22.1	(3-4-7)	(4-7-8)	55.5
(6-7-Tl)	(3-6-7)	25.6	(4-7-8)	(1-4-8)	52.7
(7-8-Tl)	(4-7-8)	24.9	(1-4-8)	(5-1-8)	52.1
(5-8-Tl)	(1-5-8)	22.9	(1-5-8)	(1-2-5)	58.1
(1-2-9)	(3-2-9)	68.3	(1-2-5)	(3-4-7)	37.4
(2-3-9)	(3-4-9)	69.5	(2-3-6)	(4-1-8)	32.5
(3-4-9)	(1-4-9)	68.5	(2-5-6)	(4-7-8)	28.6
(1-4-9)	(2-1-9)	70.0	(3-6-7)	(1-5-8)	27.9
(1-2-9)	(1-2-5)	16.5	(1-2-3)	(1-4-3)	1.3
(2-3-9)	(2-3-6)	20.4	(5-6-7)	(5-8-7)	2.5
(3-4-9)	(3-4-7)	19.2	(1-2-3-4)	(5-6-7-8)	0.8[a]
(1-4-9)	(1-4-8)	20.7			

[a] For (1-2-3-4) and (5-6-7-8) all atoms are within 0.013 and 0.025 Å of their respective, best least-squares planes.

Table III. Bond Distances (Å) and Dihedral Angles (Deg) in $TlSn_8^{3-}$ [a]

atom 1	atom 2	dist	atom 1	atom 2	dist
Tl	1	3.060 (2)	1	2	3.163 (2)
Tl	2	3.063 (2)	3	4	3.154 (2)
Tl	3	3.055 (2)	6′	8′	3.301 (5)
Tl	4	3.073 (2)	2	3	3.109 (2)
5	1	2.948 (2)	3	6′	3.160 (4)
5	2	2.945 (2)	2	6′	3.089 (4)
5	6′	2.923 (4)	1	4	3.139 (2)
5	8′	2.879 (4)	4	8′	3.130 (4)
7	3	2.987 (3)	1	8′	3.096 (4)
7	4	2.959 (2)	Tl	5	5.054 (2)
7	8′	2.899 (4)	Tl	7	5.075 (3)
7	6′	2.905 (4)	5	7	4.728 (3)
plane 1	plane 2	angle	plane 1	plane 2	angle
(1-2-Tl)	(3-2-Tl)	68.3	(2-3-Tl)	(2-3-6)	35.1
(2-3-Tl)	(3-4-Tl)	69.5	(3-4-Tl)	(3-4-7)	19.2
(3-4-Tl)	(1-4-Tl)	68.5	(1-4-Tl)	(1-4-8′)	35.6
(1-4-Tl)	(2-1-Tl)	70.0	(4-8′-7)	(1-4-8′)	40.9
(3-4-7)	(4-8′-7)	63.9	(6′-7-8′)	(5-6′-8′)	15.8
(4-8′-7)	(7-6′-8′)	66.7	(3-6′-7)	(2-3-6′)	41.8
(6′-7-8′)	(6′-3-7)	67.8	(1-8′-5)	(1-8′-4)	41.2
(3-6′-7)	(3-4-7)	63.1	(2-6′-5)	(2-6′-3)	41.8
(1-2-5)	(2-6′-5)	63.2	(1-4-8′)	(2-3-6′)	177.0
(2-6′-5)	(5-6′-8′)	67.5	(1-2-5)	(4-3-7)	142.6
(5-6′-8′)	(1-8′-5)	66.9	(1-2-Tl)	(6′-7-8′)	133.5
(1-8′-5)	(1-2-5)	64.8	(6′-5-8′)	(3-4-Tl)	135.3
(1-2-Tl)	(1-2-5)	16.5			

[a] For (1-2-6′-8′), (3-4-8′-6′), and (1-2-3-4) the atoms are within 0.001, 0.011, and 0.013 Å of their respective, best least-squares plane.

shift of any potassium atom toward one end of its 2,2,2-crypt ligand such as has been observed in the related salts of Bi_4^{2-} (0.09 Å, 3σ)[16] and $HgTe_2^{2-}$ (0.026 Å, 2.8σ).[10] The shortest anion–cation and anion–en distances indicate little interaction between the ions or with en in this structure. Those less than 4.0 Å are from Tl (in $TlSn_9^{3-}$) to C111, 3.79 (3) Å, Sn7 to C316, 3.93 (2) Å, and Sn8 (in $TlSn_9^{3-}$) to C14, 3.88 (3) Å, and to C13, 3.96 (3) Å.

