

# Arylstibonic acids $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$ ; precursors to organometallic isopolyoxostibonates $[\text{Na}_2\text{H}_9(\text{RSb})_{12}\text{O}_{30}]^-$ , (R = aryl).

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**Electrospray ionisation mass spectrometry shows that arylstibonic acids,  $\text{RSbO}_3\text{H}_2$ , give rise to oxo-bridged clusters derived from  $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$  which act as inorganic crown ligands towards  $\text{Na}^+$  cations; structure determination of one derivative revealed a cage-like anion  $[\text{Na}_2\text{H}_9(p\text{-O}_2\text{NC}_6\text{H}_4\text{Sb})_{12}\text{O}_{30}\cdot 4\text{H}_2\text{O}]^-$ .**

In contrast to the arylarsonic acids,  $\text{ArAsO}_3\text{H}_2$ , which are well-defined molecular species with four-coordinate As [1], arylstibonic acids have largely undetermined structures but are assumed to be oligomeric or polymeric in the solid state [2]. Mossbauer studies have been interpreted in terms of five-coordinate Sb [3]. Very recently, an example with a very bulky aryl group has been reported as an oxygen-bridged dimer,  $(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{Sb})_2\text{O}_2(\text{OH})_4$  [4].

We now report ESI-MS data for some arylstibonic acids which indicate high-nuclearity aggregation and show that these are a source of a novel class of well-defined polyoxometallates. The very extensive field of polyoxometallates (POMs) has been largely restricted to the early transition metals, especially Mo or W, as exemplified by the Keggin and Dawson ion families [5]. Main group elements, including As and Sb, have been incorporated into the framework to give hetero-POMs [6]. However there are very few previous reports of iso-POMs from the p-block elements [7].

A sample of  $\text{RSbO}_3\text{H}_2$  (R = *p*- $\text{ClC}_6\text{H}_4$ -) [8] was purified by dissolving in aqueous ammonia and allowing slow vapour diffusion of acetic acid to precipitate it as an off-white powder\*. This was soluble in MeCN and an ESI-MS of the resulting solution gave the spectrum shown in Fig 1. The dominant peak can be unambiguously assigned to  $[\text{H}_7(\text{RSb})_{12}\text{O}_{28}]^-$  ( $m/z$  3253.744 *c.f.* calc. 3253.756). The characteristic observed and calculated isotope patterns arising mainly from the two isotopes of Sb ( $^{121}\text{Sb}$  57%,  $^{123}\text{Sb}$  43%) and Cl ( $^{35}\text{Cl}$  75%,  $^{37}\text{Cl}$  25%) match perfectly. There was also the corresponding doubly-charged peak for  $[\text{H}_6(\text{RSb})_{12}\text{O}_{28}]^{2-}$  ( $m/z$  1626.379, calc. 1626.375). Each of these peaks had a satellite corresponding to the analogues with one  $\text{H}^+$  replaced by a  $\text{Na}^+$ . There are some less intense peaks which arise from higher nuclearities, but clearly the  $\text{Sb}_{12}$  one is most favoured under these conditions.

If the stibonic acid is not carefully purified, or if a small amount of NaOH is added\*\*, or even if the solution of the purified sample is left standing in normal glassware, the parent acid peaks are completely replaced by those of the sodium adducts  $[\text{Na}_3\text{H}_3(\text{RSb})_{12}\text{O}_{28}]^{2-}$  ( $m/z$  1659.343, calc. 1659.347),  $[\text{Na}_2\text{H}_4(\text{RSb})_{12}\text{O}_{28}]^{2-}$  ( $m/z$  1648.354 calc 1648.356), and  $[\text{NaH}_5(\text{RSb})_{12}\text{O}_{28}]^{2-}$  ( $m/z$  1637.361, calc. 1637.365). The corresponding singly-charged ions  $[\text{Na}_4\text{H}_3(\text{RSb})_{12}\text{O}_{28}]^-$  and  $[\text{Na}_3\text{H}_4(\text{RSb})_{12}\text{O}_{28}]^-$  were represented in the region around  $m/z$  3300.

Other stibonic acids  $\text{RSbO}_3\text{H}_2$  for R' = *p*- $\text{CH}_3\text{C}_6\text{H}_4$  and R'' = *p*- $\text{O}_2\text{NC}_6\text{H}_4$  under the same conditions behaved identically, giving the same series of sodium adduct ions.

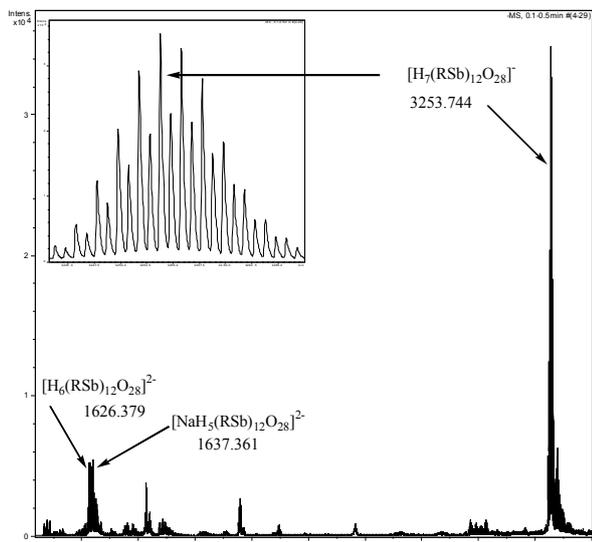


Figure 1. The ESI-MS of ' $\text{RSbO}_3\text{H}_2$ ' in MeCN showing ions derived from the cluster  $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$  (R = *p*- $\text{ClC}_6\text{H}_4$ -). The inset is an expansion of the  $m/z$  3253 envelope showing the characteristic isotope pattern.

