by gas chromatographic mass spectroscopy. No evidence was found for 7-phenylnorcarane, nor any other $C_{13}H_{16}$ isomer.

**Pyrolysis of 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo-[2.2.2]octa-2,5-diene (2) in Hexene.** 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (0.1 g, 0.37 mol) was dissolved in 1.5 g (17.5 mmol) of hexane. The solution was pyrolyzed in a nitrogen flow system at 480 °C. Analysis by GC and GCMS showed neither *trans*-stilbene nor cyclic siloxanes. Gas chromatography and GCMS identified a quantitative yield of diphenyl along with several polysilanes.

**Pyrolysis of Benzaldehyde.** Benzaldehyde (1.75 g, 16.5 mmol) was pyrolyzed under nitrogen flow at 480 °C. Analysis of the product by NMR and GCMS showed only starting benzaldehyde (96% recovery) and no evidence for *trans*-stilbene.

**Pyrolysis of 1,2-Dimethoxy-1,1,2,2-tetramethyldisilane with Benzaldehyde.** Dimethoxydisilane[9] (1.78 g, 0.1 mol) and 2.12 g (0.2 mol) of benzaldehyde were pyrolyzed in the flow system at 500 °C. The solution was analyzed by GC, and benzaldehyde (97%) was isolated (identified by GC retention time and GCMS). No evidence was found for *trans*-stilbene or cyclic siloxanes.

**Preparation of 5,6-Diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (12).** Dihydrobenzoin (2.0 g, 9.3 mmol) was dissolved in 250 ml of dry, deoxygenated benzene. Dry triethylamine (1.9 g, 18.8 mmol) and 1.75 g (9.3 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane were added, and the solution was refluxed under nitrogen for 12 h. The solution was filtered to remove triethylamine hydrochloride. The benzene was distilled from the filtrate under reduced pressure, and then under high vacuum. The residue was identified as disiladioxane **12** (80%): NMR ($CCl_4$) $\delta$ 0.30 (s, 12 H), 5.16 (s, 2 H), 6.92 (s, 10 H); infrared ($CCl_4$) 3080 (w), 3025 (w), 2950 (m), 2880 (w), 1410 (m), 1380 (w), 1250 (s), 1200 (w), 1105 (s), 1070 (b); mass spectrum (70 eV) *m/e* (rel intensity) 328 (1), 270 (17), 180 (100), 165 (25), 74 (28); mass spectrum calculated for $C_{18}H_{24}O_2Si_2$ *m/e* 328.1315; found, *m/e* 328.1310 ± 0.0016. The synthesis of **12** is very erratic and only on two occasions has gone cleanly. The product has only been identified by the above spectroscopic means and is apparently *very* unstable to the atmosphere.

**Pyrolysis of 5,6-Diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (12).** 5,6-Diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (0.5 g, 1.5 mmol) (**12**) was dissolved in 10 ml of dry, deoxygenated benzene. The solution was dripped through a pyrolysis column at 500 °C under nitrogen flow. The products were separated by gas chromatography. They were *trans*-stilbene (73%) (identified by NMR and gas chromatographic comparison with authentic sample), hexamethylcyclotrisiloxane (28%), and octamethylcyclotetrasiloxane (17%) (siloxanes identified by GC and GCMS comparison of authentic samples).

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# Stable Homopolyatomic Anions of the Post-Transition Metals, "Zintl Ions". The Synthesis and Structure of a Salt Containing the Heptantimonide(3−) Anion

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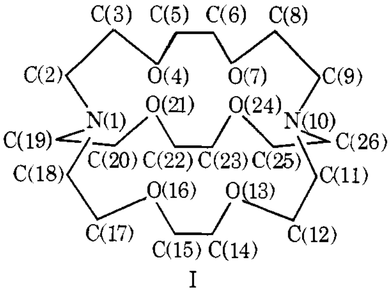
**Abstract:** The phenomenon of the formation of homopolyatomic or the so-called Zintl anions on solution of many alloys in liquid ammonia is considered, and a general route to the isolation of stable homopolyatomic anions illustrated in the case of antimony. The dark brown crystalline (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)sodium heptantimonide(3−), $(C_{18}H_{36}N_2O_6{\cdot}Na^+)_3Sb_7^{3-}$, has been prepared from the reaction of a sodium–antimony alloy with $C_{18}H_{36}N_2O_6$ (2,2,2-crypt) in ethylenediamine. Lattice constants $a$ = 23.292 (7) Å, $b$ = 13.791 (6) Å, $c$ = 25.355 (6) Å, and $\beta$ = 108.56 (2)° with four molecules per unit cell in space group $P2_1/n$ were deduced from three-dimensional x-ray data collected from a single crystal of the compound on a four-circle diffractometer using Mo K$\alpha$ radiation. The problem was phased using direct methods. Stepwise full-matrix least-squares refinement of the ten heavy atoms with anisotropic thermal parameters and of the 78 light atoms of the crypts with isotropic temperature factors resulted in converged atomic parameters with $R$ = 0.111 and $R_w$ = 0.134. Three cryptated sodium cations in which the sodium ion occupies the central cavity of the macrobicycle occur together with the $Sb_7^{3-}$ cluster anion, the first example of a well-characterized polyatomic anion for a metallic element. The polyantimony anion exhibits approximate $C_{3v}$ symmetry as an end-capped trigonal prism with the capped face substantially expanded, analogous to the isoelectronic $P_4S_3$. Bond distances in the cluster range from 2.693 (4) to 2.880 (4) Å. Possible geometries for several other reported Zintl ions of the group 5 elements are proposed on the basis of known isoelectronic ions or molecules.

