Isopolyoxometalates of Antimony: Arylstibonic Acids [H₈(RSb)₁₂O₂₈] and Derived Dodecanuclear Polyoxostibonates $[M_2H_{10-x}(RSb)_{12}O_{30}]^{x-}$, M = Na or K

Brian K. Nicholson,^{*,†} Christopher J. Clark,[‡] Cody E. Wright,[†] and Tania Groutso[§]

[†]Chemistry Department, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand, * Bioengineering Technologies, Plant and Food Research, Ruakura Research Centre, Private Bag 3123, Hamilton 3240, New Zealand, and [§]Chemistry Department, University of Auckland, PO Box 92019, Auckland, New Zealand

Received September 7, 2010

Electrospray ionization mass spectrometry shows arylstibonic acids, $p-XC_6H_4SbO_3H_2$ (X = methyl, nitro, or chloro), and 1-naphthylstibonic acid exist in MeCN as dodecanuclear aggregates $[H_8(RSb)_{12}O_{28}]$. With KOH or NaOH these form polyoxometalate ions $[M_2H_8(RSb)_{12}O_{30}]^{2-}$ (M = K or Na) with a hexagonal antiprismatic array of the Sb atoms, as shown by X-ray crystallographic structures for three new examples. There is one firmly encapsulated 10-coordinate M^+ ion within an inorganic 12-crown-6 moiety $\{Sb_6O_6\}$ in the hexagonal channel and one six-coordinate M^+ .

Introduction

Arylstibonic acids, of nominal formula RSbO₃H₂, have been known for over 100 years.¹ However, in contrast to the simple molecular arylarsonic acids, their precise form is unknown since they invariably exist as amorphous powders with limited solubility in aqueous solution, except when it is alkaline. Their titration behavior is complicated and variable.² It is generally concluded that they are polymeric species involving five- or six-coordinate Sb with μ -O linkages,³ with early Mossbauer studies favoring trigonal-bipyramidal geometry.⁴ A recent crystal structure determination⁵ of a sterically hindered compound, 2,6-Mes₂C₆H₃SbO₃H₂, showed a molecular dimer with a central Sb₂O₂ core and fivecoordinate Sb, but the bulky R groups in this instance prevent higher aggregation; thus the result cannot be used as a specific basis for deducing the arrangement in stibonic acids with smaller aryl groups.

ESI-MS is a powerful method for determining species in solution,⁶ so we decided to investigate the oligomerization of

*To whom correspondence should be addressed. E-mail: b.nicholson@ waikato.ac.nz.

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stibonic acids and now report that under appropriate conditions these acids form polyoxostibonate cages with intriguing structures. Herein we describe the mass spectrometric behavior of the acids $RSbO_3H_2$ [R = p-ClC₆H₄, p-MeC₆H₄, p-O₂NC₆H₄, and 1-naphthyl] and present the characterization and structural determinations of Na⁺ or K⁺ salts of high-nuclearity polyoxyanions formed by them.7 Preliminary details of the present work have been communicated earlier.8

ORGANOMETALLICS

Related examples of organopolyoxostibonates, or mixed oxometalates incorporating organo-antimony, have been reported only recently, prepared under different conditions from those used and described herein.9,10

Experimental Section

Preparation of the arylstibonic acids was carried out essentially using the procedure established by Doak and Steinman.11 For convenience a typical synthesis is included below. No melting point data are given, as these substances do not have well-defined melting or decomposition temperatures.¹¹ For the preparation of the derivatives of the acids the crude yield (contaminated with other salts) will be essentially quantitative. However the crystalline material from the slow evaporation of

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MeCN is variable, depending on how long the solution is left to concentrate, how much noncrystalline compound precipitates out, etc. Crystals are initially highly solvated with lattice water, some of which at least is lost as soon as the crystals are collected. This makes a formal yield somewhat difficult to define. ESI-MS was carried out on a Bruker MicrOTOF instrument, operating under standard conditions in negative ion mode, with samples made up in MeCN immediately before infusion. Assignment of ions was aided by matching the characteristic patterns generated by the ¹²¹Sb (57%) and ¹²³Sb (42%) isotopes. Peaks are reported as the *m/z* with the greatest intensity in the isotopic envelope.

Preparation and Characterization of p-ClC₆H₄SbO₃H₂. 4-Chloroaniline (6.38 g, 0.05 mol) was dissolved in ethanol (125 mL) in a 500 mL wide-mouth conical flask, surrounded by an ice-bath, with an efficient stirrer. Concentrated sulfuric acid (2.7 mL, 5 g) and SbCl₃ (11.4 g, 0.05 mol) were added. Once the latter had completely dissolved, a solution of sodium nitrite (3.5 g in 5 mL of water) was added to initiate diazotization. This thick mixture was stirred for 30 min. Cuprous bromide (1 g) was added and the ice-bath removed. As the mixture warmed, nitrogen evolved spontaneously. Stirring was continued for 24 h to ensure complete nitrogen evolution. Steam distillation was used to remove the alcohol. The residue of crude stibonic acid was collected on a Buchner funnel, washed with water, and air-dried.

The crude acid was dissolved in concentrated hydrochloric acid (ca. 1 L) and filtered, and a solution of pyridine (5 mL) in concentrated HCl (20 mL) added. The precipitated pyridinium salt, [pyH][ClC₆H₄SbCl₅], was collected on a sintered glass filter, washed several times with concentrated hydrochloric acid, and left to dry. It was dissolved in the minimum volume of dilute sodium carbonate solution (ca. 2 L of a 1% (w/v) solution) and filtered. The free acid was obtained by the dropwise addition of dilute hydrochloric acid while stirring rapidly. The precipitate was collected by filtration and washed thoroughly with water acidified with a few drops of dilute hydrochloric acid. After air drying the yield was 12.3 g, 87%, assuming a formula of *p*-ClC₆H₄SbO₃H₂.

