

[Na(2,2,2-crypt)]₃[Sb₁₁], a Salt Containing the Undecaantimonide(3-) Anion†

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Reaction of Na₃Sb₇ with 2,2,2-crypt in ethylenediamine results in the formation of [Na(2,2,2-crypt)]₃[Sb₁₁], whose structure has been determined crystallographically.

Groups 14, 15 and 16 elements show a fascinating anion chemistry,¹ which was studied by Zintl and coworkers² in the 1930s. The richness of structures available only to the Group 15 elements, in the solid state as well as in solution, is surprising. Phosphorus is the element with most striking features.³ Besides the anionic two- and three-dimensional networks of most binary polyphosphides, which are often

derivatives of black or Hittorf's (violet) phosphorus, there are discrete structural units such as P₇ⁿ⁻ (*n* = 1–4) and P₁₁³⁻ in oligomeric and polymeric structural arrangements.³

Bismuth, on the other hand, is interesting because it forms a variety of cluster cations (*e.g.*⁴ Bi₈²⁺) and anions (*e.g.*⁵ Bi₄²⁻), and for this reason it has been called the wonder metal.¹ A special aspect of the polyanionic chemistry of arsenic in solution is that besides the homopolyanions As₁₁³⁻,⁶ and As₂₂⁴⁻,⁷ several heteropolyanions such as SnAs₁₄⁴⁻,⁷ As₁₀Te₃²⁻,⁸ or As₁₁Te₃³⁻,⁹ are known.

A crucial point of Zintl-ion chemistry is the apparent instability of large polyanions of the main group metals. Pb₉⁴⁻ has never been isolated even though it was one of the first polyanions discovered by Zintl and coworkers in liquid ammonia solution.² Similarly, the existence of Sb₁₁³⁻ or Bi₇³⁻ and Bi₁₁³⁻ in solution could never be confirmed. Interestingly,

† 2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

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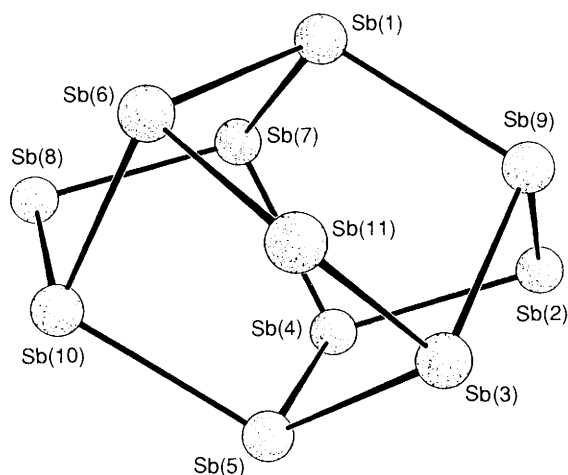
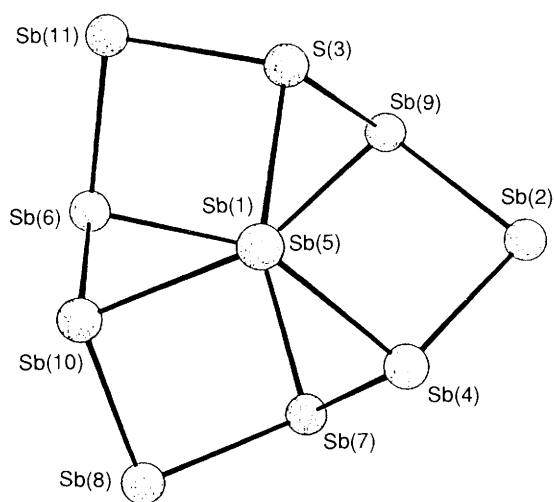


