

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

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 NaOH solution was added to a MeCN solution of purified  $[\text{H}_8(\text{RSb})_{12}\text{O}_{28}]$ .

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

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

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 NMe<sub>3</sub> group were treated isotropically because of partial disorder, again with H atoms omitted.

Four H<sub>2</sub>O molecules coordinated to Na<sup>+</sup> cations were well defined, so were included. In addition there were at least 15 lattice water molecules revealed in difference maps, some clearly having partial occupancy or loosely held positions. These 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, containing *ca* 568 electrons. This would correspond to 15-20 H<sub>2</sub>O molecules in the asymmetric unit.

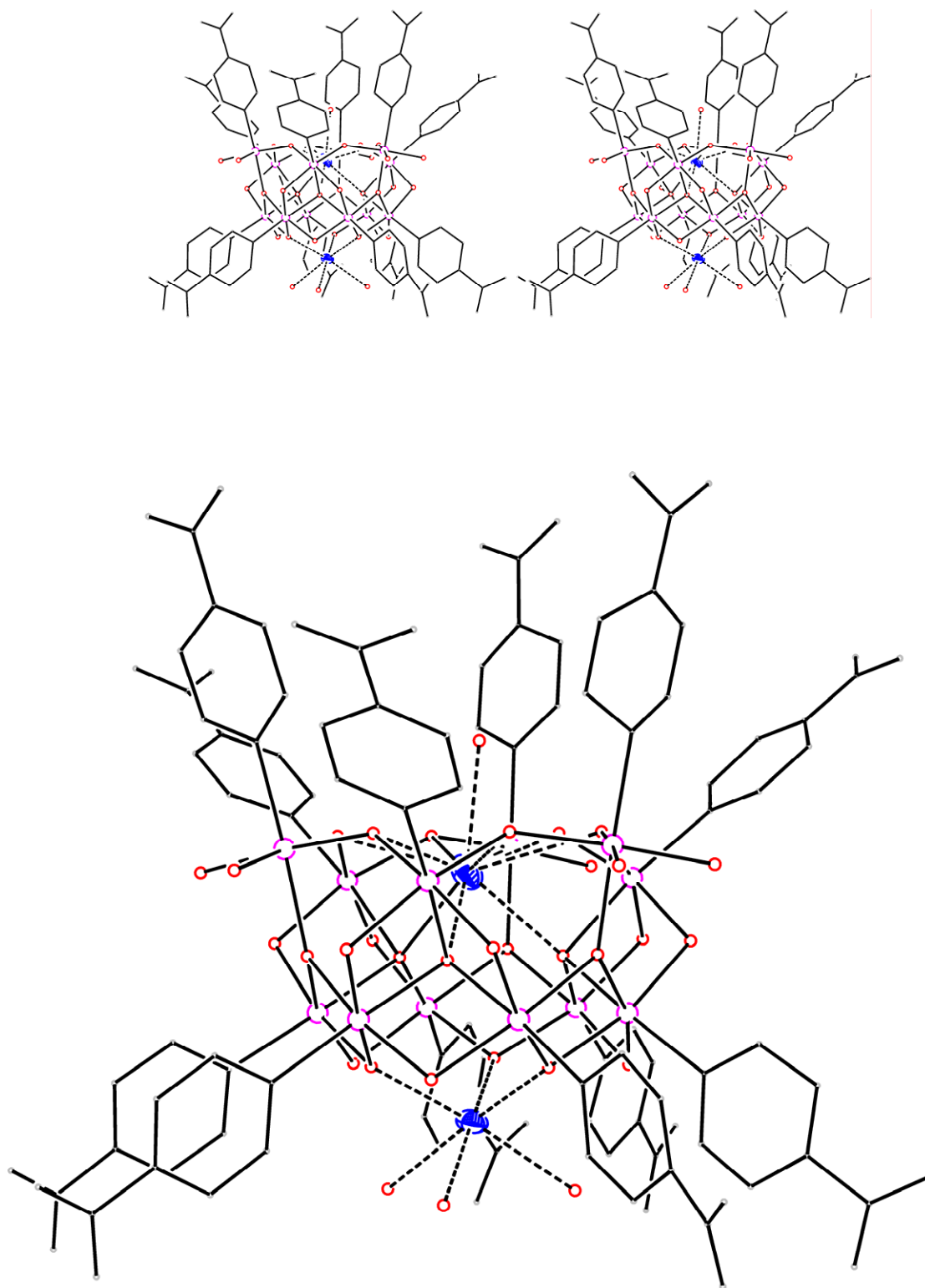
Final refinement therefore excluded this diffuse lattice water, and calculations of density etc also ignore this contribution. The H atoms were included in calculated positions for the ordered rings of the cation and anion, but those of the disordered rings, the methyl groups and the water molecules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

