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Synthesis and Structure of an $[Sb_{12}Se_{20}]^{4-}$ Salt: The Largest Molecular Zintl Ion

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The polyatomic anions of the post transition elements (the Zintl ions) have been known for many years but have only been fully characterized within the last 15 years.[1] However, these intriguing compounds have rapidly proven to be a rich source of novel chemistry, both in the chemistry of their complexation with transition metals[2] and in their own right as well.[3] We have been exploring the reactivity of main group anions with metal complexes in general and metal carbonyls in particular.[4] It was found that polychalcogenides readily induce oxidative decarbonylation of low-valent transition metal centers. The chalcogen–chalcogen bonds of the polychalcogenide chains act as the oxidant, leading to electron flow from the transition metal center, loss of some or all the coordinated carbonyls, and formation of a variety of novel metal chalcogenide clusters. We have been extending the synthetic strategy to mixed anions containing combinations of group 15 and 16 elements. These mixed clusters are intriguing in that the presence of trivalent centers creates the possibility for additional connectivity, greater cluster formation, and polymerization. While the chemistry is considerably more complex, we have been able to isolate a number of complexes and found that some patterns, such as the oxidative decarbonylation reactions, are similar to those of polychalcogenides.[5] We note that although a number of mixed 15/16 clusters have been reported in the literature, their occurrence is sporadic, especially for clusters involving combinations of heavier elements.[2,6,7] In this paper we report a significant extension of the known chemistry of the mixed main group clusters, namely the preparation of the first anionic molecular antimony selenide cluster, $Sb_{12}Se_{20}^{4-}$. By the conventional definition of a Zintl ion,[1] this compound is also, to our knowledge, the largest molecular Zintl ion reported to date.

The title compound can be prepared as its PPh_4^+ salt by the reduction of Sb_4Se_4 with potassium in DMF.[8] This results in dissolution of the antimony selenide presumably to form an anionic cluster. Upon addition of PPh_4Br, the product precipitates from solution as analytically pure, well-formed, orange, brick-shaped crystals. The product also forms from a solution containing Sb_2Se_3 reduced with potassium in similar fashion; however, no product can be isolated unless $Cr(CO)_6$ is also added. The role of $Cr(CO)_6$ is not clear, as it does not appear in the product but seems essential for product formation when Sb_2Se_3 is used as starting material. An IR spectrum of the reaction mixture after the metal carbonyl is added reveals a number of bands in the CO region,[8] indicating that some complexation has taken place, but as of yet no metal complex has been isolated. An amorphous orange powder having the same color as the title compound often also coprecipitates along with the orange crystals and is assumed to be the same product. The product is characterized by elemental analysis, far-IR, and single-crystal X-ray diffraction. The far-IR spectrum reveals a series of strong bands around 200 cm^{-1} which are presumably Sb–Se stretches.[8] Once formed, the product is slightly soluble in NMP but essentially insoluble in DMF and most other common solvents presumably because of its size and high charge density. Its general, insolubility precludes the obtaining of a ^{77}Se NMR spectrum.

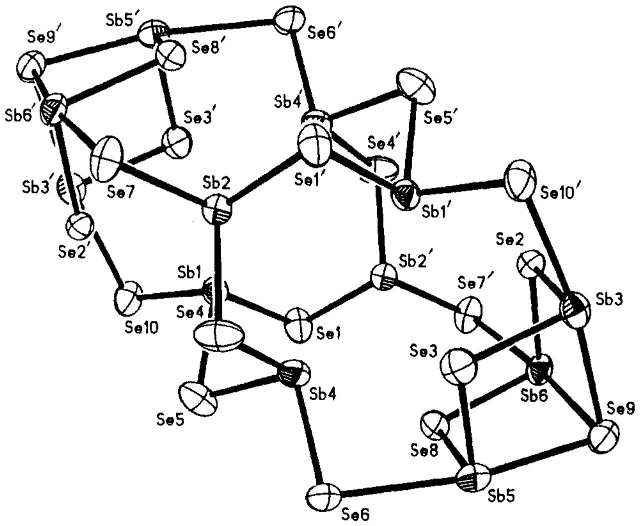

Figure 1. Thermal ellipsoid plot of the $Sb_{12}Se_{20}^{4-}$ anion (spheres at 35% probability level).