The remarkable reaction of sodium and lead or their compounds with liquid ammonia to yield an intensely colored green solution was evidently first noted by Joannis[1] about 85 years ago. Subsequent experimentation confirmed his observations and further established that the lead solute was anionic and contained about 2.25 lead atoms per charge[2] according to

Faraday's laws. Likewise, the results of equilibration of excess antimony with solutions of sodium in ammonia showed the red-brown solute contained about 2.33 Sb atoms per Na,[3] and on these bases the two anions were formulated $Pb_9^{4-}$ and $Sb_7^{3-}$.[4,5] The most thorough characterization of not only the polyatomic anions of lead and antimony but also of tin, arsenic, bismuth, sulfur, selenium, and tellurium in liquid ammonia was provided by Zintl and co-workers[6-9] in the early 1930's, principally through potentiometric titrations of the solutions and exhaustive extractions of the corresponding alkali metal alloys. Typical ions reported were $Pb_9^{4-}$ and $Pb_7^{4-}$, $Sn_9^{4-}$, $Sb_7^{3-}$, $Sb_3^{3-}$, $Bi_7^{3-}$, and $Bi_5^{3-}$. However, in no case were they able to isolate crystalline derivatives. The brightly colored amorphous products obtained at low temperatures on solvent evaporation analytically corresponded to the $Na(NH_3)_n^+$ salts of the first listed anion of the above elements, but these solids always lost $NH_3$ and reverted to the corresponding binary intermetallic phases of the alkali metal and the element under investigation. It is important to note that phase compositions (and structures) in the corresponding binary alloy systems themselves show no relationship to the compositions deduced for the solutes in ammonia. The instability of simple solid derivatives of the polymetal anions formed in liquid ammonia solution seemingly results from a pronounced tendency for electrons on the supposed anions to delocalize back onto the alkali metal cations in the dense solid state and thus to yield structures and bonding characteristic of intermetallic phases.

Intimately related to these ammonia observations were considerations by Zintl and others[10-12] of the ionic or polar properties of phases formed by these same post-transition metals with the active metals, phases which have since become known as Zintl phases.[13,14] Since the original investigations numerous related binary phases have been shown to contain clusters, ribbons, sheets, etc., of the heavy metal, representing some degree of directed covalent bonding[14-16] although none is the same as postulated in $NH_3$. Further evidence of these ionic properties has been the observation that a number of the "ionic" intermetallics are appreciably soluble in molten salts.[17] But prior to preliminary communication of the present results[18,19] no general route to the isolation of stable solid derivatives of these polyatomic anions had been available, and the only report on these polymetal anions since Zintl's time had been the note by Kummer and Diehl regarding the preparation of a red, slightly stable $Na_4Sn_9 \cdot 6\text{-}8en$ (en = ethylenediamine), an incomplete crystal structure of which has revealed a polytin anion as a distorted tricapped trigonal prism.[20] A more recent note[21] also reports the existence of the compound $(Na_3 \cdot 4en)Sb_7$. Presumably there are many unsuccessful and hence unpublished contributions on the subject of Zintl anions; in our case[22] these involved attempts at both metathetical reactions and reactions in a variety of alternate solvents. On the other hand substantial progress has been made in the stabilization and characterization of presumably related polyatomic *cations* of some of the same metals, e.g., $Bi_9^{5+}$, $Bi_5^{3+}$, $Te_4^{2+}$, etc.,[23-27] the first of which is isoelectronic with $Pb_9^{4-}$ noted above.

The key to the stabilization of the polyatomic anions was provided by the synthesis of 2,2,2-crypt (I)[28,29] and the demonstration that the strong complexing of the alkali metal cations sodium, potassium, and rubidium by this octadentate ligand not only greatly enhances the solubility of the metals themselves in ammonia, amines and ethers[30] but even allows the isolation and structural characterization of the crystalline $[Na(crypt)^+]Na^-$.[31] We have found that the presence of crypt likewise increases markedly the solubility of sodium and potassium alloys of antimony, bismuth, tin, and lead in ammonia and in ethylenediamine and, more importantly, allows the isolation of brightly colored, crystalline salts rather than intermetallic on solvent removal. The present paper reports the synthesis and crystal structure of the first of these salts, $[Na(crypt)^+]_3Sb_7^{3-}$; subsequent papers will detail the corresponding results for the anions $Pb_5^{2-}$ and $Sn_9^{4-}$.



I

## Experimental Section

**Synthesis.** The 2,2,2-crypt (Cp) was used as received from EM Laboratories (Merck) and was handled only in the drybox. The alloys were prepared as before[17] by fusion of the appropriate amounts of the elements in a welded tantalum tube followed by quenching and annealing. The phase $(NaCp^+)_3Sb_7^{3-}$ was synthesized from powdered NaSb and one-third of the stoichiometric amount of crypt in one arm of a double arm Pyrex reaction vessel in which Teflon needle valves (Fischer-Porter) were used in place of stopcocks. En (ethylenediamine) dried over Molecular Sieve gives an immediate coloration when distilled in vacuo onto the mixture. After 12–24 h at room temperature the deep red-brown solution was decanted from unreacted alloy into the other arm and the en slowly removed by vacuum distillation over ~12 h yielding dark brown, diamond- and needle-shaped crystals. The different morphologies originate from the same phase. Since only a small portion of the starting alloy will dissolve even with excess crypt, a substoichiometric amount of crypt was used to minimize the amount of unreacted (and expensive) reagent which was mixed with the product. Alloy compositions ranging from $Na_3Sb$ to NaSb + 2 Sb give only the single product save for the blue phase, presumed to be $NaCp^+(e^-)$, which also separates from the more reduced systems; green solutions have also been seen in the early stages of reaction. In comparison neither antimony alloy phase reacts with, or dissolves in, en at a significant rate in the absence of crypt. The stoichiometry of the phase was determined by the crystal structure analysis.