#### **Crystal and refinement data.**

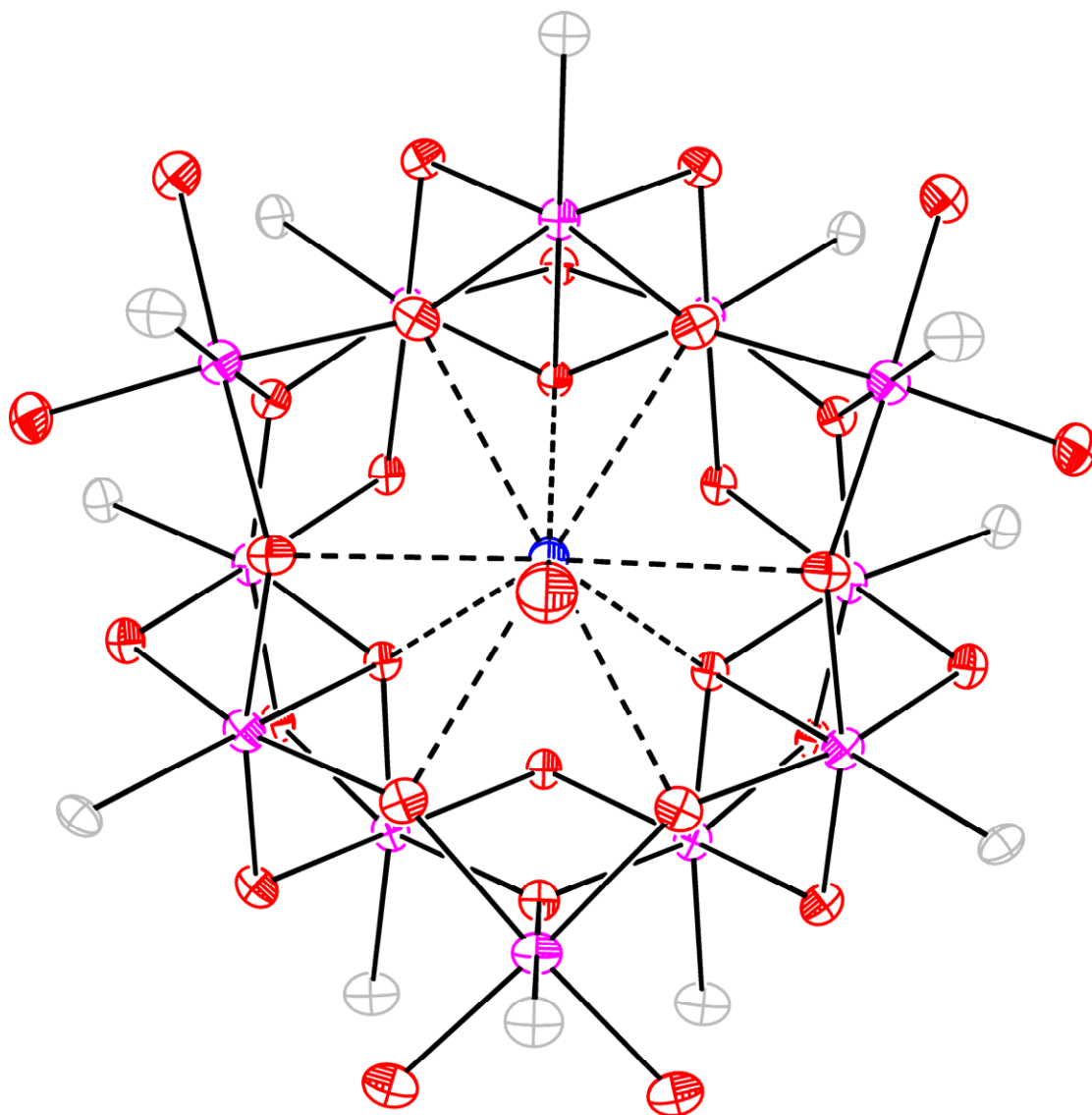
C<sub>82</sub>H<sub>81</sub>N<sub>13</sub>Na<sub>2</sub>O<sub>58</sub>Sb<sub>12</sub>, M<sub>r</sub> 3683.58, monoclinic, space group C2/m, *a* 30.6262(6), *b* 22.5295(4), *c* 25.1789(8)Å, β = 122.569(1)°, U 14641.2(6) Å<sup>3</sup>, Z = 4, D<sub>c</sub> 1.671 g cm<sup>-3</sup>\*, μ(Mo-Kα) 2.26 mm<sup>-1</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 converged with R<sub>1</sub> 0.0620 (I > 2σ(I)), wR<sub>2</sub> 0.1917 (all data), GoF 1.138, Δe = 2.3/-1.6 e Å<sup>-3</sup>.