The product was further purified by dissolving a sample (2 g)in a mixture of water and concentrated NH₃(aq) (2:1, ca. 300 mL) in a plastic beaker. The open beaker was placed in a closed desiccator containing glacial acetic acid. The acid diffused into the solution over several days, precipitating the stibonic acid as an off-white powder, which was collected by gravity filtration. Recovery was 80-90%. Anal. Found: C 26.93; H 2.46. Calcd for C₆H₆ClO₃Sb: C 25.44; H 2.14; Calcd for C₇₂H₅₆Cl₁₂O₂₈Sb₁₂: C 26.56; H 1.73. ESI-MS (m/z, assignment, (calc), intensity, R = *p*-ClC₆H₄): 3275.719, [NaH₆(RSb)₁₂O₂₈]⁻, (3275.738), 18%; 3253.744, $[H_7(RSb)_{12}O_{28}]^-$, (3253.756), 100%; 2157.189 $[H_6 (\text{RSb})_{16}\text{O}_{36}]^{2-}$, (2157.162), 9%; 1648.353, $[\text{Na}_2\text{H}_4(\text{RSb})_{12}\text{O}_{28}]^{2-}$, $(1648.356), 4\%; 1637.361, [NaH_5(RSb)_{12}O_{28}]^{2-}, (1637.365), 18\%;$ 1626.366 [H₆(RSb)₁₂O₂₈]²⁻, (1626.375), 18%. IR (KBr disk, cm⁻¹): 3400 (s, br), 3190 (s), 1634 (m), 1573 (m), 1477 (s), 1383 (s), 1182 (w), 1090 (s), 1067 (s), 1013 (s), 947 (w), 814 (s), 728 (s), 663 (s), 602 (w), 489 (s).

Preparation and Characterization of *p***-MeC₆H₄SbO₃H₂.** Similarly, from *p*-toluidine a white powder was obtained in 79% initial yield. Anal. Found: C 33.35; H 3.49. Calcd for C₇H₉O₃Sb: C 31.98; H 3.45; Calcd for C₈₄H₉₂O₂₈Sb₁₂: C 33.51; H 3.08. ESI-MS (*m*/*z*, assignment, (calc), intensity, R = p-MeC₆H₄): 3008.434, [H₇(RSb)₁₂O₂₈]⁻, (3008.419), 100%; 1993.619 [H₆(RSb)₁₆O₃₆]²⁻ (1993.604), 3%; 1503.719 [H₆(RSb)₁₂O₂₈]²⁻, (1503.706), 18%. IR (KBr disk, cm⁻¹): 3401 (s, br), 3200 (s), 1635 (m), 1593 (m), 1493 (m), 1447 (w), 1395 (s), 1310 (w), 1280 (w), 1210 (w), 1187 (m), 1073 (m), 1018 (w), 802 (s), 743 (s), 667 (s), 600 (w), 486 (s), 460 (w).

Preparation and Characterization of $p-O_2NC_6H_4SbO_3H_2$. This was prepared from *p*-nitroaniline using the same method, except that the crude acid was dissolved in a 1:1 mixture of MeOH and concentrated HCl to form the pyridinium salt. The product was an off-white powder, crude yield 92% calculated as $p-O_2NC_6H_4SbO_3H_2$. ESI-MS showed that Na⁺ was strongly incorporated even after two diffusion purifications. Anal. Found: C 26.11; H 2.76; N 4.76. Calcd for $C_6H_6NO_5Sb$: C 24.52; H 2.06; N 4.76; Calcd for $C_{72}H_{56}N_{12}O_{52}Sb_{12}$: C 25.56; H 1.67; N 4.96; Calcd for NaC₇₂H₅₅N₁₂O₅₂Sb₁₂: C 25.4; H 1.63; N 4.94. ESI-MS (m/z, assignment, (calc), intensity, R = $p-O_2NC_6H_4$): 1700.535 [NaH₅(RSb)₁₂O₂₈]²⁻, (1700.514), 100%; 1146.688, [Na₂H₅(RSb)₁₂O₂₉]³⁻, (1146.671), 100%; 1139.359, [NaH₆(RSb)₁₂- O_{29}]³⁻, (1139.344), 80%. IR (KBr disk, cm⁻¹): 3400 (s, br), 3190 (s, br), 1630 (m), 1597 (m), 1576 (m), 1516 (s), 1477 (w), 1390 (m), 1355 (s), 1315 (w) 1279 (w), 1105 (m), 1068 (m), 1014 (m), 937 (w), 854 (s), 738 (s), 710 (s), 684 (s), 600 (w), 533 (w), 466 (m).

Preparation and Characterization of (1-naphthyl)SbO₃H₂. This was prepared following the same procedure from α -naphthylamine (7.16 g, 0.05 mol) in ethanol (200 mL). The crude acid was dissolved in 1:1 MeOH/conc HCl (1.5 L) to form the pentachlorostibonate salt. The precipitation after dissolving in Na₂CO₃ solution was with dilute nitric acid. The product, (1-naphthyl)SbO₃H₂, was obtained as an off-white solid (20%), which ESI-MS showed contained very little Na⁺, so it was not purified further. Anal. Found: C 38.8; H 2.55. Calcd for C₁₀H₉O₃Sb: C 40.2; H 3.03%; Calcd for C120H92Sb12O28: C 41.9; H 2.7%. ESI-MS (m/z, assignment, (calc), intensity, R = naphthyl): 3442.413, $[H_7(RSb)_{12}O_{28}]^-$, (3442.422), 100%. IR (KBr disk, cm⁻¹): 3401 (s, br), 3052 (s), 1656 (m), 1623 (w), 1590 (m), 1558 (w), 1504 (s), 1384 (s), 1335 (m), 1300 (w), 1263 (m), 1212 (w), 1166 (w), 1136 (w), 1058 (w), 1023 (m), 953 (w), 796 (s), 768 (s), 745 (m), 680 (m), 618 (w), 514 (w), 468 (m), 407 (w).

Preparation of Crystals of K₄[H₈(*p*-ClC₆H₄Sb)₁₂O₃₀] •58H₂O. *p*-Chlorophenylstibonic acid (244 mg, 0.86 mmol) was dissolved in water (50 mL) containing KOH (0.6 mL of 2 mol L⁻¹, pH = 12.0). Potassium nitrate (50 mg, 0.5 mmol) was dissolved in 25 mL of the alkaline stibonate solution (giving overall 0.43 mmol of Sb, 1.1 mmol K⁺), and the clear solution was left to evaporate to dryness. The white residue crystallized from a MeCN (10 mL)/H₂O (0.2 mL) solution by slow evaporation, forming colorless block crystals. IR (KBr disk, cm⁻¹): 3370 (s, br), 1631 (s, br), 1572 (m), 1477 (s), 1384 (s), 1183 (w), 1090 (s), 1066 (s), 1013 (s), 821 (s), 726 (s), 654 (s), 603 (s), 491 (s), 457 (w).