The reaction products were examined under nitrogen in a specially designed drybox (Blickman) with a nearly horizontal window which facilitated the use of a stereomicroscope with a 7 in. focal length. Candidates were inserted into 0.2 mm i.d. Lindemann glass capillaries and the latter sealed with a resistance-heated wire within the box. X-ray data were taken from a crystal approximating a regular rectangular prism with dimensions 0.1 × 0.2 × 0.6 mm and utilized an automated four-circle diffractometer which was designed and built in the Ames Laboratory.[32] The diffractometer is equipped with a scintillation counter and is interfaced with PDP-15 computer in a real-time mode.

**Crystal Data.** The compound exhibits monoclinic symmetry with lattice constants $a$ = 23.45 Å, $b$ = 13.93 Å, $c$ = 25.52 Å, and $\beta$ = 108.7° according to the initial orientation.[33] Integrated intensity data were collected at ambient temperature within a $2\theta$ sphere of ($\sin\theta/\lambda$ = 0.526 Å) using ufiltered Mo K$\alpha$ radiation monochromatized with pyrolytic graphite ($\lambda$ 0.709 54 Å) at a takeoff angle of 4.5°. During data collection the intensities of three different standard reflections were monitored every 50 reflections to check for instrument and crystal stability. A total of 6717 integrated intensities were recorded in octants $HKL$ and $HK\bar{L}$ out of 11 263 reflections scanned. Since a 30% decrease in the intensities of the standards occurred during data collection, the data set was scaled linearly in time to the initial sum of the intensities of the standards. Final unit cell parameters and their estimated standard deviations $a$ = 23.292 (7) Å, $b$ = 13.791 (6) Å, $c$ = 25.355 (6) Å, and $\beta$ = 108.56 (2)° were obtained by a least-squares fit[34] to twice the $\omega$ values of 24 independent reflections, the centers of which were determined on the diffractometer by left–right, top–bottom beam splitting with the crystal used for data collection.

The observed intensities were corrected for Lorentz and polarization effects and the standard deviations calculated as previously described.[35] A total of 4662 reflections were retained with $I > 3\sigma_I$. Although the linear absorption coefficient calculated[36] for this compound

**Table I.** Final Positional and Thermal Parameters[a] for the Atoms in $(NaCp^+)_3Sb_7^{3-}$

| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Sb(1) | 0.2256 (1) | 0.1885 (2) | 0.4177 (1) | Na(1) | 0.6627 (6) | 0.285 (1) | 0.6185 (5) |
| Sb(2) | 0.1761 (1) | 0.0733 (2) | 0.4784 (1) | Na(2) | 0.5302 (6) | 0.371 (1) | 0.2843 (5) |
| Sb(3) | 0.3262 (1) | 0.2574 (2) | 0.5010 (1) | Na(3) | 0.5773 (6) | 0.829 (1) | 0.1362 (5) |
| Sb(4) | 0.3746 (1) | 0.0926 (2) | 0.5598 (1) | | | | |
| Sb(5) | 0.2628 (1) | 0.3374 (2) | 0.5689 (1) | | | | |
| Sb(6) | 0.2729 (1) | 0.0181 (2) | 0.5739 (1) | | | | |
| Sb(7) | 0.1993 (1) | 0.1803 (2) | 0.5806 (1) | | | | |

| | $\beta_{11}$[b] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Sb(1) | 5.9 (1) | 12.7 (2) | 2.22 (5) | 3.9 (1) | 0.36 (6) | 0.34 (9) |
| Sb(2) | 3.27 (7) | 11.3 (2) | 3.26 (6) | 0.4 (1) | −0.14 (5) | −1.88 (9) |
| Sb(3) | 3.91 (8) | 11.6 (2) | 4.46 (8) | 0.3 (1) | 1.39 (6) | 2.2 (1) |
| Sb(4) | 2.68 (6) | 10.9 (2) | 3.64 (6) | 1.8 (1) | 0.57 (5) | 0.7 (1) |
| Sb(5) | 4.50 (9) | 8.5 (2) | 5.32 (9) | 0.5 (1) | 1.15 (7) | −1.9 (1) |
| Sb(6) | 3.95 (8) | 10.2 (2) | 3.05 (6) | 0.5 (1) | 0.55 (5) | 0.92 (9) |
| Sb(7) | 3.78 (8) | 11.3 (2) | 3.43 (6) | 1.0 (1) | 1.57 (6) | −0.2 (1) |
| Na(1) | 3.8 (3) | 6.8 (8) | 2.8 (3) | 2.0 (4) | 1.0 (2) | 0.7 (4) |
| Na(2) | 3.5 (3) | 12 (1) | 2.8 (3) | 2.0 (5) | 1.1 (2) | 1.0 (4) |
| Na(3) | 3.0 (3) | 13 (1) | 3.1 (3) | −1.6 (6) | 0.8 (2) | 0.1 (5) |