Even though the two clusters $TlSn_9^{3-}$ and $TlSn_8^{3-}$ can be refined only with seven-atom positions common to both anions their individual geometries are very reasonable, and the only possible problems result in the resolution of the divergent atoms 6 and 8. The ten-atom cluster, the first one of this size isolated with heavy elements, is essentially a bicapped square antiprism similar to the familiar *closo*-$B_{10}H_{10}^{2-}$, and the nine-atom unit approximates a tricapped trigonal prism analogous to *closo*-$B_9H_9^{2-}$[17-19] and to Ge_9^{2-}.[6] Both clusters are somewhat distorted from their ideal geometries, especially because of the thallium substitution, and this is discussed below. The charge assignment is pertinent first.

Anion Charges. Since the unit cell contains six 2,2,2-crypt-K^+ cations, the two anions must have a total charge of −6, and the refinement indicates that there is 50:50 proportion of each anion. This distribution would be necessary if the anionic charges were not equal (such as 4− and 2−) but of course it is not mandatory when both bear 3− charges. There are nonetheless very compelling reasons for a 3− charge on each anion, since these would then formally have skeletal electron counts ($2n + 2$) for closo species,[17] in perfect agreement with their observed geometries. Allocation of charges of 4− and 2− to $TlSn_9$ and $TlSn_8$ in either way would make both ions paramagnetic, for which there is no precedent in anionic clusters of this type. Furthermore, ESR measurements on the compound at 20 and −196 °C gave no evidence for any unpaired spin density.

The only other possibility would be to allocate charges of 5− and 1− to the anions. One choice, $TlSn_9^{5-}$ and $TlSn_8^{-}$, would provide a skeletal electron count ($2n + 4$) for a nido configuration for the former and an unprecedented $2n$ skeletal electron count for the latter. The alternative assignment would, in turn, give an unprecedented $2n$ count for $TlSn_9^-$ and a nido prediction for $TlSn_8^{5-}$. In neither case does the anion have the expected nido geometry as for $B_{10}H_{13}^-$ or $B_7C_2H_9(CH_3)_2$.[18] And very few examples with $2n$ skeletal electron counts are actually known. One is B_9Cl_9 with D_{3h} geometry,[20] but this comparison is clouded by the probable back-donation from chlorine to the cluster, a process not feasible in Tl–Sn anions. We do note in passing that Rudolph and co-workers[12] recently deduced the formation of the fluxional species $TlSn_8^{5-}$ from ^{119}Sn NMR studies in en solution, the charge assignment coming from chemical analysis of a precipitate derived by en extraction of the alloy composition $NaSnTl_{1.5}$. The species was speculated to be a nido unicapped antiprism as it would be isoelectronic with Sn_9^{4-}. Presumably the difference in starting alloy and absence of 2,2,2-crypt is responsible for the formation of a different product in this instance.

The conclusion that the crystals studied consist of substantially a 50:50 mixture of two anions of equal charge means this is not a unique composition but a particular point in a solid solution region of presumably some width. We suspect that it represents the most insoluble composition. And since the solution likely did not contain exactly equal proportions of the anions a second but minor component was presumably also precipitated. But at least 90% of the product is the phase reported here, and all crystals examined on the diffractometer (about five) had the same lattice parameters to ±0.01 Å and ±0.1°. We have also seen crystals of very similar dimensions from studies of other systems and suspect that a family of compounds occur in this structure. Most interesting is a binary potassium–tin product which would appear to fit in only if it contains Sn_9^{4-} and Sn_{10}^{2-} in equal proportions.[21]

Anion Configurations. Although the $TlSn_9^{3-}$ anion exhibits a nominal bicapped square-antiprismatic geometry it appears slightly

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(17) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(18) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.

(19) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.

(20) Hursthouse, M. B.; Kane, J.; Massey, A. G. *Nature (London)* **1970**, *228*, 659.

(21) Critchlow, S. C.; Corbett, J. D., unpublished research.