Preparation of Crystals of Rb_{0.67}Na_{2.33}[H₉(*p*-MeC₆H₄Sb)₁₂-O₃₀]·20H₂O. *p*-Tolylstibonic acid (221 mg, 0.84 mmol) was dissolved in water containing NaOH (0.6 mL of 2 mol L⁻¹, pH 11.2). A 10 mL aliquot of this solution was combined with RbI (43 mg, 0.2 mmol) in water (1 mL) (ratio of Sb:Na:Rb 17:24:20), and the clear solution was left to evaporate to dryness. The resulting white solid was crystallized from MeCN/H₂O solution (4:1 v/v, 5 mL) by slow evaporation to give clear, truncated square-pyramidal crystals after three weeks. IR (KBr disk, cm⁻¹): 3414 (s, br), 3015 (w), 2920 (w), 1638 (m), 1593 (m), 1492 (s), 1472(w), 1455 (m), 1392 (m), 1308 (w), 1210 (w), 1186 (m), 1074 (s), 1018 (w), 974 (w), 891 (w), 803 (s), 726 (m), 658 (s), 605 (m), 581 (m), 488 (s), 450 (m).

Preparation of Crystals of $[Ph_4P][Na_2H_9(p-MeC_6H_4Sb)_{12}-O_{30}] \cdot xH_2O. p$ -Tolylstibonic acid (221 mg, 0.84 mmol) was dissolved in water (50 mL) containing NaOH (0.6 mL of 2 mol L⁻¹, pH 11.2). A 10 mL aliquot of this solution was combined with a solution of $[Ph_4P]Br$ (84 mg, 0.2 mmol) in water (5 mL), giving a fine white suspension, which was left to evaporate to dryness. The resulting powder was crystallized from MeCN (4 mL)/H₂O (0.2 mL) by slow evaporation to give colorless crystals within four weeks.

ESI-MS of the crystals redissolved in MeCN: m/z 1525.689, calc for $[H_4Na_2(p-MeC_6H_4Sb)_{12}O_{28}]^{2-}$ 1525.688; m/z 3390.494, calc for $[H_4Na_2 (p-MeC_6H_4Sb)_{12}O_{28}+Ph_4P]^{-}$ 3390.507.

X-ray Crystal Structure Determinations. Crystals were rapidly transferred from the mother liquor onto the diffractometer and cooled immediately to ca. 90 K, since they invariably lost crystallinity on exposure to air, presumably due to loss of lattice solvent (water and/or MeCN). Data were collected on a Bruker Apex II CCD diffractometer and processed routinely, including absorption corrections using a multiscan method (SADABS).¹² Because of the relatively poor diffraction, the size of the molecules, and the presence of extensive lattice water molecules, the refinements were not routine. Each was treated differently, as presented below. Structures were solved using the SHELXS97 program¹³ and refinement on F_o^2 was with SHELXL97¹³ operating under the WinGx interface.¹⁴

Solution and Refinement for K₄[H₈(p-ClC₆H₄Sb)₁₂O₃₀]. 58H₂O. The structure was solved by direct methods to reveal the 24 Sb atoms in the asymmetric unit. Subsequent difference maps revealed the remainder of the complex anions and the K^{+} cations. Further analysis gave the positions of 77 O atoms from the lattice water molecules, and these refined cleanly with isotropic temperature factors. Another 39 O atoms were located in sensible positions, but were less well defined; thus these were refined with a common, isotropic temperature factor. All the included water molecules formed a reasonable H-bonded network with sensible $O \cdots O$ distances. There are probably only a few extra water molecules unaccounted for because of the relatively small (ca. 600 Å³, 4%) remaining void volume in the cell. The aryl-ring H atoms were included in calculated positions, but the H atoms of the water molecules and the eight that must be associated with each of the anions for charge neutrality were not included.

Crystal and refinement data: $C_{72}H_{144}Cl_{12}K_4O_{88}Sb_{12}$, M_r 4446.6, triclinic, space group $P\overline{1}$, a = 20.3732(6) Å, b = 23.0650(7) Å, c = 34.213(1) Å, $\alpha = 87.386(2)^{\circ}$, $\beta = 86.265(2)^{\circ}$, $\gamma = 83.649(2)^{\circ}$; U = 15932.5(8) Å³, Z = 4, $D_c = 1.854$ g cm⁻³, μ (Mo K_{α}) = 2.4 mm⁻¹, F(000) = 8632. T = 89(2) K. Crystal size: $0.44 \times 0.28 \times 0.20$ mm³. Total data 359 194, unique data 72 182 ($R_{int} 0.070$), θ range 1–27.5°. Refinement converged with $R_1 = 0.0918$ ($I > 2\sigma(I)$), $wR_2 = 0.2430$ (all data), GoF = 1.085, $\Delta e = 3.1/-4.9$ e Å⁻³.

Solution and Refinement for Rb_{0.67}Na_{2.33}[H₉(*p*-MeC₆H₄Sb)₁₂-O₃₀]·20H₂O. The crystals diffracted weakly, giving data with an average $I/\sigma(I)$ of only 3.6. The structure was solved by direct methods to give the positions of the 12 Sb atoms. A subsequent difference map showed all the anion O atoms and the three cations. These were refined as mixed Na⁺/Rb⁺ with tied occupancy factors summing to 1.0 and with temperature factors constrained to be the same. Ultimate refinement showed only Na⁺/Rb⁺(3) had significant (50%) contribution from Rb⁺, the other two cation sites being solely Na⁺. With further cycles the tolyl rings were located, but some were clearly disordered. The aryl rings were constrained as rigid hexagons using AFIX 66, with temperature factors constrained by the SIMU and DELU options of SHELXL97.¹³

Four H_2O molecules coordinated to Na^+ cations were welldefined. In addition there were another 16 lattice water molecules included in the refinement, some reasonably well-defined,





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others clearly having partial occupancy or loosely held positions. Although some of them refined with unrealistic temperature factors, this appeared to model the included solvent reasonably well since PLATON¹⁵ indicated only small voids left in the unit cell. All non-H atoms were treated anisotropically, but H atoms were not included given the poor quality of the data.