| | $x$ | $y$ | $z$ | $B$ | | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|---|---|---|---|---|
| N(101)[c] | 0.606 (1) | 0.095 (2) | 0.618 (1) | 8.8 (8) | C(214) | 0.518 (2) | 0.605 (3) | 0.310 (2) | 11 (1) |
| C(102) | 0.602 (2) | 0.084 (3) | 0.677 (2) | 10.6 (13) | C(125) | 0.561 (2) | 0.579 (4) | 0.357 (2) | 13 (1) |
| C(103) | 0.583 (2) | 0.181 (3) | 0.695 (2) | 9.9 (11) | O(216) | 0.550 (1) | 0.482 (2) | 0.366 (1) | 11 (1) |
| O(104) | 0.628 (1) | 0.252 (2) | 0.703 (1) | 8.6 (6) | C(217) | 0.591 (2) | 0.452 (4) | 0.418 (2) | 13 (1) |
| C(105) | 0.681 (2) | 0.245 (3) | 0.754 (2) | 10.6 (6) | C(218) | 0.645 (2) | 0.413 (4) | 0.414 (2) | 13 (1) |
| C(106) | 0.720 (2) | 0.324 (3) | 0.762 (2) | 10.9 (13) | C(219) | 0.623 (2) | 0.236 (4) | 0.399 (2) | 13 (1) |
| O(107) | 0.737 (1) | 0.333 (2) | 0.712 (1) | 10.4 (7) | C(220) | 0.587 (3) | 0.173 (5) | 0.361 (3) | 18 (2) |
| C(108) | 0.772 (2) | 0.424 (4) | 0.718 (2) | 12.8 (15) | O(221) | 0.526 (2) | 0.205 (2) | 0.331 (1) | 12 (1) |
| C(109) | 0.770 (3) | 0.463 (4) | 0.672 (2) | 15.2 (16) | C(222) | 0.476 (3) | 0.209 (4) | 0.336 (2) | 15 (2) |
| N(110) | 0.719 (2) | 0.468 (2) | 0.622 (1) | 9.2 (8) | C(223) | 0.427 (3) | 0.243 (6) | 0.319 (3) | 18 (2) |
| C(111) | 0.730 (2) | 0.481 (3) | 0.572 (2) | 9.9 (13) | O(224) | 0.417 (2) | 0.319 (4) | 0.289 (2) | 20 (2) |
| C(112) | 0.761 (2) | 0.399 (3) | 0.558 (2) | 10.0 (11) | C(225) | 0.374 (4) | 0.335 (6) | 0.229 (4) | 21 (3) |
| O(113) | 0.728 (1) | 0.315 (2) | 0.556 (1) | 8.3 (6) | C(226) | 0.387 (4) | 0.415 (6) | 0.203 (3) | 19 (2) |
| C(114) | 0.757 (2) | 0.228 (4) | 0.548 (2) | 9.6 (12) | N(301) | 0.591 (2) | 0.953 (3) | 0.229 (2) | 12 (1) |
| C(115) | 0.725 (2) | 0.144 (3) | 0.558 (2) | 7.7 (10) | C(302) | 0.565 (2) | 0.919 (4) | 0.267 (2) | 12 (2) |
| O(116) | 0.727 (1) | 0.150 (1) | 0.615 (1) | 6.9 (5) | C(303) | 0.498 (3) | 0.966 (4) | 0.218 (2) | 14 (2) |
| C(117) | 0.714 (2) | 0.060 (3) | 0.635 (1) | 7.8 (9) | O(304) | 0.482 (2) | 0.864 (2) | 0.182 (1) | 12 (1) |
| C(118) | 0.650 (2) | 0.024 (3) | 0.610 (1) | 7.8 (9) | C(305) | 0.458 (3) | 0.949 (5) | 0.142 (2) | 17 (2) |
| C(119) | 0.546 (2) | 0.093 (3) | 0.578 (2) | 9.4 (10) | C(306) | 0.424 (2) | 0.882 (4) | 0.104 (2) | 11 (1) |
| C(120) | 0.550 (2) | 0.135 (3) | 0.523 (2) | 11.6 (12) | O(307) | 0.469 (2) | 0.862 (3) | 0.066 (1) | 13 (1) |
| O(121) | 0.562 (1) | 0.240 (2) | 0.532 (1) | 9.0 (7) | C(308) | 0.441 (3) | 0.768 (4) | 0.058 (2) | 14 (2) |
| C(122) | 0.517 (2) | 0.299 (4) | 0.545 (2) | 12.5 (14) | C(309) | 0.480 (3) | 0.743 (4) | 0.004 (2) | 13 (2) |
| C(123) | 0.536 (2) | 0.404 (3) | 0.547 (1) | 8.8 (9) | N(310) | 0.549 (2) | 0.694 (3) | 0.031 (2) | 11 (1) |
| O(124) | 0.588 (1) | 0.424 (2) | 0.589 (1) | 10.4 (7) | C(311) | 0.600 (2) | 0.726 (4) | 0.016 (2) | 11 (1) |
| C(125) | 0.614 (3) | 0.520 (4) | 0.595 (2) | 14.2 (16) | C(312) | 0.587 (3) | 0.839 (4) | 0.001 (2) | 13 (2) |
| C(126) | 0.669 (3) | 0.532 (4) | 0.629 (2) | 13.4 (15) | O(313) | 0.630 (2) | 0.843 (3) | 0.054 (2) | 14 (1) |
| N(201) | 0.639 (2) | 0.329 (3) | 0.372 (1) | 11 (1) | C(314) | 0.656 (2) | 0.953 (4) | 0.060 (2) | 12 (2) |
| C(202) | 0.688 (2) | 0.323 (4) | 0.349 (2) | 12 (1) | C(315) | 0.610 (3) | 0.006 (4) | 0.066 (2) | 13 (2) |
| C(203) | 0.683 (3) | 0.390 (4) | 0.308 (2) | 15 (2) | O(316) | 0.599 (2) | 0.017 (3) | 0.124 (1) | 14 (1) |
| O(204) | 0.632 (2) | 0.396 (2) | 0.257 (1) | 14 (1) | C(317) | 0.651 (2) | 0.009 (4) | 0.178 (2) | 11 (2) |
| C(205) | 0.638 (2) | 0.324 (4) | 0.217 (2) | 12 (1) | C(318) | 0.629 (2) | 0.030 (4) | 0.219 (2) | 10 (1) |
| C(206) | 0.584 (3) | 0.332 (4) | 0.178 (2) | 13 (1) | C(319) | 0.656 (3) | 0.898 (5) | 0.258 (3) | 18 (2) |
| O(207) | 0.537 (2) | 0.289 (3) | 0.194 (2) | 17 (1) | C(320) | 0.621 (3) | 0.767 (4) | 0.254 (2) | 14 (2) |
| C(208) | 0.465 (4) | 0.284 (6) | 0.153 (3) | 20 (2) | O(321) | 0.672 (2) | 0.762 (3) | 0.224 (2) | 16 (1) |
| C(209) | 0.426 (5) | 0.364 (9) | 0.154 (4) | 28 (4) | C(322) | 0.691 (3) | 0.685 (4) | 0.204 (2) | 16 (2) |
| N(210) | 0.433 (3) | 0.447 (5) | 0.187 (2) | 18 (2) | C(323) | 0.653 (3) | 0.633 (5) | 0.166 (3) | 16 (2) |
| C(211) | 0.453 (4) | 0.552 (6) | 0.185 (3) | 20 (2) | O(324) | 0.596 (2) | 0.616 (3) | 0.141 (2) | 14 (2) |
| C(212) | 0.465 (7) | 0.569 (1) | 0.238 (7) | 38 (8) | C(325) | 0.582 (3) | 0.579 (4) | 0.081 (2) | 13 (2) |
| O(213) | 0.514 (2) | 0.557 (3) | 0.265 (2) | 16 (1) | C(326) | 0.528 (3) | 0.625 (4) | 0.059 (2) | 12 (2) |