The crystal structure reveals that the unit cell contains the $Sb_{12}Se_{20}^{4-}$ ion along with well-separated Ph_4P^+ cations and two DMF molecules of solvation.[9] The anionic cluster contains two cubanes, each of which are missing a vertex, forming an Sb_3Se_7 terminus to each end of the molecule (Figures 1 and 2). The

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(8) The starting materials with nominal compositions Sb_2Se_3 and Sb_4Se_4 were prepared by heating stoichiometric quantities of the elements in a quartz tube at 650 °C for 10 h. In a typical reaction, 0.300 g (0.374 mmol) of Sb_4Se_4 and 0.029 g (0.748 mmol) of K were dissolved in 15 mL of dry DMF and the mixture was stirred at 23 °C overnight. The orange solution was filtered onto 0.313 g (0.748 mmol) of PPh_4Br, and the mixture was stirred for 1 h. The solution was filtered, and the filtrate was layered with 3 mL of diethyl ether. Storage at 4 °C for 4 days produced 90 mg of orange crystals (27% yield based on Se). In the alternative method, gray Sb_2Se_3 glass (0.300 g, 0.635 mmol) and elemental potassium (0.049 g, 12.25 mmol) were stirred in 10 mL of dry DMF overnight. To the resulting orange solution was added $Cr(CO)_6$ (0.137 g, 0.625 mmol), and resultant the solution was stirred for 5 h (solution IR 2031 (m), 1977 (s), 1920 (s), 1875 (m), 1860 (m), 1813 cm^{-1} (w)). After addition of Ph_4PBr (0.262 g, 0.625 mmol), the orange solution was filtered, and the filtrate was stored at 4 °C overnight. Orange powder and well-formed brick-shaped crystals could be isolated 20% yield (85 mg). Anal. Calcd for $C_{102}H_{94}N_2O_2P_4Sb_{12}Se_{20}$: C, 26.96; H, 2.09; N, 0.62. Found: C, 26.89; H, 2.19; N, 0.92. IR (cm^{-1}, Nujol mull): 352 (m), 225 (s), 199 (s), 181 (s).

(9) Crystal structure data for $C_{102}H_{94}N_2O_2P_4Sb_{12}Se_{20}$: triclinic space group $P\bar{1}$, $a = 14.127(3)$ Å, $b = 15.135(3)$ Å, $c = 16.234(6)$ Å, $\alpha = 69.32(2)°$, $\beta = 77.78(2)°$, $\gamma = 89.25(2)°$, $V = 3166$ Å^3, $Z = 1$, $D_x = 2.383$ g/cm^3, number of reflections observed 4259 ($F_o > 2\sigma(F_o)$), empirical absorption correction $\mu = 8.36$ mm^{-1}, $R = 0.0672$, $R_w = 0.0784$.

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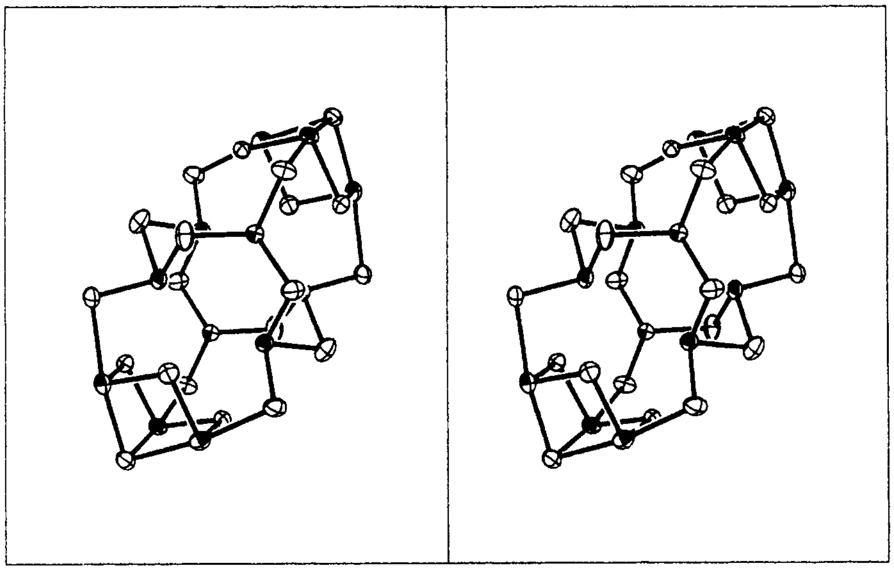

Figure 2. Stereoview of the $Sb_{12}Se_{20}^{4-}$ anion: shaded ellipsoids, antimony; unshaded ellipsoids, selenium.