We have not yet obtained single crystals of the parent acid suitable for structure determination, but when the solution formed by dissolving *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{SbO}_3\text{H}_2$  in NaOH was treated with  $[\text{PhCH}_2\text{NMe}_3]\text{Br}$ , slow evaporation provided crystals\*\*\* suitable for X-ray

structure determination<sup>††</sup>. This revealed the anion shown in Fig 2, as part of an overall formula of  $\text{PhCH}_2\text{NMe}_3[\text{Na}_2\text{H}_9(p\text{-O}_2\text{NC}_6\text{H}_4\text{Sb})_{12}\text{O}_{30}\cdot 4\text{H}_2\text{O}]\cdot x\text{H}_2\text{O}$ . The nine H atoms of the anion were not located directly, but are required for charge neutrality; six of them will probably be associated with the terminal O atoms (see below) as  $-\text{OH}$  groups, while the other three are presumably attached to cage O atoms. In addition to the four  $\text{H}_2\text{O}$  molecules closely associated with the anion by coordination to  $\text{Na}^+$ , there are also many other

water molecules in the lattice which are poorly defined, as is common in structures of this type. The anion is a cage formed by twelve hexa-coordinate  $\text{R}^{\text{''}}\text{Sb}$  groups at the apices of a hexagonal antiprism, linked by O atoms. Six of the Sb atoms are arranged in a puckered hexagonal array (av.  $\text{Sb}\dots\text{Sb}$  3.640 Å), with the other six in a planar hexagonal array (av.  $\text{Sb}\dots\text{Sb}$  3.135 Å) parallel to it, and *ca* 3 Å apart. The oxygen atoms can be divided into eighteen  $\mu_2\text{-O}$ , six  $\mu_3\text{-O}$  and six terminal ones (presumably  $-\text{OH}$ s). The average Sb-O distances are 1.980, 2.088 and 1.979 Å respectively for the  $\mu_2$ ,  $\mu_3$  and terminal examples.

The overall symmetry of the cage, ignoring the conformation of the aryl rings, is  $\text{C}_{3v}$ ; with the rings included the anion has crystallographically-imposed mirror symmetry.

Held within the cage are two  $\text{Na}^+$  ions. Na(1) has an unusual 10-coordination. Six of the coordination sites are occupied by a planar hexagonal array of the  $\mu_2\text{-O}$  atoms from the puckered Sb layer ( $\text{Na}\dots\text{O}$  (av.) 2.777 Å). The  $\text{Na}^+$  is displaced 0.76 Å out of the oxygen plane towards the interior of the cage. The remaining coordination is from three of the  $\mu_3\text{-O}$  atoms that link the two Sb layers together ( $\text{Na}\dots\text{O}$  (av.) 2.570 Å), with a coordinated  $\text{H}_2\text{O}$  occupying the 10<sup>th</sup> site on the other side of the hexagon ( $\text{Na}\dots\text{O}$  2.68(3) Å). This hexagonal-planar site is clearly analogous to those in ligands such as crown ethers while the truncated conical void within which the ion is embraced suggests a cavitated cage. A similarly-held cation site was described by Cronin *et al* [9] for the inorganic crown POM  $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$ , though for their example the O atoms were from terminal oxo ligands which formed a puckered ring in contrast to crown-ethers which have a planar array of bridging oxygens. Our example is a closer analogue with a planar array of  $\mu\text{-O}$  atoms providing coordination, and with average cross-ring  $\text{O}\dots\text{O}$  distances of 5.34 Å compared with values of *ca* 5.5 Å in 18-crown-6 ligands [10].

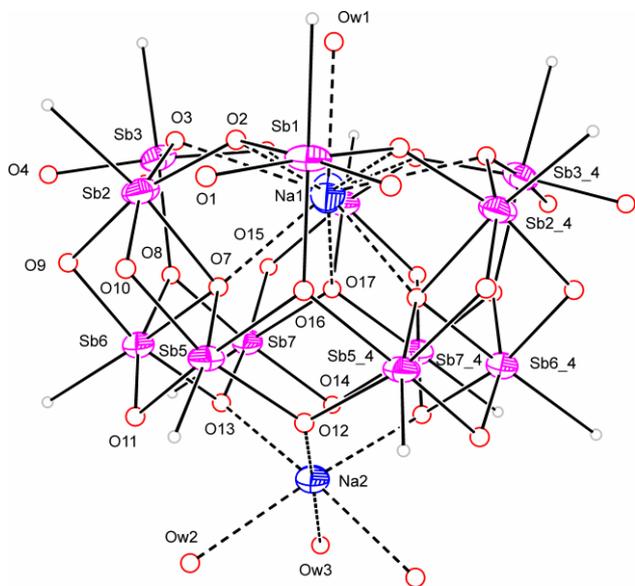


Figure 2. The core structure of the anion revealed in the crystal structure determination of  $(\text{PhCH}_2\text{NMe}_3)[\text{Na}_2\text{H}_9(\text{R}^{\text{''}}\text{Sb})_{12}\text{O}_{30}(\text{H}_2\text{O})_4]\cdot x\text{H}_2\text{O}$  ( $\text{R}^{\text{''}} = p\text{-O}_2\text{NC}_6\text{H}_4\text{-}$ ). The red circles are oxygen atoms, and the small grey circles represent the *ipso* carbon atoms of the  $p\text{-O}_2\text{NC}_6\text{H}_4\text{-}$  rings.