[a] Estimated standard deviations in least significant figures given in parentheses. [b] $\beta \times 10^3$ is listed. [c] The first digit indexes the crypt molecule and sodium, the second and third number the crypt atoms, as in the introductory section.

is only 25 cm$^{-1}$, an absorption correction was still applied[37] to each reflection because of the needle shape of the crystal. The conditions $k = 2n$ and $h + l = 2n$ for observation of $0k0$ and $h0l$ reflections, respectively, fix the space group uniquely as $P2_1/n$, a nonstandard setting of $P2_1/c$ ($C_{2h}^5$, No. 14).

**Structure Determination and Refinement.** The heavy atoms were located by direct methods. The output from the Fourier step of MULTAN[38] contained seven large peaks which described a potential antimony cluster having interpeak distances on the order of 2.8 Å, and three cycles of full-matrix least-squares refinement[39] of positional and isotropic thermal parameters resulted in a residual (agreement factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.398. An electron density map[40] contained three additional peaks of appropriate height for sodium atoms with smaller peaks clustered about them indicative of the light

**Table II.** Interatomic Distances and Angles in the $Sb_7^{3-}$ Anion

| Sb atoms | *d* (Å) | *d*(thermal[a]), Å | Sb atoms | *d* (Å) | *d*(thermal[a]), Å |
|---|---|---|---|---|---|
| 1–2 | 2.711 (4) | 2.773 (4) | 1–6 | 4.432 (3) | 4.487 (3) |
| 1–3 | 2.776 (4) | 2.855 (4) | 1–7 | 4.365 (4) | 4.418 (4) |
| 2–6 | 2.838 (3) | 2.917 (3) | 2–3 | 4.209 (4) | 4.261 (4) |
| 2–7 | 2.880 (4) | 2.956 (4) | 2–4 | 4.431 (3) | 4.483 (4) |
| 3–4 | 2.755 (4) | 2.838 (4) | 2–5 | 4.435 (4) | 4.493 (4) |
| 3–5 | 2.824 (4) | 2.903 (4) | 3–6 | 4.159 (4) | 4.214 (4) |
| 4–6 | 2.706 (4) | 2.775 (4) | 3–7 | 4.210 (4) | 4.264 (4) |
| 5–7 | 2.693 (4) | 2.769 (4) | 4–5 | 4.313 (4) | 4.371 (4) |
| 6–7 | 2.856 (4) | 2.928 (4) | 4–7 | 4.446 (3) | 4.497 (4) |
| 1–4 | 4.339 (4) | 4.397 (4) | 5–6 | 4.409 (4) | 4.463 (4) |
| 1–5 | 4.191 (4) | 4.253 (4) | | | |

| Sb atoms | Angle (deg) | Sb atoms | Angle (deg) | Sb atoms | Angle (deg) | Sb atoms | Angle (deg) |
|---|---|---|---|---|---|---|---|
| 2–1–3 | 100.2 (1) | 3–5–7 | 99.5 (1) | 1–3–4 | 103.4 (1) | 2–7–5 | 105.4 (1) |
| 1–2–6 | 106.0 (1) | 2–6–4 | 106.1 (1) | 1–3–5 | 96.9 (1) | 2–7–6 | 59.3 (1) |
| 1–2–7 | 102.6 (1) | 2–6–7 | 60.8 (1) | 4–3–5 | 101.3 (1) | 5–7–6 | 105.2 (1) |
| 6–2–7 | 59.9 (1) | 4–6–7 | 106.1 (1) | 3–4–6 | 99.2 (1) | | |

[a] Distances averaged for thermal motion of independent atoms.

atoms of the crypt ligands. The 26 independent nonhydrogen atoms of one crypt were readily located from a difference electron density map using a program which automatically searches the map after the Fourier calculation.[41] The complete sets of atoms making up the other two independent crypts proved to be more difficult to locate and refine via successive least-squares refinements and Fourier syntheses. Both showed generally higher thermal parameters. Several of the carbon atoms were assigned with difficulty as the peaks were broad and not very large, and there was evidence for disordering of the ethylene groups at the bridgeheads in crypt three. Thermal parameters of the bridgehead ethylene groups in crypt two were particularly large, as also observed in the $Sn_9^{4-}$ phase.[19]

The initial stages of the full refinement were carried out using a block diagonal least-squares program;[42] the refined parameters therefrom normally agreed with those from ORFLS within the respective estimated standard deviations. The scattering factors used with both programs were those of Hanson et al.,[43] and those for antimony and sodium were corrected for both the real and imaginary parts of anomalous dispersion.[36] In both cases the reflections were weighted by $\sigma_F^{-2}$ to account for the reliability of each measurement. Refinement of all 88 atoms with isotropic temperature factors resulted in converged positional and thermal parameters at $R = 0.172$. After conversion of the isotropic temperature factors of the heavy atoms to anisotropic factors of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$, three cycles of block-diagonal least-squares refinement resulted in well-behaved positional and thermal parameters, an unweighted residual of 0.130, and a weighted residual $R_w = [(\Sigma w(|F_o| - |F_c|)^2)/\Sigma w|F_o|^2]^{1/2} = 0.168$.