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

Table IV. Some Dihedral Angles (δ) in Nine-Atom Polyhedra

		Trigonal prism	Cap to cap			Prism end to cap					
D_{3h}	Type face	(opposed)	(vicinal)			(vicinal)					
	Example, Figure 3	1-4-8′, 2-3-6′	5-6′-8′, 6′-7-8′			2-3-6′, 2-5-6′					
	Bi_9^{5+} [a]	180°	22° (x3)			43° (x6)					
C_{2v} [b],	$TlSn_8^{3-}$ [c, d]	177°	16°	17° [e]	19° [e]	35° [e]	36° [e]	41°	41°	42°	42°
$C_{2v'}$	Ge_9^{2-} [f]	171°	8°	25°	23°	38°	36°	44°	47°	45°	45°
$\sim C_{4v'}$	Ge_9^{4-} [f]	162°	5°	32°	24°	32°	33°	51°	54°	53°	51°
C_{4v}	Sn_9^{4-} [g]	158° (x2)	3°	30°	29° (x2)		32°	52°	53°	54°	55°
	Type face	opposed, waist	base	cap to antiprism				vicinal, waist			

[a] Reference 22. [b] Anion is close to D_{3h} symmetry if thallium is not considered unique. [c] This work. [d] Vicinal angles around capping atoms Sn5, Sn7, and Tl (Figure 3) are not included. [e] Defining planes contain one thallium atom, which has the effect of reducing δ relative to that in unsubstituted species. [f] Reference 6. [g] Reference 5.

distorted even with respect to the fourfold axis. The plane 5–6–7–8 adjacent to the thallium atom in the cap is not square but "kite-shaped" ($\sim D_{2h}$) and exhibits alternating long and short distances between atoms in that plane and the thallium (see Table II and Figure 2) and in the interbond angles at tin atoms 5, 6, 7, and 8, 85.51 (8), 92.25 (8), 89.18 (9), and 93.00 (8)°, respectively. However, this result *may* be rooted not in some fundamental electronic or packing effect but in positional correlations occurring during the refinement of the pairs of atoms Sn6–Sn6′ and Sn8–Sn8′ which end up only 0.720 (5) and 0.715 (5) Å apart, respectively. The apparent distortions and observed distances are consistent with (but do not prove) an artificially small separation of the pairs in each composite atom, thereby giving a 6–8 separation (in $TlSn_9^{3-}$) which is too small and a 6′–8′ distance (in $TlSn_8^{3-}$) which is too great. Accordingly, all interatomic distances in $TlSn_9^{3-}$ associated with atoms 6 and 8 (2.862–2.898 Å) are found to be somewhat smaller than those involving atoms 5 and 7 (2.945–2.987 Å) (Figure 2). On the other hand, a possible indication of a real distortion is found in the other plane of four atoms in the square antiprism, 1–2–3–4, which is slightly rectangular rather than square. Here the intraplanar distances between atoms that are bonded to 5 and 7 (1–2 and 3–4, average 3.159 Å) are a little larger than those between atoms bonded to 6 and 8 (1–4 and 2–3, average 3.124 Å).

The greatest separations in $TlSn_9^{3-}$ are those in the plane 5–6–7–8 adjacent to the capping thallium atom, 3.204–3.253 Å, presumably a direct consequence of this substitution. Interestingly, the next largest group of interatom distances are in the other plane 1–2–3–4 capped by tin, 3.109–3.163 Å, which does lend credence to the supposition that increased size of the plane 5–6–7–8 is to a large degree caused by a capping thallium. In Sn_9^{4-} the largest distances are also those in the four atom plane adjacent to the capping tin atom, though all distances in this square pyramid are about 0.1 Å shorter than observed here with the same number of valence electrons. The other distances in $TlSn_9^{3-}$ fall in regular groups, 3.093–3.164 Å to the capping thallium atom, 3.055–3.073 Å to the capping tin atom, and 2.862–2.987 Å for the group of interplanar or waist distances.

As with $TlSn_9^{3-}$, the tricapped trigonal-prismatic geometry of $TlSn_8^{3-}$ can also be interpreted in terms of a slight distortion through coupling in the refinement. A projection along the best pseudo threefold axis is shown in Figure 3. The 3.301 (5) Å separation of 6′ and 8′, which defines one edge of the trigonal prism, is significantly greater (0.142 Å, 26σ) than the average of the other two distances which define the height of the prism (though the difference is not as great as in the diagonals 5–7 and 6–8 in $TlSn_9^{3-}$ or in the prism observed for Ge_9^{2-}[6]). The elongation of 6′–8′ leads to a dihedral angle of 177.0° between the two fairly regular triangular faces defining the prism, 1–4–8′ and 2–3–6′. Also associated with atoms 6′ and 8′ are the shortest distances in the cluster—those to the capping tin atoms 5 and 7 (see Figure 3), 2.879 (4)–2.923 (4) Å, which are somewhat less than the other capping distances to atoms 5 and 7, 2.945 (2)–2.987 (3) Å. However, it is difficult in these to distinguish between artificial distortions and real inductive effects of thallium substitution in one capping position. If the aforementioned correlation effect is important, then atoms 6′ and 8′ should be closer together and the geometry, closer to what is already clearly a tricapped trigonal-prismatic geometry.

