

# Novel polyoxometalates: is antimony the new molybdenum?

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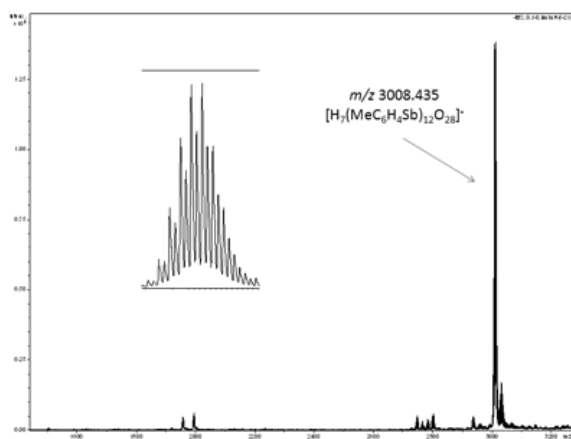
**Key words:** Polyoxometalates; Antimony; ESI mass spectrometry

Polyoxometalates based on Mo, W or V have been known for a long time and present a diverse range of structures, with the  $[XMo_{12}O_{40}]^{n-}$  Keggin ions ( $X = P, Si, \dots$ ) perhaps the best known.<sup>1</sup> They are still subject to intense research with >4000 papers published in the past five years.

Following on from our study<sup>2</sup> of aryl arsonic acids  $RAsO_3H_2$ , which are straightforward molecular species based on four-coordinate As(V), we became interested in the corresponding antimony compounds. Although aryl stibonic acids of nominal formula  $RSbO_3H_2$  have been known for over 100 years,<sup>3</sup> their composition has remained uncertain, as they form only amorphous solids, have complicated titration behaviour and only limited solubility. The presumption has been that they are polymeric, based on 5- or 6-coordinate Sb with Sb-O-Sb linkages, though direct evidence is sparse.<sup>4</sup> Recently, it has been shown by Beckman that if very bulky R groups are used, then relatively simple dimers such as  $(2,6-Mes_2C_6H_3Sb_2O_2(OH)_4)$  (Mes=mesityl) can be isolated, but these represent a special case.<sup>5</sup>

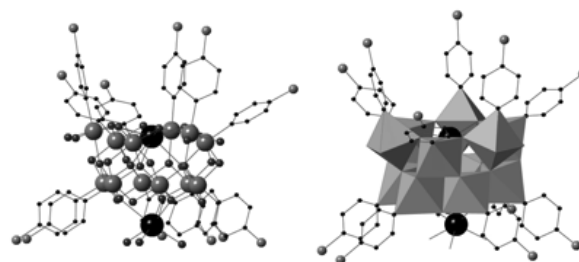
Using electrospray ionisation mass spectrometry (ESI-MS), we were able to show conclusively that  $RSbO_3H_2$  acids ( $R = p\text{-tolyl}, p\text{-ClC}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4$ ), rather than being ill-defined polymers, existed mainly as discrete aggregates of overall formula  $[H_{12}(RSb)_{12}O_{30}]$ , see Fig. 1.<sup>6</sup> There was some evidence for other nuclearities ( $Sb_{14}$ ,  $Sb_{16}$ , etc.) but these were invariably minor.

While the ESI-MS results indicated the formulae, no structural conclusions could be drawn, and attempts to grow single crystals for X-ray analysis have been singularly unsuccessful.



**Fig. 1.** The negative-ion ESI mass spectrum of *p*-tolyl stibonic acid in MeCN showing the specificity of the aggregation to give  $[H_7(MeC_6H_4Sb)_{12}O_{28}]^-$ . The inset shows the characteristic isotope envelope arising mainly from the twelve Sb atoms ( $I = 1/2$ ).