Fig. 1 Two views of the Sb_{11}^{3-} anion in $[\text{Na}(2,2,2\text{-crypt})]_3[\text{Sb}_{11}]$. Pertinent interatomic distances: (Type A) $\text{Sb}(1)\text{-Sb}(9)$ 2.809(4), $\text{Sb}(1)\text{-Sb}(6)$ 2.810(3), $\text{Sb}(1)\text{-Sb}(7)$ 2.874(4), $\text{Sb}(5)\text{-Sb}(3)$ 2.822(3), $\text{Sb}(5)\text{-Sb}(4)$ 2.797(3), $\text{Sb}(5)\text{-Sb}(10)$ 2.853(4); (Type B) $\text{Sb}(9)\text{-Sb}(3)$ 2.815(4), $\text{Sb}(6)\text{-Sb}(10)$ 2.787(4), $\text{Sb}(4)\text{-Sb}(7)$ 2.787(4); (Type C) $\text{Sb}(2)\text{-Sb}(4)$ 2.769(3), $\text{Sb}(2)\text{-Sb}(9)$ 2.742(4), $\text{Sb}(8)\text{-Sb}(7)$ 2.716(4), $\text{Sb}(8)\text{-Sb}(10)$ 2.776(4), $\text{Sb}(11)\text{-Sb}(6)$ 2.771(4), $\text{Sb}(11)\text{-Sb}(3)$ 2.761(4); (height h) $\text{Sb}(1)\cdots\text{Sb}(5)$ 4.717(3) Å.

however, a metallated derivative of the Pb_9^{4-} cluster anion, $[\text{Pb}_9\text{Cr}(\text{CO})_3]^{4-}$,¹⁰ has been reported recently. Therefore, a possible synthetic route to large polyanions of the main group metals may involve their stabilization by appropriate transition metal fragments. We have pursued this synthetic approach and report here the synthesis and crystal structure of the salt-like compound $[\text{Na}(2,2,2\text{-crypt})]_3[\text{Sb}_{11}]$ containing the Sb_{11}^{3-} anion. §

§ *Crystal data* for $[\text{Na}(2,2,2\text{-crypt})]_3[\text{Sb}_{11}]$: $\text{C}_{54}\text{H}_{108}\text{N}_6\text{Na}_3\text{O}_{18}\text{Sb}_{11}$, $M = 2536.8$, triclinic, space group $P1$, $a = 13.865(5)$, $b = 17.852(8)$, $c = 18.143(7)$ Å, $\alpha = 94.78(3)$, $\beta = 94.34(3)$, $\gamma = 98.97(3)^\circ$, $V = 4402(2)$ Å³, $D_c = 1.91$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 3.41$ mm⁻¹, $Z = 2$, $\lambda = 0.71073$ Å, crystal needle shape, dimensions $0.25 \times 0.12 \times 0.30$ mm³, $2\theta_{\text{max}} = 54^\circ$, data collected at 150 K on a Siemens R3 four-circle diffractometer: structure solved and refined using the SHELXTL PLUS program system, no absorption correction. 20 038 unique reflections of which 7641 are 'observed' [with $I \geq 2\sigma(I)$]. Full-matrix least-squares refinement with hydrogen atoms constrained to chemically reasonable positions. Final $R = 0.094$, $R_w = 0.088$ for all Sb, Na, O, and N atoms anisotropic and all C atoms isotropic. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

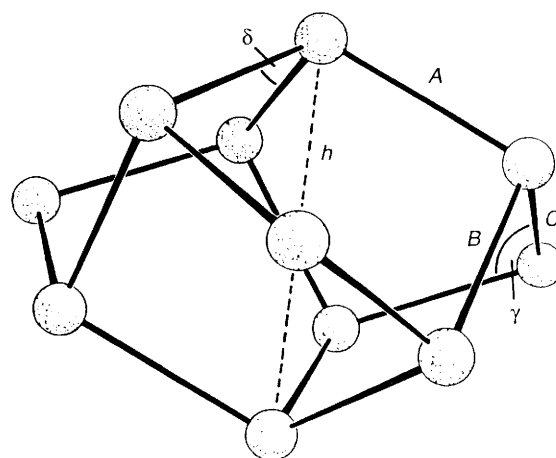


Fig. 2 Schematic representation of the Y_{11}^{3-} anion with labels for groups of pertinent bond lengths and bond angles as well as the height h of the polyanion