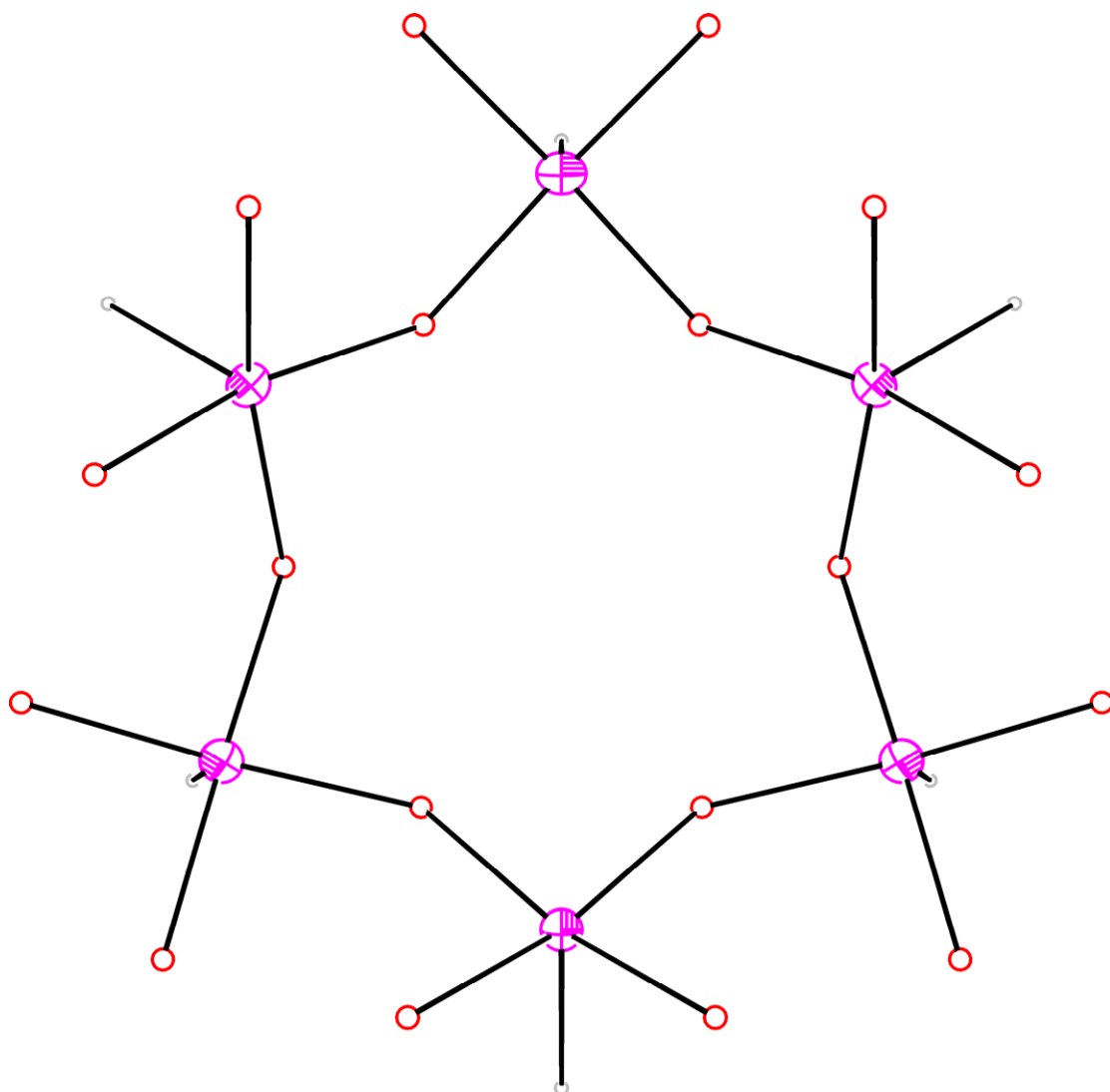
\* These are calculated ignoring the diffuse water of crystallisation in the lattice so will be under-estimated



Supplementary figure 1.  
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.



Supplementary Figure 3.

Part of the pucker 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.