It was noted from the mass spectral results that, unless special precautions were taken, there was a strong tendency for the acids to entrain  $Na^+$  carried over from the syntheses, and even carefully purified samples developed ions containing  $Na^+$  by adventitious leaching from glassware.<sup>6,7</sup> We therefore embarked on a systematic survey of the acid salts formed with a variety of metal cations in the hope of providing crystalline samples for X-ray diffraction. The only prior report in this area came from Winpenny's group, who had shown that a number of complex polyhedra based on antimony could be prepared using solvothermal methods.<sup>8</sup> Their studies, along with ours and some parallel ones from Baskar's group,<sup>9,10</sup> have now established an expanding range of novel polyoxostibonate structures, some of which have direct parallels with polyoxomolybdates and some of which are unique.



**Fig. 2.** The structure of  $[K_2H_{10}(p\text{-ClC}_6\text{H}_4Sb)_{12}O_{30}]$  as stick-and-ball and in polyhedral representations.

With medium-sized cations  $Na^+$  or  $K^+$  the characteristic structures are as shown in Fig. 2.<sup>6,11</sup> They consist of a hexagonal antiprism of six-coordinate Sb atoms with a planar lower layer and a puckered upper one. The framework is completed by thirty oxygen atoms, comprising six triply-bridging, eighteen doubly bridging and six terminal ones. There are two main cation sites. One is 10-coordinate, lying within the hexagonal channel, attached to nine framework O atoms, with an  $H_2O$  coordinated in the final position. This encapsulated cation is very firmly attached within the cavity, which serves as an inorganic equivalent of a crown ether.

A second cation site is six-coordinate, lying below the channel entrance, connected to three framework O atoms and three  $H_2O$  molecules. This position is more promiscuous and can be occupied by  $Rb^+$  or  $Ba^{2+}$  as well as by  $Na^+$  or  $K^+$ .<sup>12</sup> Additional cations may be involved in less well-defined sites depending on the crystallisation conditions, either loosely attached to the main core or as fully solvated cations in the crystal lattice. The differing numbers of cations and their charges is compensated for by differing degrees of protonation of the cluster. These hex-

agonal antiprismatic species have a precedent in one of the components in a complex structure.<sup>8</sup>

With the larger cations, Ba<sup>2+</sup> or Rb<sup>+</sup>, a more open structure forms, with an Sb<sub>14</sub> framework, generating a bowl that cradles the cation in an eleven-coordinate site.<sup>13, 14</sup> The overall formula is [MH<sub>10</sub>(RSb)<sub>14</sub>O<sub>34</sub>]<sup>x-</sup> (M= Ba<sup>2+</sup> x = 0; M = Rb<sup>+</sup> x = 1) and the six-coordinate antimony atoms are linked to six triply-bridging O atoms, twenty four doubly-bridging O atoms and four terminal OH groups (Fig. 3). This geometry is unique to polyoxostibonates.<sup>13</sup>

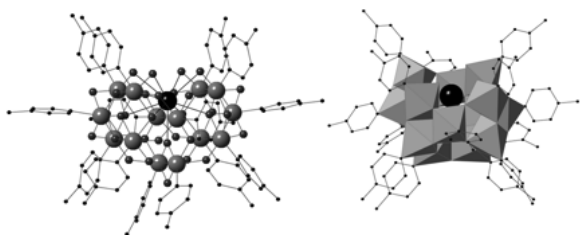


Fig. 3. The structure of bowl-shaped [BaH<sub>10</sub>(*p*-MeC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>34</sub>].

Sb<sub>16</sub> examples been established which have a geometry that can be generated from our Sb<sub>14</sub> examples by removing the cation and capping the open face with two extra edge-shared {RSbO<sub>6</sub>} octahedra.<sup>8, 10</sup> In contrast, with the smaller cation Li<sup>+</sup> a complex was isolated with a more condensed core and overall formula Li<sub>4</sub>[LiH<sub>3</sub>(RSb)<sub>12</sub>O<sub>28</sub>].<sup>13</sup> One of the Li<sup>+</sup> ions is fully encapsulated within the cluster core in a tetrahedral site, and the overall geometry corresponds to the rare  $\gamma$  isomer of the Keggin ion [XMo<sub>12</sub>O<sub>40</sub>]<sup>n-</sup>, Fig. 4.<sup>15</sup> The remaining Li<sup>+</sup> cations are attached to external faces of the polyoxometalate.