Crystal and refinement data: C₈₄H₁₂₄Na_{2.66}O₅₀Rb_{0.67}Sb₁₂, *M*_r 3498, monoclinic, space group *P*2₁/*n*, *a* = 17.7337(5) Å, *b* = 24.9225(8) Å, *c* = 27.4111(9) Å, *β* = 98.190(2)°, *U* = 11991.3(6) Å³, *Z* = 4, *D*_c = 1.938 g cm⁻³, μ (Mo Kα) = 2.95 mm⁻¹, *F*(000) = 6756. *T* = 89(2) K. Crystal size 0.22 × 0.12 × 0.12 mm³. Total data 125 562, unique data 21 102 (*R*_{int} 0.098), observed (*I* > 2*σ*(*I*)) data 11 852, *θ* range = 2–25°. Refinement converged with *R*₁ = 0.0970 (*I* > 2*σ*(*I*)), *wR*₂ = 0.2878 (all data), GoF = 1.082, $\Delta e = 3.4/-2.1$ e Å⁻³.

Solution and Refinement for $[Ph_4P][Na_2H_9(p-MeC_6H_4Sb)_{12}-O_{30}] \cdot xH_2O$. Unfortunately the crystals diffracted weakly, giving data with an average $I/\sigma(I)$ of only 2.2. The structure was solved by direct methods (SHELXS97) to give the positions of the 12 Sb atoms. A subsequent difference map showed all the anion O atoms and the two Na⁺ cations. With further cycles the tolyl rings and the Ph_4P⁺ cation were located, but were not well defined. The phenyl carbon atoms of the cation were constrained as rigid hexagons using the AFIX 66 option of SHELXL97, while the tolyl rings were constrained using the SAME, SIMU, and DELU options.

The four H_2O molecules coordinated to Na^+ cations were well defined, as was one lattice water that links two anions through H bonding. However the rest of the lattice solvent (presumably H_2O though it may also include MeCN) was very diffuse and could not be modeled sensibly.

Without the solvent included the refinement converged with $R_1 = 0.166$, $wR_2 = 0.435$. To remove the diffuse solvent contribution, the SQUEEZE¹⁶ routine of PLATON was invoked. This allowed refinement to give $R_1 = 0.125$ and $wR_2 = 0.346$.

While the results were sufficient to demonstrate that the anion has the same structure as that found for the PhCH₂NMe₃⁺ example in our earlier report,⁸ and the Rb⁺ example above, the quality of the determination precludes any detailed analysis of bond parameters.

Crystal and refinement data: C₁₀₈H₁₂₃Na₂O₃₅PSb₁₂, M_r = 3519.01, orthorhombic, space group *Pcab*, *a* = 28.5319(7) Å, *b* = 29.5235(7) Å, *c* = 38.2815(10) Å, *U* = 32246.9(14) Å³, *Z* = 8, *D_c* = 1.450 g cm⁻³, μ (Mo Kα) = 2.05 mm⁻¹, *F*(000) = 13 600. *T* = 90(2) K. Crystal size 0.44 × 0.29 × 0.13 mm³. Total data 27 4 394, unique data 25 318 (R_{int} 0.133), observed ($I > 2\sigma(I)$) data 14 781, θ range = 2–24°. (Data are calculated from the refinement against the SQUEEZED data, so ignore contributions from the diffuse lattice solvent.) Refinement converged with R_1 = 0.125 ($I > 2\sigma(I)$), wR_2 = 0.346 (all data), GoF = 1.101, Δe = 3.4/–1.8 e Å⁻³.

Results and Discussion

Preparation of Arylstibonic Acids 1–4. Arylstibonic acids are traditionally prepared using the Scheller reaction, as modified by Doak and Steinman (Scheme 1).¹¹ The key to the procedure is the conversion of the initial crude acid (which contains Sb_2O_3 as an impurity, among others) to a well-defined pyridinium salt [pyH][RSbCl₅], which can be purified by recrystallization.

Hydrolysis of this salt under mildly alkaline conditions precipitates the acid as an amorphous powder, which can be collected and dried. The purity of the arylstibonic acids thus formed was assessed by Doak and Steinman only by elemental analysis for Sb, varying amounts of water of crystallization being assigned to achieve matching data. Given the

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Figure 1. Negative ion ESI mass spectrum of *p*-tolylstibonic acid in MeCN, showing the dominant peak assigned to $[H_7(MeC_6H_4Sb)_{12}O_{28}]^-$ (calcd *m/z* 3008.419). The inset shows the characteristic isotope envelope for the parent ion arising mainly from the two isotopes of Sb.

strong affinity that the acids appear to have for cations (see below), it seems likely that material prepared by the published method would have contained some Na⁺ from the hydrolysis step. To avoid this, we have added an extra purification step that involves dissolving the acid in the minimum amount of aqueous NH₃ and allowing CH₃COOH to slowly diffuse in to precipitate the acid. This works successfully with p-ClC₆H₄ and p-MeC₆H₄, examples 1 and 2, but the p-O₂NC₆H₄ example 3 still contained significant amounts of Na⁺ even after two such purification cycles. Modification of the preparation by using a sequence of NH₃(aq) in place of the Na₂CO₃, followed by HCl for the hydrolysis of the pyridinium (p-nitrophenyl)pentachlorostibonate, gave material that was free of Na⁺ adducts in the ESI-MS, but the overall purity of the sample was compromised. Further attempts to purify it led to incorporation of adventitious sodium, showing a particularly strong affinity for complexation with this example. In contrast, $(1-naphthyl)SbO_3H_2(4)$ showed a much lower affinity for Na⁺ and did not need the extra purification step to provide ESI-MS spectra with little contribution from adducts. Compounds 1-3 are well known, but the 1-naphthyl compound 4 has not been characterized previously.