The reaction of a dark-red ethylenediamine (en) solution of the alloy Na_3Sb_7 with $[\text{Mo}(\text{bipy})(\text{CO})_4]$ (bipy = 2,2'-bipyridyl) and 2,2,2-crypt leads to the formation of $[\text{Na}(2,2,2\text{-crypt})]_3[\text{Sb}_7\text{Mo}(\text{CO})_3]$.¹¹ Initially, the title compound was isolated as an unexpected side product from this reaction. However, subsequent studies showed that it can be synthesized in high yields by the reaction of an en solution of the alloy Na_3Sb_7 with 2,2,2-crypt in a 1:1 ratio.

Structurally, the Sb_{11}^{3-} anion, which is shown in two different views in Fig. 1, belongs to the 'ufosane' type system described by von Schnering¹² and Belin⁶ for P_{11}^{3-} (found in Na_3P_{11}) and As_{11}^{3-} (the only undeca-Group 15 element isolated from solution so far). It is a hexacyclic system of polyanion species five-membered rings, which possesses idealized D_3 symmetry. From another point of view this cluster might be described as a derivative of a hypothetical Sb_8 cubane [made from the atoms $\text{Sb}(1)$, $\text{Sb}(3)$, $\text{Sb}(4)$, $\text{Sb}(5)$, $\text{Sb}(6)$, $\text{Sb}(7)$, $\text{Sb}(9)$, $\text{Sb}(10)$], where three of twelve edges are bridged by additional antimony atoms [$\text{Sb}(2)$, $\text{Sb}(8)$, $\text{Sb}(11)$]. Those Sb atoms of the cubane system which are bridged by $\text{Sb}(2)$, $\text{Sb}(8)$ and $\text{Sb}(11)$ are not bonded to each other.

The structural details are in accordance with a topological scheme^{3a} that has been given for Y_{11} clusters (Fig. 2, $\text{Y} =$ Group 15 element). For neutral 'ufosane-type' systems the relation $A > B > C$ and $\gamma > \delta$ is valid, whereas for ionic cages the sequence $A > C > B$ is observed. These significant differences in the structural parameters are a clear indication of repulsive coulombic interactions between the twofold-bridging atoms of the cluster.

The anions P_{11}^{3-} and As_{11}^{3-} show similar behaviour in terms of bond distances and bond angles. For both species $A > C > B$ and $\delta > \gamma$ hold, and the values for the ratio $Q = h/A$ (1.69 for P_{11}^{3-} and 1.65 for As_{11}^{3-}) are only slightly different. Although the negative charge of the undecaantimonide anion should be mainly localized at the (2b)-bridging atoms there seems to be to some extent a delocalisation of charge. The distances C of the (2b)-bridging atoms are significantly reduced in the Sb_{11}^{3-} anion; therefore the ordering $A > C > B$ is reversed and $A > B > C$ is observed instead. The ratio $Q = h/a$ (1.68) is almost identical to that found in the P_{11}^{3-} and As_{11}^{3-} anions.

Since the cluster is not electron deficient, its bonding can be explained in a straightforward fashion using the picture of 2-electron, 2-centre-bonds. The total electron count of the cluster is 58. 28 electrons are tied up in 14 lone pairs while the remaining 30 electrons are used in 15 (2e,2c)-bonds. In terms of Wade's rules the bonding within the cluster can be rationalized by assuming that each Sb atom has one lone pair

of electrons and contributes the remaining three electrons for cluster bonding. The 36 cluster electrons ($11 \times 3 + 3$) form 18 bonding pairs. Thus, the parent structure of the Sb_{11} cage should be a 17 vertex *closo* polyhedron.¹³

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