Final refinements were completed on an expanded version of ORFLS. At the finish one cycle of refinement was carried out on the ten heavy atoms with anisotropic temperature factors plus the atoms of the first crypt with isotropic factors. Two cycles of refinement on the second crypt with isotropic thermal parameters resulted in converged parameters. Further refinement of the third crypt was not considered worthwhile since earlier refinements of this portion using ORFLS had not resulted in improved parameters over those obtained from block least squares. Finally two cycles of refinement on the heavy atoms with the refined parameters of the light atoms resulted in converged positional parameters for the heavy atoms with $R = 0.111$ and $R_w = 0.134$. The ratio of the largest shift in coordinates to the respective standard deviation in the last refinement cycle was 0.07. A difference Fourier map showed only a randomly fluctuating background of $\leq \pm 1$ $e^-/Å^3$ except in the neighborhood of the heavy atoms where there were two ripples of less than 3 and 5 $e^-/Å^3$ in the vicinity of Sb(5) and one ripple of less than 3 $e^-/Å^3$ near Sb(6). This is not unreasonable since scattering factors for $Sb^0$ were used. No hydrogen atoms were discerned or assigned and therefore 10.7% of the total electron density remains unassigned.

Interatomic distances and angles for the anion and for the first and second crypts were calculated using ORFFE,[44] the standard deviations being estimated from the variance-covariance matrix calculated from the final least-squares cycle. The program FBOND[42] was used to obtain these for the third crypt.

## Results and Discussion

The final positional and thermal parameters for all atoms are listed in Table I. Distances and angles in $Sb_7^{3-}$ are given in Table II, and for crypt-sodium(1) cation, in Table III. The somewhat repetitious and less precise distance and angle data for the other two crypt cations are contained in the supplementary material together with the structure factor comparisons. A stereoscopic [010] view of the packing in the unit cell is given in Figure 1, the cations being simplified by showing the (numbered) sodium atoms with only the nitrogen atoms of the ligands.

The most significant part of the compound investigated, the $Sb_7^{3-}$ ion, is illustrated in Figure 2. The species is well approximated as having $C_{3v}$ symmetry (Table II); the principal deviations therefrom are distances and angles around Sb(3), plausibly because of closeness of crypt-1 to Sb(1) and Sb(4). The configuration is similar to that known not only for nortricyclane but also for $P_4S_3$[46] where sulfur occupies the bridge positions of Sb(1), Sb(4), and Sb(5), and for the $P_7^{3-}$ ion described more recently in $Sr_3P_{14}$ and $Ba_3P_{14}$.[47] The proportioning of distances in $Sb_7^{3-}$ and $P_7^{3-}$ is quite similar. As might be expected from this similarity to a nonmetal species, a localized two-center bonding picture is possible for $Sb_7^{3-}$ as well, consisting of the nine $\sigma$ bonds implied in the figure plus an extra nonbonding electron pair on the bridging Sb(1), Sb(4), and Sb(5) atoms. The results of CNDO calculations[48] trend toward this charge distribution, namely, about −0.35, −0.55, and −0.25 charge on each basal, bridging, and apex atom, respectively, in both $Sb_7^{3-}$ and $P_7^{3-}$. The distance distribution observed in $Sb_7^{3-}$ is interesting, the longest distances in the base plausibly reflecting strain (or poorer overlap) therein, the apex atom also being trivalent and forming somewhat longer bonds. The short (2.70 Å) bridge to basal bonds presumably are a reflection of the poorer bonding within the base.

The sodium-crypt cations found in this structure are relatively similar to that reported and illustrated for the iodide salt[49] and so these will not be considered in detail. In the iodide the N(1)-Na-N(10) linkage of the complex cation lies on a three-fold axis, whereas the present examples occur as enantiomeric pairs in general positions and exhibit little accidental symmetry, as is demonstrated by the variations in Na(1) dis-

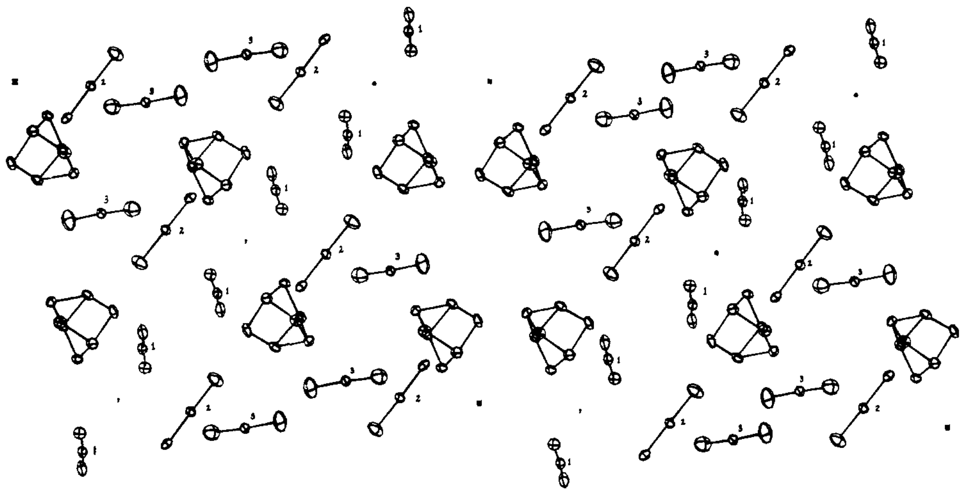


Figure 1. Stereoview of the unit cell of $[(2,2,2\text{-crypt})Na^+]_3Sb_7^{3-}$ along [010], from ORTEP;[45] only (numbered) sodium and nitrogen atoms are shown for the cations.