Na(2) is six-coordinate with three sites occupied by  $\mu_2\text{-O}$  atoms from the anion and the other three by coordinated water molecules. The mass spectrometry experiments indicate that the coordinated water molecules are readily lost, and one  $\text{Na}^+$ , presumably Na(2), can be extruded, but the remaining  $\text{Na}^+$  is held tenaciously and no ions were observed in the ESI-MS where this had been removed, even under quite severe conditions.

There is a difference in the apparent degree of hydration of the core-cluster unit between the ESI-MS results in MeCN, which indicate a parent formula  $[\text{H}_9(\text{RSb})_{12}\text{O}_{28}]$ , and the crystal structure result which is derived from  $[\text{H}_{12}(\text{RSb})_{12}\text{O}_{30}]$  after crystallisation from aqueous solutions, a difference of  $2\text{H}_2\text{O}$ . It is not yet clear whether this arises from the different solvent conditions or from very facile loss of two  $\text{H}_2\text{O}$  in the mass spectrum, possibly by condensation of four of the terminal  $-\text{OH}$  groups to give two more  $\mu\text{-O}$  units. Previous reports suggest that ESI-MS results for POMs usually, but not always, provide a good correlation between species in solution, and those subsequently crystallised [11].

The core structure of the  $p\text{-O}_2\text{NC}_6\text{H}_4\text{Sb}$  polyoxometallate has been reported before as part of a complex structure assigned the overall formula  $[\text{Na}_{21}(\text{PhSb})_{48}\text{O}_{114}]\cdot 46\text{H}_2\text{O}\cdot 4\text{MeCN}$ , isolated in small yields from a reaction mixture consisting of  $\text{PhSbO}_3\text{H}_2$ ,  $\text{Ni}^{2+}$  and  $\text{NaOMe}$  in  $\text{MeCN}/\text{H}_2\text{O}$  [12]. The  $[\text{Na}_2\text{H}_9(\text{ArSb})_{12}\text{O}_{30}\cdot 4\text{H}_2\text{O}]$  cores of both structures are essentially superimposable, despite the different aryl groups and crystal packing arrangements. We also have preliminary crystal structures of the corresponding  $\text{Rb}[\text{Na}_2\text{H}_9(p\text{-MeC}_6\text{H}_4\text{Sb})_{12}\text{O}_{30}\cdot 4\text{H}_2\text{O}]$  and  $\text{Ph}_4\text{P}[\text{Na}_2\text{H}_9(p\text{-MeC}_6\text{H}_4\text{Sb})_{12}\text{O}_{30}\cdot 4\text{H}_2\text{O}]$  analogues and they also have the same core structure, so this appears to be a highly conserved arrangement.

The stability of this (ArSb)<sub>12</sub> unit is further shown by related structures formed with other cations. When *p*-MeC<sub>6</sub>H<sub>4</sub>SbO<sub>3</sub>H<sub>2</sub> was dissolved using KOH in place of NaOH a solid was obtained for which the dominant signal in ESI-MS was assigned to [K<sub>3</sub>H<sub>7</sub>(*p*-MeC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>30</sub>]<sup>2-</sup> (*m/z* 1579.647 calc. 1579.651). Similarly with Ca(OH)<sub>2</sub> as base, the product gave ESI-MS peaks for [Ca<sub>2</sub>H<sub>6</sub>(*p*-MeC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>30</sub>]<sup>2-</sup> (*m/z* 1560.679 calc. 1560.664). Conversely LiOH or CsOH gave a different range of polyoxostibonates which have yet to be characterised fully, suggesting Li<sup>+</sup> is too small, and Cs<sup>+</sup> too large, to be complexed within the same species.

The strong affinity for Na<sup>+</sup> was illustrated when *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SbO<sub>3</sub>H<sub>2</sub> was dissolved using Et<sub>3</sub>N as base; the main product was shown by ESI-MS to be the sodium adduct [Na<sub>2</sub>H<sub>4</sub>(*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup> presumably formed from adventitious Na<sup>+</sup> from the glassware, or carried over from synthesis of the acid. Similarly when the [Na<sub>2</sub>H<sub>4</sub>(*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup> complexes are mixed with an aqueous solution of Rb<sup>+</sup>, there is little if any exchange of cations, as shown by ESI-MS.

In conclusion, we have shown that RSbO<sub>3</sub>H<sub>2</sub> forms an aggregate [H<sub>8</sub>(RSb)<sub>12</sub>O<sub>28</sub>], at least when crystallised from NH<sub>3</sub>(aq)/HOAc. This serves as a parent for a novel range of isopolyoxostibonates, stable under alkaline conditions (it is noteworthy that transition-metal POMs form under *acid* conditions). The cage behaves as an inorganic crown ligand, with a strong affinity for Na<sup>+</sup> and other similarly-sized cations. The new species can be synthesised with a variety of different aryl groups which should allow some tuning of electronic and steric properties. There is ESI-MS evidence for other high-nuclearity POMs based on polyoxostibonates, as yet not fully characterised, which may be optimised with different cations or conditions. There is also clearly potential to use arylstibonic acids for a range of hetero-POMs.