Elemental analysis cannot reliably distinguish between the nominal mononuclear formula $RSbO_3H_2$ and the polynuclear form $[H_8(RSb)_{12}O_{28}]$ that is indicated from the mass spectra (see below), though there is a better match for the latter in each case.

ESI-MS of Arylstibonic Acids. Samples of each of the arylstibonic acids were dissolved in MeCN and examined using ESI-MS. In every case, the dominant peaks could be assigned from mass measurements and from the distinctive isotope patterns to the anions derived from a parent acid of

formula $[H_8(RSb)_{12}O_{28}]$. These were mainly $[H_7(RSb)_{12}O_{28}]^$ and/or the corresponding doubly charged species $[H_6-(RSb)_{12}O_{28}]^{2-}$. Figure 1 shows a typical spectrum.

Interestingly, the p-Me and 1-naphthyl examples gave mainly the 1⁻ ions, while the *p*-Cl compound gave both 1⁻ and 2⁻ ions in a ratio of ca 2:1. In contrast, the p-NO₂ species gave mainly 2^{-} and 3^{-} ions, which incorporated Na⁺ ions, such as $[NaH_5(RSb)_{12}O_{28}]^{2-}$, showing the difficulty of complete purification for this compound. The specificity for the dodecanuclear aggregation for all these derivatives was remarkable. Other minor peaks appeared to arise from Sb₁₁, Sb₁₃, Sb₁₆, and Sb₂₈ species, but these were barely significant. The main peaks were usually accompanied by satellites corresponding to species where one or more H⁺ had been replaced by Na⁺ to give, for example, [NaH₆(RSb)₁₂- O_{28}]⁻. For very fresh samples these were relatively minor and presumably arose either from traces of Na⁺ carried over from the preparation or from adventitious Na⁺ from the mass spectrometer source. However if the samples were left in standard glassware for any length of time, the Na⁺ species increased as cations were leached from the glassware, indicating a strong affinity for complexation by the acid cluster. As noted above, the p-NO2 example had an especially high affinity for cations. There is clearly some dependence on the relative electron-withdrawing nature of the R groups controlling the charge on the ions, and for all examples the sodium salts showed a greater tendency to form the 2- or 3ions than did the parent acids, which appeared mainly as 1ions under the same conditions.

The $[Na_xH_y(RSb)_{12}O_{28}]^{z^-}$ aggregates appeared indefinitely stable in MeCN solution, with ESI-MS unchanged

Table 1. Negative Ion ESI-MS Data for Arylstibonic Acids in MeCN Obtained from the NCI Chemotherapeutics Repository^a

NCI code	formula	m/z	assignment
NSC13735	$4-Cl-3-O_2NC_6H_4SbO_3H_2$	3793.64	$[H_7(RSb)_{12}O_{28}]^-$
	2 0 1 3 2	2051.72	$[H_6(RSb)_{13}O_{30}]^{2-}$
		1896.28	$[H_6(RSb)_{12}O_{28}]^{2-1}$
NSC13742	$2-O_2NC_6H_4SbO_3H_2$	3402.04	$[NaH_6(RSb)_{12}O_{28}]^-$
NSC13743	$3-O_2NC_6H_4SbO_3H_2$	3380.07	$[H_7(RSb)_{12}O_{28}]^{-1}$
	2 0 1 3 2	1827.98	$[H_6(RSb)_{13}O_{30}]^{2-}$
		1818.98	$[H_8(RSb)_{12}O_{29}]^{2-}$
		1689.52	$[H_6(RSb)_{12}O_{28}]^{2-}$
NSC13746	Na[4-HO ₃ SC ₆ H ₄ SbO ₃ H]	no significant high-mass peaks in MeCN ^{b}	
NSC13748	4-(H ₂ N)O ₂ SC ₆ H ₄ SbO ₂ H ₂	1683.18 (in MeCN)	$[NaH_4(RSb)_{16}O_{36}]^{3-1}$
		1675.87 (in H ₂ O)	$[H_5(RSb)_{16}O_{36}]^{3-1}$
NSC13776	$4\-[(HOC_2H_4)NH]O_2SC_6H_4SbO_3H_2$	no significant high mass peaks in $MeCN^b$	[5()1050]
NSC13778	3-(HO ₂ CCHCH)C ₆ H ₄ SbO ₃ H ₂	no significant peaks in MeCN or H ₂ O	
NSC13782	$4\text{-}(HOC_2H_4NH)C(O)C_6H_4SbO_3H_2$	no significant peaks in MeCN or H ₂ O	

^{*a*} The provenance of the archived samples is largely unknown, and the samples may not be pure (R. H. Shoemaker, personal communication). ^{*b*} [RSbO₃H.nH₂O]⁻ signals in low-mass region in H₂O.

after 24 h in MeCN in the absence of a source of cations. Furthermore, a mixture of MeCN solutions of the *p*-Cl- and *p*-Me-phenylstibonic acids showed peaks corresponding to the individual dodeca-clusters with no scrambling to give mixed species even after a week at room temperature.

MeCN was the solvent of choice for running ESI-MS. MeOH could also be used and gave the same species initially, but slow development of peaks arising from esterification gave ions such as $[H_5(RSb)_{12}O_{27}(OMe)]^{2-}$. 1,2-Dichloroethane or MeCN/H₂O (1:1) gave the same species as in MeCN, but overall ionization efficiency was lower, while tetrahydrofuran caused breakdown of the cluster units.

These results initially seemed to conflict with reports that arylstibonic acids could be analyzed by HPLC/ESI-MS, giving peaks assignable to monomeric Sb species.¹⁷ However these chromatographic analyses were carried out by dissolving the solid acids in 0.05 M NaOH at 45 °C for 30 min before eluting with aqueous NH₄OAc at pH 9. These conditions apparently served to hydrolyze the Sb₁₂ aggregates to monomeric species. To confirm this supposition, a sample of *p*-chlorophenylstibonic acid was dissolved in 0.05 M NaOH under the reported conditions. This solution then gave peaks in the low mass region assignable to [RSbO₃H · nH₂O]⁻ (*m*/*z* 282.899, 300.911, and 318.923, respectively, for n = 0-2) and related dimers and trimers.