Table III. Bond Distances and Bond Angles for the Crypt-Sodium(1) Cation

| | | | |
|---|---|---|---|
| **Bonded Distances (Å)** | | | |
| N(1)-C(2) | 1.52 (5) | C(18)-N(1) | 1.49 (4) |
| C(2)-C(3) | 1.52 (5) | N(1)-C(19) | 1.43 (4) |
| C(3)-O(4) | 1.40 (4) | C(19)-C(20) | 1.52 (5) |
| O(4)-C(5) | 1.47 (4) | C(20)-O(21) | 1.49 (5) |
| C(5)-C(6) | 1.40 (5) | O(21)-C(22) | 1.45 (5) |
| C(6)-O(7) | 1.44 (4) | C(22)-C(23) | 1.50 (5) |
| O(7)-C(8) | 1.47 (5) | C(23)-O(24) | 1.37 (4) |
| C(8)-C(9) | 1.29 (6) | O(24)-C(25) | 1.45 (6) |
| C(9)-N(10) | 1.44 (5) | C(25)-C(26) | 1.30 (6) |
| N(10)-C(11) | 1.38 (5) | | |
| N(10)-C(26) | 1.51 (5) | Na-N(1) | 2.94 (3) |
| C(11)-C(12) | 1.45 (5) | Na-N(10) | 2.83 (4) |
| C(12)-O(13) | 1.39 (4) | Na-O(4) | 2.56 (3) |
| O(13)-C(14) | 1.43 (5) | Na-O(7) | 2.55 (3) |
| C(14)-C(15) | 1.44 (5) | Na-O(13) | 2.55 (3) |
| C(15)-O(16) | 1.43 (4) | Na-O(16) | 2.40 (2) |
| O(16)-C(17) | 1.42 (4) | Na-O(21) | 2.71 (3) |
| C(17)-C(18) | 1.50 (5) | Na-O(24) | 2.54 (3) |
| **Bond Angles (deg)** | | | |
| N(1)-C(2)-C(3) | 109 (3) | N(1)-Na-N(10) | 178 (1) |
| C(2)-C(3)-O(4) | 112 (4) | N(1)-Na-O(4) | 65 (1) |
| C(3)-O(4)-C(5) | 117 (3) | N(1)-Na-O(16) | 66 (1) |
| O(4)-C(5)-C(6) | 114 (4) | N(1)-Na-O(21) | 62 (1) |
| C(5)-C(6)-O(7) | 106 (4) | N(10)-Na-O(7) | 64 (1) |
| C(6)-O(7)-C(8) | 105 (3) | N(10)-Na-O(13) | 61 (1) |
| O(7)-C(8)-C(9) | 114 (5) | N(10)-Na-O(24) | 66 (1) |
| C(8)-C(9)-N(10) | 126 (6) | O(4)-Na-O(7) | 64 (1) |
| C(9)-N(10)-C(11) | 117 (4) | O(4)-Na-O(13) | 163 (1) |
| C(9)-N(10)-C(26) | 113 (4) | O(4)-Na-O(16) | 105 (1) |
| C(11)-N(10)-C(26) | 114 (4) | O(4)-Na-O(21) | 102 (1) |
| N(10)-C(11)-C(12) | 113 (4) | O(4)-Na-O(24) | 91 (1) |
| C(11)-C(12)-O(13) | 110 (4) | O(7)-Na-O(13) | 100 (1) |
| C(12)-O(13)-C(14) | 115 (3) | O(7)-Na-O(16) | 89 (1) |
| O(13)-C(14)-C(15) | 110 (4) | O(7)-Na-O(21) | 165 (1) |
| C(14)-C(15)-O(16) | 106 (3) | O(7)-Na-O(24) | 106 (1) |
| C(15)-O(16)-C(17) | 111 (2) | O(13)-Na-O(16) | 67 (1) |
| O(16)-C(17)-C(18) | 116 (3) | O(13)-Na-O(21) | 94 (1) |
| C(17)-C(18)-N(1) | 111 (3) | O(13)-Na-O(24) | 100 (1) |
| C(18)-N(1)-C(2) | 110 (3) | O(16)-Na-O(21) | 101 (1) |
| C(18)-N(1)-C(19) | 116 (3) | O(16)-Na-O(24) | 162 (1) |
| C(19)-N(1)-C(2) | 111 (3) | O(21)-Na-O(24) | 67 (1) |
| N(1)-C(19)-C(20) | 110 (4) | | |
| C(19)-C(20)-O(21) | 107 (3) | Na-N(1)-C(2) | 105 (2) |
| C(20)-O(21)-C(22) | 117 (3) | Na-N(1)-C(18) | 105 (2) |
| O(21)-C(22)-C(23) | 109 (4) | Na-N(1)-C(19) | 110 (2) |
| C(22)-C(23)-O(24) | 113 (3) | Na-N(10)-C(9) | 104 (3) |
| C(23)-O(24)-C(25) | 120 (4) | Na-N(10)-C(11) | 108 (3) |
| O(24)-C(25)-C(26) | 118 (5) | Na-N(10)-C(26) | 99 (3) |
| C(25)-C(26)-N(10 | 119 (5) | | |

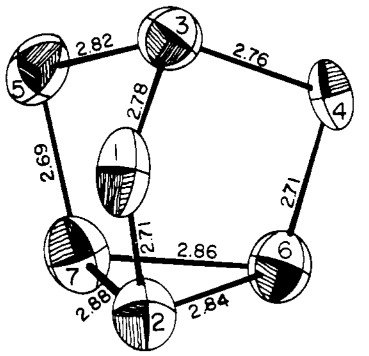


Figure 2. ORTEP[45] drawing of the configuration of $Sb_7^{3-}$ in the compound $[(2,2,2\text{-crypt})Na^+]_3Sb_7^{3-}$.

tances to the "equivalent" O(4), O(16), and O(21) atoms, 2.56 (3), 2.40 (2), and 2.71 (3) Å, respectively, and by the N-Na-N angles in the three cations, 178 (1), 168 (2), and 175 (1)°. The N-N distances in the present cations and in some of those found in $(NaCp^+)_4Sn_9^{4-}$ [19] appear to be about 0.26 Å or more longer than those found with iodide. As already noted,[49] the evident strain in and sizeable twist between the oxygen "planes" (7-13-24 and 4-16-21) of crypt necessary for adequate complexing of the somewhat undersized $Na^+$ ion are also reflected both in larger than expected Na-N and Na-O distances and in an enhanced difference between these two distances relative to the potassium complex.