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† C<sub>82</sub>H<sub>81</sub>N<sub>13</sub>Na<sub>2</sub>O<sub>58</sub>Sb<sub>12</sub>.xH<sub>2</sub>O, *M<sub>r</sub>* 3683.58, monoclinic, space group C2/m, *a* 30.6262(6), *b* 22.5295(4), *c* 25.1789(8)Å, β = 122.569(1)°, *U* 14641.2(6) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* 1.671 g cm<sup>-3</sup>, μ(Mo-Kα) 2.26 mm<sup>-1</sup>, *F*(000) 7048. *T* 90(2) K. Crystal size 0.31 x 0.17 x 0.14 mm<sup>3</sup>. Total data 165946, unique data 16399 (*R<sub>int</sub>* 0.083), observed (*I* > 2σ(*I*)) data 10514, θ range 2-27°. Refinement (on *F<sub>o</sub>*<sup>2</sup>) converged with *R<sub>1</sub>* 0.0620 (*I* > 2σ(*I*)), *wR<sub>2</sub>* 0.1917 (all data), *GoF* 1.138, Δ*e* = 2.3/-1.6 e Å<sup>-3</sup>. Only the four H<sub>2</sub>O molecules coordinated to the Na<sup>+</sup> cations have been included in the formula and *M<sub>r</sub>* calculation; lattice H<sub>2</sub>O molecules (approximately 15 of them) were poorly defined so were removed from the refinement using the SQUEEZE procedure of PLATON<sup>13</sup>.

\* Preparation of [H<sub>8</sub>(RSb)<sub>12</sub>O<sub>28</sub>] (R = *p*-ClC<sub>6</sub>H<sub>4</sub>-). A sample of RSbO<sub>3</sub>H<sub>2</sub> (R = *p*-ClC<sub>6</sub>H<sub>4</sub>-) was purified by suspending a small sample (*ca* 0.5 g) in water, and adding NH<sub>3</sub>(aq) (2 mol L<sup>-1</sup>) dropwise until dissolution was just effected. The open flask was placed in a desiccator containing conc. CH<sub>3</sub>COOH, which was allowed to diffuse into the stibonic acid solution, and precipitate the product as an off-white powder. Found: C 26.93; H 2.46. Calc. for C<sub>72</sub>H<sub>56</sub>Cl<sub>12</sub>O<sub>28</sub>Sb<sub>28</sub> C 26.56; H 1.73%. ESI-MS (a fresh sample in MeCN): (*m/z* (calc), assignment, relative intensity): 3275.719 (3275.738), [NaH<sub>6</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>-</sup>, 18%; 3253.744 (3253.756), [H<sub>7</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>-</sup>, 100%; 3025.866, 3007.859, 2989.844, 2969.837, (all 1<sup>-</sup> ions, unassigned, appear to be Sb<sub>11</sub> species) 2565.054 (3<sup>-</sup> ion, unassigned, appears to be Sb<sub>28</sub> species); 2157.189 (2157.162) [H<sub>6</sub>(RSb)<sub>16</sub>O<sub>36</sub>]<sup>2-</sup>, 9%; 1826.314 (2<sup>-</sup> ion, unassigned, appears to be Sb<sub>13</sub> species); 1648.353 (1648.356), [Na<sub>2</sub>H<sub>4</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup>, 4%; 1637.361 (1637.365), [NaH<sub>5</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup>, 18%; 1626.366 (1626.375), [H<sub>6</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup>, 18%.

\*\* Preparation of sodium salt solutions from [H<sub>8</sub>(RSb)<sub>12</sub>O<sub>28</sub>] (R = *p*-ClC<sub>6</sub>H<sub>4</sub>-). RSbO<sub>3</sub>H<sub>2</sub> (R = *p*-ClC<sub>6</sub>H<sub>4</sub>-) was suspended in water and an aqueous solution of NaOH (2 mol L<sup>-1</sup>) was added dropwise until the solid had dissolved. This solution was allowed to evaporate until a white powder formed. This was filtered and dried. A small portion of the solid was dissolved in MeCN and examined by ESI-MS: (*m/z* (calc), assignment): 3341.684 (3341.642) [Na<sub>4</sub>H<sub>3</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>-</sup>; 3319.702 (3341.664) [Na<sub>3</sub>H<sub>4</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>-</sup>; 1659.343 (1659.347) [Na<sub>3</sub>H<sub>3</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup>; 1648.354 (1648.356) [Na<sub>2</sub>H<sub>4</sub>(RSb)<sub>12</sub>O<sub>28</sub>]<sup>2-</sup>. The same peaks were observed if a drop of NaOH solution was added to a MeCN solution of purified [H<sub>8</sub>(RSb)<sub>12</sub>O<sub>28</sub>].

\*\*\* Isolation of crystals of (PhCH<sub>2</sub>NMe<sub>3</sub>) [Na<sub>2</sub>H<sub>9</sub>(R"SB)<sub>12</sub>O<sub>30</sub>(H<sub>2</sub>O)<sub>4</sub>].xH<sub>2</sub>O. (R" = *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-). *p*-Nitrophenylstibonic acid (245 mg, 8.4 x 10<sup>-4</sup> mol) was dissolved in water (50 ml) containing 0.6 ml 2 M NaOH (pH = 11.2). Ten ml of this solution (1.7 x 10<sup>-4</sup> mol stibonic acid, 2.4 x 10<sup>-4</sup> mol Na<sup>+</sup>) was subsequently combined with benzyltrimethyl ammonium bromide (46 mg, 2 x 10<sup>-4</sup> mol) dissolved in water (1 ml) forming a fine pale-yellow precipitate. The solution was left to evaporate to dryness. The dried precipitate crystallised from 2:1 (v/v) acetonitrile/water solution (6 ml) by slow evaporation, where-upon pale-yellow needles formed within 3 weeks.