During the course of the present study, Rishi et al. described the inhibition of DNA binding to B-ZIP dimers, using 12 arylstibonic acids that were sourced from the National Cancer Institute archives.¹⁸ To extend our ESI-MS investigation, we requested some of the same samples and analyzed these in MeCN. Results are summarized in Table 1 and generally indicate that these examples also aggregate. The 2-nitro-, 3-nitro-, and 3-nitro-4-chlorophenylstibonic acids all showed clean ions from the equivalent Sb₁₂ species discussed above, although interestingly, reasonably abundant signals from Sb₁₃ clusters were also present for the latter two examples.

The other compounds listed in Table 1 gave no equivalent peaks in MeCN, possibly because of low solubility. In H₂O

or MeCN, the *p*-sulfamoylphenylstibonic acid uniquely gave signals assigned to an Sb₁₆ cluster derived from $[H_8(RSb)_{16}-O_{36}]$, with only traces of Sb₁₂ species. The other examples in H₂O gave only low mass ions associated with mainly monomers $[RSbO_3H]^-$ and related dimers.

In summary, it appears that, rather than variable polymeric species, solid arylstibonic acids are well-defined aggregates of formula $[H_8(RSb)_{12}O_{28}]$ and that these dissolve intact in MeCN solutions. Other nuclearities, especially Sb₁₃ and Sb₁₆ species, are often present but are only minor contributors, except for the one example described above. In water, these clusters are initially intact but hydrolyze to give monomeric RSbO₃H⁻, and this breakdown is enhanced at higher pH.

Unfortunately we have been unable as yet to grow single crystals of any of these acids for full structural characterization, but the possible structures can perhaps be deduced from the structures of salts derived from the acids, as described below. We note that formally the species $[H_8(RSb)_{12}O_{28}]$ is the equivalent of the well-known isopolytungstate [H₂W₁₂- O_{40} ⁶⁻ [with the R group on Sb(V) a surrogate for the O on W(VI)],¹⁹ providing a possible analogy for structural prediction. There is also comparison with the Keggin ion structural isomers such as $[PMo_{12}O_{40}]^{3-}$, which would also indicate a cuboctahedron, dodecahedral core for the Sb atoms in arylstibonic acid clusters if the α -isomer was to be formed. However analogies between polyoxometalates with main group (Sb) and transition metals (Mo or W) may be complicated by the recent theoretical findings that imply that the stability order of $[PW_{12}O_{40}]^{3-}$ Keggin species ($\alpha > \beta > \gamma > \delta > \varepsilon$) is completely reversed for $[Mn(MeSb)_{12}O_{28}]^{6-}$ aggregates.20

Structure of $K_2[K_2H_8(p-ClC_6H_4Sb)_{12}O_{30}]$ ·58H₂O. Crystals of a potassium salt of *p*-chlorophenylstibonic acid suitable for X-ray structural analysis were grown from MeCN/H₂O solution. These were found to correspond to the tetrapotassium salt $K_4[H_8(p-ClC_6H_4Sb)_{12}O_{30}]$.

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Figure 2. Hexagonal antiprismatic arrangement of the 12 Sb atoms in the $[K_2H_8(p-ClC_6H_4Sb)_{12}O_{30}]^{2-}$ anion. The same arrangement is found for the two sodium-containing anions.



Figure 3. Two views of the $[K_2H_8(p-ClC_6H_4Sb)_{12}O_{30}]^{2-}$ anion, with the K⁺ ions omitted and only the *ipso* carbon atoms of the aryl rings included. Purple = Sb, red = O, gray = C.

The lattice contains two independent anions in the asymmetric unit, but these have very similar structures; hence the following discussion is based on average parameters. Figures 2–4 show views of the anion. The core unit consists of 12 six-coordinate Sb atoms, each with one p-ClC₆H₄ group attached and five O atoms. The basic arrangement of the Sb₁₂ unit is an irregular hexagonal antiprism (Figure 2).

The lower Sb₆ array is planar, while the upper Sb₆ array is a puckered chair arrangement. The Sb atoms are linked by 30 O atoms, divided into 18 double-bridging, six triple-bridging, and six terminal ones (presumably Sb–OH). The overall symmetry of the oxostibonate framework (stripped of the attached aryl rings and cations) is $C_{3\nu}$ (Figure 3a). There must be an extra two H⁺ associated with the cluster from charge considerations, but their positioning is undefined.

The aryl rings are of two types. Those attached to Sb atoms in the planar array form three pairs arranged face-to-face, while those from the puckered array of Sb atoms are splayed out to form a bowl-shaped cavity (Figure 4), which may function as a cavitand.

There are four distinct sites for the potassium cations. Each of the anions has a firmly encapsulated K⁺. This sits within the puckered hexameric face, coordinated in a planar hexagonal array by six of the μ -O atoms from the anion (average $O \cdots K^+$ 2.79 Å). There are further interactions with three of the interlayer μ_3 -O atoms ($O \cdots K^+$ 2.72 Å), and the coordination of this cation is completed by a loosely held H₂O molecule sitting above the face ($O \ldots K^+$ 3.47 Å). This generates a 10-coordinate K⁺ in total. For this site the anion is behaving as an inorganic crown ligand, as illustrated in Figure 5, with cross ring O...O distances of 5.46 Å, compared with *ca* 5.55 Å in 18-crown-6 K⁺ complexes.²¹

For each anion there is a second K^+ sitting below the other face of the hexagonal antiprism, coordinated to three μ -O



Figure 4. Full structure of the $[K_2H_8(p-ClC_6H_4Sb)_{12}O_{30}]^{2-}$ anion, showing the coordination of three different K⁺ ions (the fourth K⁺ is not closely associated with the anion). Purple = Sb, green = Cl red = O, yellow = K, light gray = C.

atoms (average $O \cdots K^+$ 2.62 Å) from the anion, with three water molecules (average $O \cdots K^+$ 2.48 Å) making up octahedral coordination.