As shown previously,[5,6] dihedral angles for nine-atom clusters provide a better delineation of the degree of distortion from an ideal model (D_{3h} or C_{4v}) than do comparisons of bond distances which may also be influenced by changes in the elements involved, particularly if these belong to different periods. The relevant dihedral angles are compared with those for other pertinent nine-atom clusters in Table IV. The most important of the dihedral angles is that between the opposite faces of the trigonal prism, 1–4–8′ and 2–3–6′, which is 180° for an ideal D_{3h} geometry such as Bi_9^{5+}, dropping progressively to 171° in Ge_9^{2-} ($\sim C_{2v}$), 162° in Ge_9^{4-} ($\sim C_{4v}$), and 158° in Sn_9^{4-} (C_{4v}). The value of 177.0° for $TlSn_8^{3-}$ indicates relatively little distortion, but in this case the angle involves atoms 6′ and 8′. More telling is the alternate prism angle between 1–2–5 and 4–3–7 which does not involve atoms 6′ and 8′. This angle in $TlSn_8^{3-}$ is 142.6°, much less than for the C_{4v} geometries of Sn_9^{4-} (158°) and Ge_9^{4-} (156°) but quite comparable for opposed faces parallel to the threefold axis in the near D_{3h} and D_{3h} geometries of Ge_9^{2-} (134, 136, and 147°) and Bi_9^{5+} (142° (×3)), respectively. The two other equivalent dihedral angles are 133.5 and 135.3° which, although they involve atoms 6′ and 8′, are also similar to the above values for Ge_9^{2-} and Bi_9^{5+}. Other dihedral angles which are useful for comparison are those between vicinal triangles between capping atoms which do not involve atoms 6′ and 8′ (e.g., 1–2–Tl and 1–2–5), which are 16.5 and 19.2° here vs. 22 for Bi_9^{5+} (D_{3h}), 23 and 25° in Ge_9^{2-}, 24 and 32° in Ge_9^{4-}, and 29 and 30° in Sn_9^{4-}. The somewhat lower values in the case of $TlSn_8^{3-}$ presumably result from the inclusion of the capping thallium atom with its relatively longer bonds.

Thallium Placement. The factors governing the heteroatom placement in these clusters are highly pertinent. In both $TlSn_9^{3-}$ and $TlSn_8^{3-}$ the thallium atom occupies a capping position (coordination number 4) rather than a position in a capped face (CN = 5). Rudolph and co-workers[12] have suggested that the thallium atom in a *nonfluxional* $TlSn_8^{5-}$ anion of presumed C_{4v} symmetry

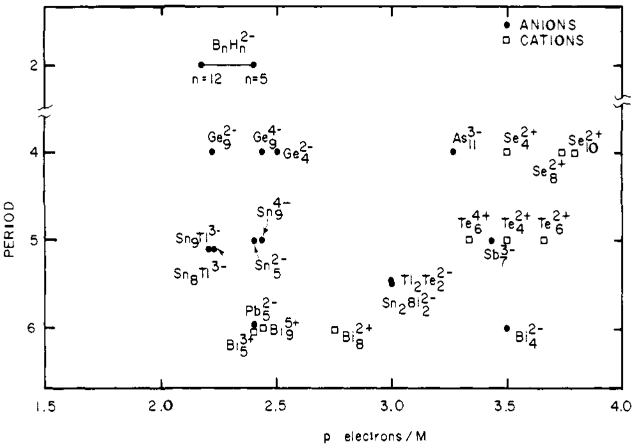

Figure 4. The total number of skeletal p electrons per element in polyatomic anions and cations as a function of period number. The lower limit for heavy element ions is close to 2.2 electrons per atom.

(nido) occurs in the capped square, that is, at a higher order vertex similar to the behavior of an electron-poor element (of the same period) in a heteroborane instead of a low-order vertex usually preferred by heteroatoms rich in electrons.[18,19] This is clearly at odds with the configurations of both $TlSn_9^{3-}$ and $TlSn_8^{3-}$ where the thallium atoms occur at the lower order (capping) vertices. We do note, however, that the recent relativistic, extended Hückel calculations of Lohr[23] seem to support the postulated positioning of the thallium atom in $TlSn_8^{5-}$. Substitution of the thallium atom at the waist (CN = 5) gives the most favorable total energy, followed by substitution at the apex (cap) and then at the base, although the differences are slight (<0.5 eV). Identical calculations were also performed on a $TlSn_8^{3-}$ cluster in the same monocapped square-antiprismatic geometry (although the present study shows this is not the most stable configuration) and interestingly, the calculations again gave the same magnitudes of stability differences for the isomers and a preference for the waist position. Since changes in total energy with configuration along the $C_{4v} \rightleftarrows D_{3h}$ pathway for Sn_9^{4-} and Ge_9^{4-} seem to be small,[6] the predicted unfavorability for substitution of thallium at the capping positions in the above calculations is hard to reconcile. Since fluxionality appears to be the rule for tin clusters observed in solution by NMR,[11,12] we do not consider it likely that we have isolated other than the thermodynamically stable isomers of these clusters.