\*\*\*\* This formula does not appear complete from charge neutrality considerations; [Na<sub>21</sub>H<sub>15</sub>(PhSb)<sub>48</sub>O<sub>114</sub>] is more probable.

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## Supplementary Information.

The arylstibonic acids, nominally  $\text{RSbO}_3\text{H}_2$ , were synthesised using the method described by Doak and Steinman, *J. Am. Chem. Soc.*, 1946, **68**, 1987, for  $\text{R} = p\text{-H}_3\text{CC}_6\text{H}_4\text{-}$ ,  $p\text{-ClC}_6\text{H}_4\text{-}$  and  $p\text{-O}_2\text{NC}_6\text{H}_4\text{-}$ .

This involves purification as crystalline  $[\text{pyH}]^+[\text{RSbCl}_5]^-$ , then hydrolysing to the acid with  $\text{NaHCO}_3$  so the acid is formed in the presence of excess  $\text{Na}^+$  cations and precipitates as an amorphous powder.

ESI-MS were carried out on a Bruker MicroTOF, operating in negative-ion mode, using direct injection of the solutions via a syringe pump ( $3 \mu\text{L min}^{-1}$ ).

### Preparation of $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$ ( $\text{R} = p\text{-ClC}_6\text{H}_4\text{-}$ ).

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A sample of  $\text{RSbO}_3\text{H}_2$  ( $\text{R} = p\text{-ClC}_6\text{H}_4\text{-}$ ) was purified by suspending a small sample (*ca* 0.5 g) in water, and adding  $\text{NH}_3(\text{aq})$  ( $2 \text{ mol L}^{-1}$ ) dropwise until dissolution was just effected. The open flask was placed in a desiccator containing conc.  $\text{CH}_3\text{COOH}$ , which was allowed to diffuse into the stibonic acid solution, and precipitate the product as an off-white powder. Found: C 26.93; H 2.46. Calc. for  $\text{C}_{72}\text{H}_{56}\text{Cl}_{12}\text{O}_{28}\text{Sb}_{12}$  C 26.56; H 1.73%. ESI-MS (a fresh sample in MeCN): (*m/z* (calc), assignment, relative intensity): 3275.719 (3275.738),  $[\text{NaH}_6(\text{RSb})_{12}\text{O}_{28}]^-$ , 18%; 3253.744 (3253.756),  $[\text{H}_7(\text{RSb})_{12}\text{O}_{28}]^-$ , 100%; 3025.866, 3007.859, 2989.844, 2969.837, (all  $1^-$  ions, unassigned, appear to be  $\text{Sb}_{11}$  species) 2565.054 ( $3^-$  ion, unassigned, appears to be  $\text{Sb}_{28}$  species); 2157.189 (2157.162)  $[\text{H}_6(\text{RSb})_{16}\text{O}_{36}]^{2-}$ , 9%; 1826.314 ( $2^-$  ion, unassigned, appears to be  $\text{Sb}_{13}$  species); 1648.353 (1648.356),  $[\text{Na}_2\text{H}_4(\text{RSb})_{12}\text{O}_{28}]^{2-}$ , 4%; 1637.361 (1637.365),  $[\text{NaH}_5(\text{RSb})_{12}\text{O}_{28}]^{2-}$ , 18%; 1626.366 (1626.375),  $[\text{H}_6(\text{RSb})_{12}\text{O}_{28}]^{2-}$ , 18%.

### Preparation of sodium salt solutions from $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$ ( $\text{R} = p\text{-ClC}_6\text{H}_4\text{-}$ ).

$\text{RSbO}_3\text{H}_2$  ( $\text{R} = p\text{-ClC}_6\text{H}_4\text{-}$ ) was suspended in water and an aqueous solution of  $\text{NaOH}$  ( $2 \text{ mol L}^{-1}$ ) was added dropwise until the solid had dissolved. This solution was allowed to evaporate until a white powder formed. This was filtered and dried.

A small portion of the solid was dissolved in MeCN and examined by ESI-MS: (*m/z* (calc), assignment): 3341.684 (3341.642)  $[\text{Na}_4\text{H}_3(\text{RSb})_{12}\text{O}_{28}]^-$ ; 3319.702 (3341.664)  $[\text{Na}_3\text{H}_4(\text{RSb})_{12}\text{O}_{28}]^-$ ; 1659.343 (1659.347)  $[\text{Na}_3\text{H}_3(\text{RSb})_{12}\text{O}_{28}]^{2-}$ ; 1648.354 (1648.356)  $[\text{Na}_2\text{H}_4(\text{RSb})_{12}\text{O}_{28}]^{2-}$ .

The same peaks were observed if a drop of  $\text{NaOH}$  solution was added to a MeCN solution of purified  $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$ .

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**Isolation of crystals of  $(\text{PhCH}_2\text{NMe}_3)[\text{Na}_2\text{H}_9(\text{RSb})_{12}\text{O}_{30}(\text{H}_2\text{O})_4]\cdot 15\text{H}_2\text{O}$ . ( $\text{R} = p\text{-O}_2\text{NC}_6\text{H}_4\text{-}$ ).**

*p*-Nitrophenylstibonic acid (245 mg,  $8.4 \times 10^{-4}$  mol) was dissolved in water (50 ml) containing 0.6 ml 2 M NaOH (pH = 11.2). Ten ml of this solution ( $1.7 \times 10^{-4}$  mol stibonic acid,  $2.4 \times 10^{-4}$  mol  $\text{Na}^+$ ) was subsequently combined with benzyltrimethyl ammonium bromide (46 mg,  $2 \times 10^{-4}$  mol) dissolved in water (1 ml) forming a fine pale-yellow precipitate. The solution was left to evaporate to dryness. The dried precipitate crystallised from 2:1 (v/v) acetonitrile/water solution (6 ml) by slow evaporation, where-upon pale-yellow needles formed within 3 weeks.