The third K^+ in each case is within the bowl-shaped cavity generated by the protruding aryl rings above the puckered six-membered face. There are small differences in this case between the two independent anions in the asymmetric unit. There are two interactions with μ -O from the anion and three coordinated H₂O molecules (one or two of which are also weakly bridging to the K⁺ ion in site 1). In addition there is a weak interaction with a Cl atom from a *p*-ClC₆H₄ group from the adjacent anion (Cl···K⁺ 3.49/3.64 Å), and the K⁺ is positioned so that it lies above the face of one of the *p*-ClC₆H₄ rings, (K⁺···ring plane 3.32/3.37 Å). This interaction places the K⁺ to one side of the cavity, breaking the $C_{3\nu}$ symmetry of the rest of the anion.

The fourth K^+ in each case is in a general lattice position, each coordinated by five H₂O (average $K^+ \cdots OH_2$ distances 2.78 Å), and each is positioned symmetrically above one of the aryl rings of an anion ($K^+ \cdots$ ring-plane distances 3.75 and 3.25 Å for K(4) to the ring attached to Sb(6) and K(8) to the ring attached to Sb(16), respectively).

The remainder of the structure consists of solvent within the lattice. A total of 116 H₂O molecules in the asymmetric unit were located and refined, and these gave sensible $O \cdots O$ distances for an H-bonded array, linking the anions and cations together. Analysis gives ca. 4% remaining void volume,



Figure 5. Cross-section of the 10-coordinate K^+ site in the $[K_2H_8(p-ClC_6H_4Sb)_{12}O_{30}]^{2-}$ anion, showing the 12-crown-6 $\{Sb_6O_6\}$ feature. The O···O cross-ring distance is 5.46 Å. The same arrangement is found for the Na⁺ derivatives, with O···O distances of ca. 5.31 Å. Purple = Sb, red = O, yellow = K (or Na).

so there are probably a few extra molecules not accounted for, but overall the solvent molecules are unusually well behaved.

Structure of $Rb_{0.67}Na_{0.33}[Na_2H_9(p-MeC_6H_4Sb)_{12}O_{30}] \cdot 20H_2O$. The structure of a mixed Rb^+/Na^+ salt was determined and was found to be closely related to the K⁺ salt discussed above. The same core hexagonal antiprism was found, with three cation sites similar to those already described. Despite the crystals growing from a solution where the $Rb^+:Na^+$ ratio was ca. 1:1, refinement showed that the two sites most

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Figure 6. Cubane-like H-bonding moiety that links two anions via the six-coordinate Na⁺ ions in all of the known sodium derivatives of arylstibonic acids. O_w and O_w' are coordinated water molecules, O and O' are μ -oxygen atoms from the anion framework.

closely associated with the anion were occupied only by Na⁺ cations, with the third site having $^{2}/_{3}$:¹/₃ mixed Rb⁺:Na⁺ occupancy.

Once again there is one cation, Na(1), that is firmly encapsulated in the crown face of the anion. In this case the $O \cdots O$ is 5.31 Å (cf. 5.46 Å for the larger K^+ example), and the Na⁺ is displaced by 0.83 Å from the O_6 plane toward the interior of the anion (0.61 Å in the K⁺ example). There are three links to μ_3 -O atoms from the middle of the anion, and there is a single H₂O attached on the upper site. The second Na⁺ occupies the lower Sb₆ face, again coordinated to three μ -O from the anion framework, with a further three H₂O molecules completing six-coordination. This unit is involved in an aesthetically pleasing link to the equivalent site on an adjacent anion via the H-bonded cubic arrangement illustrated in Figure 6, with $Na^+ - O - H \cdots O - Na^+$ bridges. We are unaware of a precedent for this type of linking of Na⁺, which would more usually be joined by μ -OH₂ bridges, an arrangement that may be precluded here by the bulk of the anion.

The third cation site is in the pocket formed by the aryl rings and contains mixed Rb⁺/Na⁺ (2:1). It is linked to Na(1) by a bridging H₂O ligand and is coordinated to two μ -O from the anion. The remaining sites around the cation are occupied by three of the *p*-tolyl rings which sandwich the cation with distances of 3.30, 3.49, and 3.55 Å from the cation to the least-squares planes of the rings, indicating weak π -bonding. This type of π -interaction between aryl rings and group 1 cations is now well-established for other systems.²²

The lattice water in this structure was less well-defined. Twenty H_2O were located, and these refined reasonably well to give a H-bonding network holding the main units together. However there still remained significant electron density that could not be modeled sensibly.

Structure of $(Ph_4P)[Na_2H_9(p-MeC_6H_4Sb)_{12}O_{30}](H_2O)_4$. xH_2O . This crystal structure was of poor quality, with lattice water that could not be modeled successfully. It is less reliable than the others, but the overall features are clear. It consists of separated Ph_4P^+ cations and the same $[(RSb)_{12}-O_{30}]$ anion as found for the other two examples. In this case there are only two Na⁺ cations, one occupying the 10-coordinate inorganic crown site and one on the opposite face with six-coordination made up from three μ -O atoms and three H_2O . This latter Na⁺ is again involved in linking two anions together through the same cubic arrangement found for the Rb⁺ compound (cf. Figure 6). The third cation site found for the K⁺ and Rb⁺ compounds is now vacant, which allows for overall $C_{3\nu}$ symmetry to be retained for the anions.

The bond parameters are very similar to those of the Rb compound, with $O \cdots O$ cross-ring distances of 5.28 Å, and again the Na⁺ is displaced by 0.83 Å from the least-squares plane of the six crown-type oxygen atoms.

Discussion

When the acids $[H_8(RSb)_{12}O_{28}]$ are dissolved in alkaline solution, salts are formed. If KOH is used, crystals containing a tetra-anion are formed, namely, $[K_4H_8(RSb)_{12}O_{30}]$. If NaOH is used and other cations are added, then salts of a trianion are formed, including so far [PhCH₂NMe₃][Na₂H₉-(RSb)₁₂O₃₀],⁸ [Ph₄P][Na₂H₉(RSb)₁₂O₃₀], and Rb_{0.67}Na_{0.33}-[Na₂H₉(RSb)₁₂O₃₀]. As an interesting historical note, as early as 1921 Fargher and Gray isolated solids from the reaction of arylstibonic acids with NaOH and found Na:Sb ratios of up to 1:3, consistent with our present results, though they were unable to provide an explanation.⁷

The anions found in the crystal structures correspond to a parent acid of formula $[H_{12}(RSb)_{12}O_{30}]$, which contrasts with the formula for the precursor acids indicated from the ESI-MS study of $[H_8(RSb)_{12}O_{28}]$. Possibly formation of the salts has concomitantly added two H₂O to the core unit, presumably via opening of two Sb–O–Sb bridges to generate sites for coordination of the tightly held cations. Alternatively, two H₂O may be readily lost in the mass spectrometer from an acid of formula $[H_{12}(RSb)_{12}O_{30}]$, since the major peaks in the mass spectra of the salts correspond to two H₂O fewer than found by X-ray crystal structure; for example, for $[Ph_4P][Na_2H_9(RSb)_{12}O_{30}]$ the most intense peak corresponded to $[Na_2H_4(RSb)_{12}O_{28}]^{2^-}$, though $[Na_2H_8(RSb)_{12}O_{30}]^{2^-}$ was also present.