The $Sb_7^{3-}$ species is evidently the first homopolyatomic anion of a "metal" to be isolated and characterized by means of a complete crystal structure, and subsequent studies have now led to comparable syntheses and structures for $Sn_9^{4-}$, $Pb_5^{2-}$, and $Sn_5^{2-}$ as well.[18,19,48] The effect of crypt in stabilizing the "ionic" constitution vis-a-vis the normal intermetallic phase can be attributed to an effective blocking of the partial electron transfer from the anion back onto the alkali metal ions which would otherwise occur in the dense solid state. The stabilization of the ionic state through complexation of the cation is often quite striking. For example, sodium-antimony alloys show only a very slow reaction with or solubility in ethylenediamine, yet they rapidly dissolve in the presence of crypt to yield dark red-brown solutions from which the crystalline phase may be isolated. The solvent ethylenediamine has proven to be both adequate and convenient for most syntheses, and the use of ammonia or other simple amines appears to offer little advantage. Several other alloy systems are presently under investigation.

The original structural proposals of Zintl for these anions

**Table IV.** Configurations of Known and Possible Polyanions of Antimony and Bismuth

| Zintl ion | Proposed Stoichiometry | Proposed Geometry | Isoelectronic species | Reference |
|---|---|---|---|---|
| $Sb_3^{3-}$, $Bi_3^{3-}$ | Same | $C_{2v}$ | $O_3$ | |
| $Bi_5^{3-}$ | $Bi_5^{3.33-}$ $= Bi_6^{4-}$ | $D_{6h}$ | $Te_6^{2+}$ | Prince, Corbett, and Garbisch[50] |
| | | | $P_6^{4-}$ | Schmettow, Lipka, von Schnering[51] |
| $Sb_7^{3-}$ | $Sb_7^{3-}$ | $C_{3v}$ | | This work |
| | | | $P_7^{3-}$ | Dahlmann and von Schnering[47] |
| "$Bi_7^{3-}$" | $Bi_{5.85}^{3-}$ $\simeq Bi_4^{2-}$ | $D_{4h}$ | $Te_4^{2+}$ | Couch, Lokken, and Corbett[26] |

were based on views then held on valence structures of the polysulfides, viz., $Na_2S(S)_x$, leading to an interpretation of these polymetal anions in terms of a central metal anion symmetrically bonded to neutral metal atoms, that is, as octahedral $[Sb^{3-}(Sb)_6]$ and cubic $[Pb^{4-}(Pb)_8]$. The apparent charges for all of the polyanions then known did follow the group negative valency. Although current bonding views would favor other descriptions, the original work by Zintl and co-workers was achieved with what would now be viewed as fairly rudimentary facilities and remains a tribute to their skill, patience, and foresight.

For the metals of group 5, Zintl and co-workers deduced the formation of the valence compounds $Na_3Sb$ and $Na_3Bi$ plus the ions $Sb_3^{3-}$, $Sb_7^{3-}$, $Bi_3^{3-}$, and $Bi_5^{3-}$ from potentiometric titrations,[6] while they later obtained evidence for $Bi_7^{3-}$ as well as $Sb_7^{3-}$ from exhaustive alloy extractions.[8] A prediction of geometries for all of these at the present time is encouraged not only by recent successes in confirming the existence of some of these Zintl ions but also by synthesis and structural characterization recently achieved from some possibly isoelectronic polycations. Table IV summarizes these possibilities. Although $Bi_3^{3-}$ and $Sb_3^{3-}$ derivatives may never by isolated (the solution equilibria are predictably highly concentration dependent, favoring the heavier polyanions on concentration) the triantimony(3−) anion does seem to have an unequivocal existence in molten sodium halides as well.[17] Both species are isoelectronic relatives of $O_3$. Although no congeners of $Bi_5^{3-}$ immediately come to mind, the composition determined is not very different from $Bi_5^{3.33-}$, that is, $Bi_6^{4-}$, this ion which would be isoelectronic with the known $Te_6^{2+}$, predicted to have $D_{6h}$ symmetry, and with the $P_6^{4-}$ ion of which has recently been shown to have that symmetry in the phase $Rb_4P_6$.[51] Finally, it is worth noting that the reported $Bi_7^{3-}$ may not necessarily be a simple analogue of $Sb_7^{3-}$ but could relate to another polycation. This speculation is based on the fact that the composition obtained from alloy extractions by Zintl and Dullenkopf[8] actually corresponded to $Bi_{5.85}^{3-}$, and they rounded this to $Bi_7^{3-}$ based on the general observation that all of the group 5 anions observed had a negative three charge and an odd number of atoms. However, the composition $Bi_{5.85}^{3-}$ is much closer to that of $Bi_4^{2-}$, an anion which would be isoelectronic with the known $Te_4^{2+}$.[26] The same analogies should apply to the three arsenic species reported, $As_{3,5,7}^{3-}$, though at present these seem less novel since the element is more characteristically nonmetallic. To date alkali metal-crypt complexes of polybismuth anions have been isolated only as relatively poor crystals, but experiments are continuing.

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**Supplementary Materials Available:** Bond distance and angle data for the second and third sodium-crypt cations (Tables V, VI) together with a listing of the observed and calculated structure factors are available (16 pages). Ordering information is given on any current masthead page of this journal.

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