**X-ray crystal structure determination of  $(\text{PhCH}_2\text{NMe}_3)\text{Na}_2[\text{H}_3(p\text{-O}_2\text{NC}_6\text{H}_4\text{SbO}_2)_{12}(\text{OH})_6(\text{H}_2\text{O})_4]\cdot \text{ca } 15\text{H}_2\text{O}$ .**

Crystals needed to be kept moist or they rapidly lost crystallinity, presumably through loss of water from the lattice.

Crystal and intensity data were collected on a Bruker APEX II diffractometer at 90 K, and corrected for absorption using a multi-scan method (SADABS). The crystals gave moderate diffraction, with an average  $I/\sigma(I)$  of 4.99.

The structure was solved by direct methods (SHELXS97) to give the positions of the Sb atoms, showing the anion was on the mirror plane of space group  $C2/m$ . A subsequent difference map showed all the anion O atoms and the two  $\text{Na}^+$  cations. With further cycles the aryl rings were located, but some were partially disordered. The two aryl rings that are bisected by the mirror plane were disordered across the plane so were refined as rigid hexagons with isotropic temperature factors, and no H atoms included. The other aryl rings were linked via SAME constraints, with temperature factors constrained by the SIMU and DELU options of SHELXL97.

The  $\text{PhCH}_2\text{NMe}_3$  cation was found to be disordered over two symmetry equivalent sites, with 50% occupancy, and the phenyl ring was constrained to a rigid hexagon with the AFIX 66 instruction, and the N and C atoms of the  $\text{NMe}_3$  group were treated isotropically because of partial disorder, again with H atoms omitted.

Four  $\text{H}_2\text{O}$  molecules coordinated to  $\text{Na}^+$  cations were well defined, as was one that was firmly H-bonded to the anion. In addition there were at least 15 lattice water molecules revealed in difference maps, some clearly having partial occupancy or loosely held positions. These

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could not be sensibly modelled so the data was treated using the SQUEEZE option of PLATON. This indicated a total void volume of *ca* 3594 Å<sup>3</sup> in the unit cell.

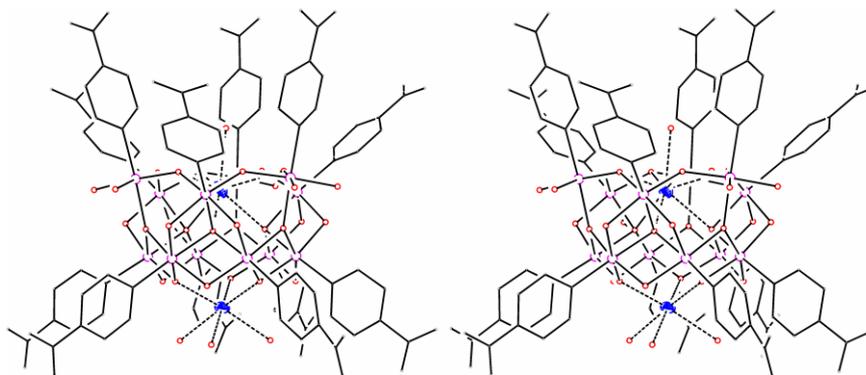
Final refinement therefore excluded this diffuse lattice water, and calculations of density etc also ignore this contribution. The H atoms were included in calculated positions for the ordered rings of the cation and anion, but those of the disordered rings, the methyl groups and the water molecules were omitted.