Despite differing aryl groups and different crystal packing, the structures of all of these derivatives (five independent Na⁺ species, two independent K⁺ ones) show a remarkably conserved anion configuration. Interestingly, this geometry was first reported by Baskar et al. as one subunit of a very complex compound assigned the formula $[Na_{21}(PhSb)_{48}-O_{114}]\cdot 46H_2O\cdot 4MeCN$, which made it unclear as to the overall charge state, though there were three Na⁺ cations associated with the Sb₁₂ subunit.²³ For all of the known examples the basic unit is a hexagonal antiprism with one puckered and one planar array of μ -O linked Sb atoms, with overall $C_{3\nu}$ symmetry. The distance between the leastsquares planes through the two Sb₆ arrays is 3.0 Å, and the Sb…Sb distances in the planar array are shorter (ca. 3.15 Å) than those in the puckered array (ca. 3.64 Å for Na⁺ salts, 3.67 Å for K⁺ ones).

The Sb–O (terminal) bond lengths average around 1.99 Å in all examples, consistent with being single bonds and hence Sb–OH groups. The doubly bridging O atoms have similar

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Sb–O distances (1.97-2.00 Å), while the triply bridging ones are longer, as expected (ca. 2.1 Å).

Two cation sites are intimately associated with the anion. With the first, one hexagonal face acts as a $\{Sb_6O_6\}$ crown ligand, providing six in-plane O atoms for bonding with a further three framework oxygens attaching below the cation and a water molecule making up the tenth site above the cation, the polyoxometalate framework effectively acting as a corand.²⁴ For the K^+ example the cation is slightly less displaced from the hexagonal plane than in the Na⁺ case, and the cross-ring $O \cdots O$ distances have expanded a little to accommodate the larger cation. The presence of a crown ligand moiety contained within the structure of a discrete polyoxometallate molecule appears unusually rare, but the $\{Sb_6O_6\}$ entity is closely similar, albeit slightly smaller, to those found in niobates $\{Nb_6O_6\}$ and the pores of large cluster molecules ${Fe_3W_3O_6}, {Mo_6O_6}, {Mo_3V_3O_6}, and {Mo_4VKO_6}.^{25} All$ contain a ring of six oxygen atoms that are essentially coplanar to within 0.013-0.083 Å, as in our case, and crossring $O \cdots O$ distances that range from 5.502 to 5.639 Å. Cations (K^+ or NH_4^+) ensnared by these ligands may be as little as 0.271 or as far as 1.523 Å from the plane of the oxygen atoms.

In contrast, the other hexagonal face is attached to the cation by only three framework oxygen atoms, with a further three terminal H_2O molecules completing the coordination. Whereas either Na^+ or K^+ can occupy these sites, there was no exchange with Rb^+ when crystallization was carried out in the presence of the larger cation.

When the remaining cations are large organic ones (PhCH₂NMe₃⁺, Ph₄P⁺), these are separate from the anions, occupying general lattice sites. However if there is a third small cation available, this is found in a pocket formed by the aryl groups above the puckered hexagonal face. This is attached to two μ -O from the framework and is bridged by a H₂O molecule to the high-coordinate cation in site 1. Remaining interactions are with the faces of the aryl rings in weak π -type bonding.²² These interactions displace the cation from the $C_{3\nu}$ axis toward one side of the pocket. In the case of the K⁺ example, the fourth cation is only loosely associated with the outside of the anion through a weak π -interaction with an aryl ring.

For all the Na⁺-containing examples the anions are linked through the cubic $\{O_3Na(H_2O)_6NaO_3\}$ H-bonded units (Figure 6), despite different crystal packing interactions. However this is not conserved for the K⁺ compound, where the $O_3K(H_2O)_3$ moiety links indirectly to the adjacent anion via a network of H-bonded water molecules.

We have obtained crystals prepared from $Ca(OH)_2$, though the quality was such that only the basic core geometry could be determined. The same hexagonal-antiprism structure as found for the K⁺ or Na⁺ species was indicated, with Ca²⁺ ions in the two usual sites. This arrangement is obviously favored for these medium-sized cations.

The compounds reported herein represent new polyoxometalates that have a number of novel features: (i) they are formed from alkaline solutions, whereas the polyoxometalates formed by Mo, W, V, etc., are formed under acid conditions;²⁶ (ii) the anions form with an open structure, which generates a hexagonal channel; (iii) there is a very strong affinity for cations, particularly in the 10-coordinate site, which acts as an inorganic crown moiety; (iv) the same structure is adopted for Ph, *p*-ClC₆H₄, *p*-MeC₆H₄, and *p*-O₂NC₆H₄ derivatives, with either K⁺ and Na⁺ counterions, and probably also with Ca²⁺; (v) the structural integrity of the anionic clusters is maintained in solution since ESI mass spectra indicate Sb₁₂ species dominate.

We note that Baskar et al. have very recently characterized a Sb_{16} polyoxostibonate from *p*-chlorophenylstibonic acid in the presence of dimethylpyrazole, under thermal conditions in nonaqueous solvents,¹⁰ so the aggregation processes of organostibonic acids can apparently be controlled using different templating cations and bases and different conditions. In future papers we will report results of our studies with other metal ions.

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Supporting Information Available: Full details of the crystal structure determinations, cif files, and extra structure diagrams are available free of charge via the Internet at http://pubs.acs.org.

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