In order to locate some common ground regarding heteroatom placement in $TlSn_9^{3-}$ and $TlSn_8^{3-}$, a number of semiempirical SCF-MO-CNDO[24] calculations have been made on the parent (but presently unconfirmed) species Sn_{10}^{2-} and Sn_9^{2-}, thereby avoiding problems associated with the actual heteroatom substitution at various vertices. Regular Sn_{10}^{2-} and Sn_9^{2-} anions were dimensioned according to those parts of the $TlSn_9^{3-}$ and $TlSn_8^{3-}$ anions which do not involve the capping thallium atoms. Thus Sn_{10}^{2-} was taken with 3.141-Å distances within the capped squares, 2.960 Å for interplanar distances, and 3.063 Å for capping distances. For Sn_9^{2-} the trigonal prism had triangular faces of 3.121 Å and a height of 3.159 Å, while the capping distances were 2.960 Å. The calculated charge distributions in Sn_{10}^{2-} were −0.376 for the capping atoms and −0.156 for the atoms in the square antiprism, while Sn_9^{2-} had calculated charges of −0.351 for the capping atoms and −0.158 for the atoms in the trigonal prism. The results are seen to depend *a great deal more* on coordination number than on configuration. Thallium therefore appears to substitute into those vertices with the higher (negative) charge density although an appreciable charge flow from the thallium to the rest of the cluster is expected based on probable electronegativities.[23] Thallium clearly does not follow the generalization developed for boranes that heteroatoms which are electron poorer than boron prefer higher order vertices. On the other hand, the electron-richer vertex may well provide compensation for what would be weaker bonding by a sixth period element.

Bonding Generalities. One final point concerns the stability of polyatomic cluster anions and cations of the main-group elements. The electronic requirements of these species place a considerable limitation on which ions may be formed with the immediate post-transition elements. A minimum of just over two electrons per element is evidently required for stability when it is assumed that each atom in the cluster also has an exo-skeletal lone pair which is primarily s^2 and not involved in the bonding.[9] All known examples, including the *closo*-borane anions, fall into this category. The lower limit is emphasized by Figure 4, where species are plotted period by period against the number of p electrons per atom. Of all of the heavy element ions, $TlSn_9^{3-}$, $TlSn_8^{3-}$, and Ge_9^{2-} have the smallest number of p electrons per element and define a line of demarkation below which polyatomic species of this type are presently not known.

A second way of treating the data would be to plot the species (period by period) against the number of skeletal *bonding* electrons per atom, making conventional assumptions regarding nonbonding electron pairs. In this case *all* cage and cluster species (anions, cations, and neutral species) are observed to contain between 2.0 and 3.0 bonding skeletal electrons per atom. Thus a limited range of skeletal electrons per atom is actually required for the formation of cluster species, irrespective of the size of the cluster or its geometry. Any extra valence electrons formally appear in lone pairs and actually determine the shape of the cluster. For example, $TlSn_9^{3-}$ and Se_{10}^{2+} are both ten-atom species but they are drastically different in geometry, being a bicapped square-antiprismatic structure in the former and the more open bicyclo[4.2.2]decane configuration in the latter.[25] Importantly, these ions formally have 22 skeletal (p) electrons each (2.2 electrons per atom), and the obviously large difference in configuration is dictated by the 16 extra valence electrons in Se_{10}^{2+} which are presumably localized in lone pairs and so produce the more open structure.

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Registry No. $(2,2,2\text{-crypt-K}^+)_3(TlSn_9^{3-}\text{-}TlSn_8^{3-})_{1/2}\cdot en$, 81423-11-2.

Supplementary Material Available: Interbond angles in the two cluster anions, distances and angles for the cryptated cations and ethylenediamine, and a listing of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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(23) Lohr, L. L. *Inorg. Chem.* **1981**, *20*, 4229.

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

(25) Burns, R. C.; Chan, W.-C.; Gillespie, R. J.; Luk, W.-C.; Sawyer, J. F.; Slim, D. R. *Inorg. Chem.* **1980**, *19*, 1432.