### Crystal and refinement data.

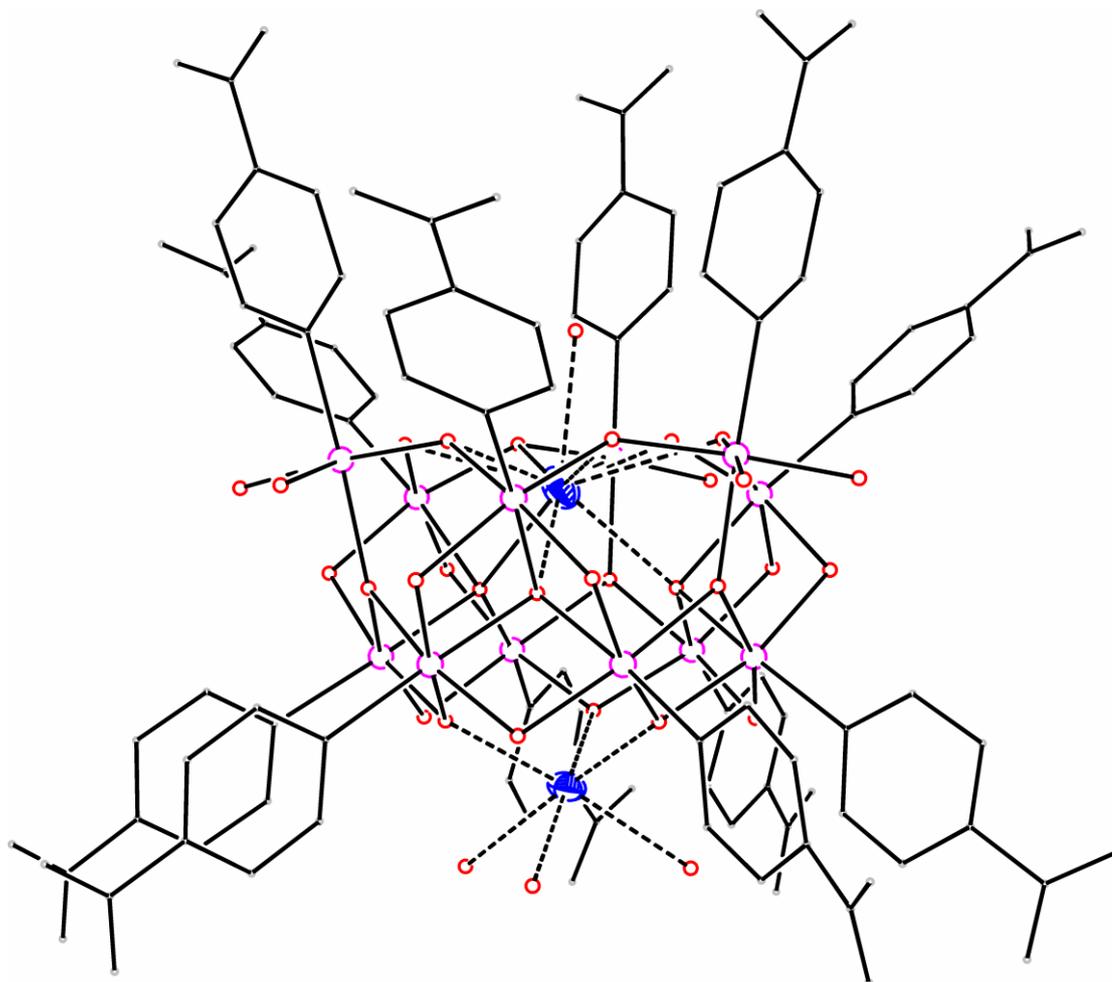
<sup>10</sup> C<sub>84</sub>H<sub>111</sub>N<sub>13</sub>Na<sub>2</sub>O<sub>73</sub>Sb<sub>12</sub>, M<sub>r</sub> 3960.37, monoclinic, space group C2/m, *a* 30.6262(6), *b* 22.5295(4), *c* 25.1789(8)Å, β = 122.569(1)°, U 14641.2(6) Å<sup>3</sup>, Z = 4, D<sub>c</sub> 1.797 g cm<sup>-3</sup>, μ(Mo-Kα) 2.27 mm<sup>-1</sup>, F(000) 7674. T 90(2) K. Crystal size 0.31 x 0.17 x 0.14 mm<sup>3</sup>. Total data 165946, unique data 16399 (R<sub>int</sub> 0.092), observed (I>2σ(I)) data 10514, θ range 2-27°.

Refinement converged with R<sub>1</sub> 0.0683 (I>2σ(I)), wR<sub>2</sub> 0.2356 (all data), GoF 1.051, Δe = 3.6/-2.0 e Å<sup>-3</sup>.