Table 1. Selected Distances (Å) and Angles (deg) for $Sb_{12}Se_{20}^{4-}$

Se9–Sb3	2.796(5)	Sb6–Se9–Sb3	84.5(1)
Se9–Sb5	2.723(4)	Sb6–Se9–Sb5	86.4(1)
Se9–Sb6	2.969(4)	Sb3–Se9–Sb5	86.9(1)
Sb6–Se7′	2.719(4)	Se9–Sb6–Se7′	168.3(1)
Sb6–Se8	2.600(4)	Sb6–Se8–Sb5	97.6(1)
Sb6–Se2	2.583(5)	Sb6A–Se7–Sb2	95.0(1)
Sb2–Se1′	2.582(4)	Se7–Sb2–Se1′	97.2(1)
Sb2–Se4	2.587(5)	Se1A–Sb2–Se4	99.1(1)
Sb2–Se7	2.544(4)	Sb1–Se1–Sb2′	90.2(1)
		Se7–Sb2–Se4	97.1(1)

antimony atoms of the open cubes are four-coordinate and are connected to the antimony atoms of a Sb_6Se_6 ring by bridging selenides. The molecule is symmetrical in that it contains a crystallographic inversion center and a noncrystallographic 3-fold rotation axis. The overall effect is that of two three-legged spiders capping opposite sides of a 12-membered corrugated ring. The four-coordinate antimony atoms in the open cubes contain a lone pair of electrons occupying an equatorial position of a slightly distorted trigonal bipyramid (Table 1) (average Se_{ax}–Sb–Se_{ax} angle 169.8(1)°), in agreement with VSEPR predictions.[10,11] The antimony atoms in the 12-membered rings at the waist of the molecule are all trivalent and three-coordinate, with the lone pairs causing a small distortion from ideality (Se–Sb–Se angles ranging from 97.1(1) to 99.2(1)°). The Sb–Se distances (2.723(5)–2.969(4) Å) involving the selenides capping the end cubes are considerably longer than those involving the other selenides in the cubes or the selenides in the 12-membered rings (2.498(6)–2.610(4) Å). The Sb–Se distances for the selenides involved in bridging the uncapped cubes to the ring are also significantly longer (2.719(4)–2.825(5) Å). These distances and angles are comparable to those of a number of solid-state anionic antimony selenide chains which contain similar structural features.[12] It should be noted that there are examples of solid-state compounds containing open cubes as building blocks in these types of systems, although the connectivity is different.[12b,13]

There are a large number of outstanding polymeric solids containing mixed 15/16 chains along with a countercations, usually an alkali metal cation.[12-15] These compounds are usually combinations of arsenic or antimony and sulfur or selenium. The tendency of the group 15 element to assume tri- or tetravalent coordination along with the propensity of chalcogenides to bridge leads to the ready formation of complex one-dimensional chains and two-dimensional layers. Antimony in particular is of interest, since it has a greater tendency to expand its coordination environment compared to the lighter pnictides, having apparently equal desires to form both three- and four-coordinate environments. The presence of both φ-tetrahedral ME_3 and φ-trigonal bipyramidal ME_4 in various combinations leads to an enormous variety of structural possibilities. The two structural types can bridge and share vertices in any number of ways, leading to some very complex and elegant structures. The presence of vacant coordinate sites often leads to the formation of occlusions and microporous solids.[15a,b]

The title compound is strictly molecular but can be viewed as a fragment of a solid, since it has many of the structural features of solid alkali metal antimony chalcogenides.[12,14,15] In addition, its arachnid type structure creates two openings within the body of the molecule where the missing vertex of the cube should be. Such an enclosed lacunar structure is rare among molecules of this type. However, the large number of solid-state structures built of interconnected φ-tetrahedra and φ-trigonal bipyramids and the conceptually related molecular compound described here hint at the enormous number of discrete clusters awaiting characterization and study.

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Supplementary Material Available: Tables giving crystallographic information, atomic positional parameters, isotropic and anisotropic thermal parameters, and complete bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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