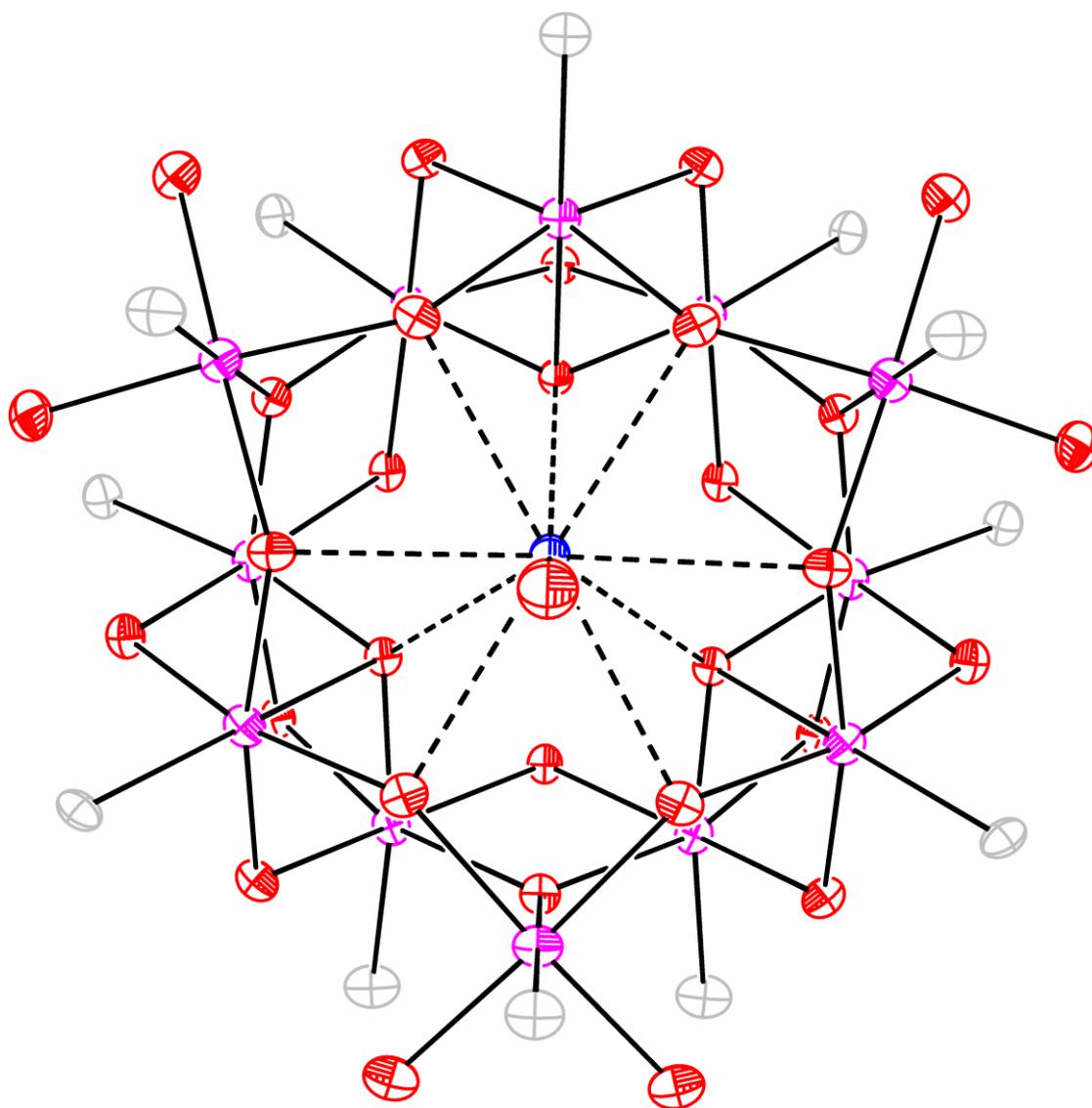
<sup>15</sup>



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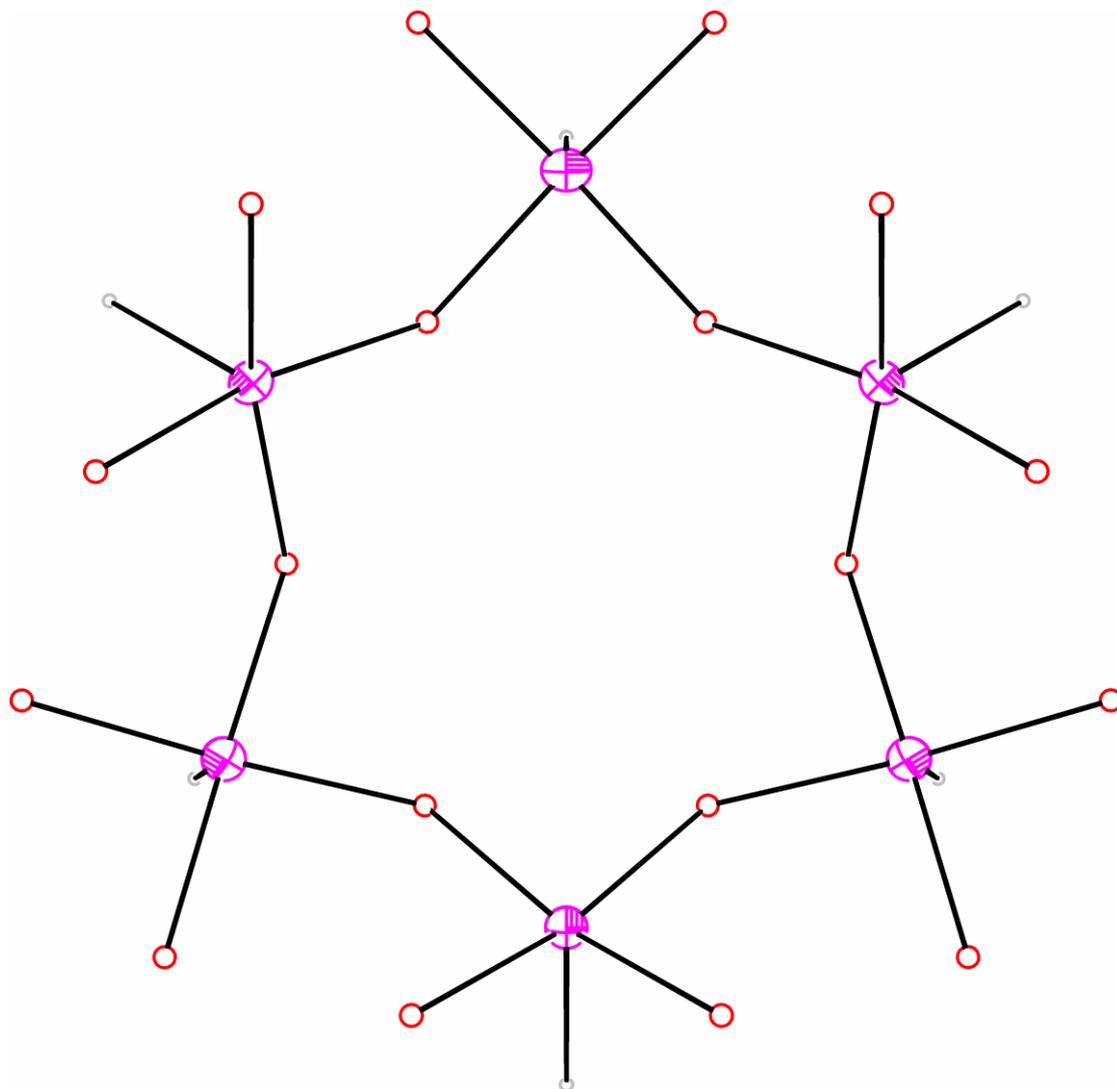


Supplementary figure 1.  
10 Stereo and mono views of the anion with aryl rings included.



Supplementary figure 2. A view of the cluster along the Na1...Na2 vector, showing the C<sub>3v</sub> symmetry of the anion with aryl rings omitted.

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Supplementary Figure 3.

10 Part of the lower layer of the anion with the  $\text{Na}^+$  cation omitted, showing the similarity to a crown-6 ligand. The larger circles are O atoms, the smaller ones are the *ipso* C atoms of the aryl rings.