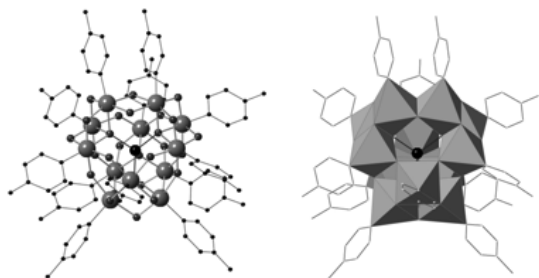


Fig. 4. Two representations of the structure of [LiH<sub>3</sub>(*p*-MeC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>28</sub>]<sup>4-</sup>.

Other isomers of Keggin ions ( $\delta$  and  $\epsilon$ ) are formed<sup>8, 16</sup> when transition metal ions Mn<sup>2+</sup>, Co<sup>2+</sup> or Zn<sup>2+</sup> are incorporated, giving [M(RSb)<sub>12</sub>O<sub>28</sub>]<sup>6-</sup> species which have the transition metal in the centre and the main group metal Sb as the framework atoms (Fig. 5); hence, these have been dubbed ‘inverse Keggin ions’.<sup>8</sup> The overall charge is compensated for by other cations coordinated to the external surface of the cluster via framework O atoms.

So far then, we and others have established an intriguing family of polyoxostibonates with geometries based on four different Sb<sub>12</sub>, one Sb<sub>14</sub> and one Sb<sub>16</sub> core polyhedra (Fig. 6). There is mass spectral evidence for other core nuclearities but these have so far defied isolation.

It is noteworthy that we have found that these compounds

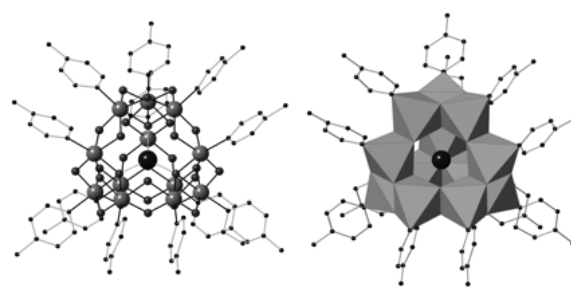


Fig. 5. The structure of the [Co(MeC<sub>6</sub>H<sub>4</sub>Sb)<sub>12</sub>O<sub>28</sub>]<sup>6-</sup> ion, corresponding to the tetrahedral  $\epsilon$ -isomer of the ‘reverse-Keggin ion’ type.

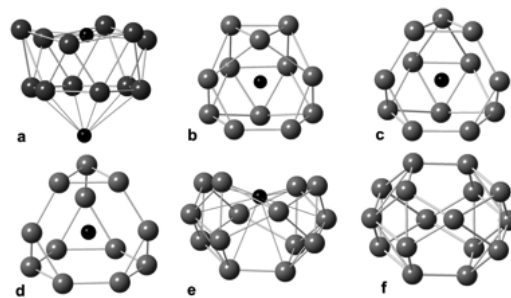


Fig. 6. The range of polyhedral so far known for polyoxostibonates; (a) hexagonal antiprism with cations Na<sup>+</sup> or K<sup>+</sup>; (b)-(d) the  $\gamma$ ,  $\delta$  and  $\epsilon$  isomers of the reverse-Keggin ions found for the Li<sup>+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> examples; (e) the bowl shaped Ba<sup>2+</sup> complex and (f) the empty Sb<sub>16</sub> cluster.

form readily under ambient conditions; the more stringent solvothermal conditions used earlier are unnecessary.<sup>8</sup> Another point of contrast is that the polyoxostibonates are formed from alkaline solutions, whereas traditional Mo or W species are generated under acidic conditions. The polyhedra that are generated appear to be templated by different sized cations but at this stage syntheses are serendipitous, based on trial and error rather than any systematic approach. Future work will undoubtedly provide extra novel examples of polyoxostibonates, and should further determine the importance of cation size, the effects of changing the steric properties of the R group, and the relevance of pH and other parameters on producing particular species. The physical properties of these new materials are so far completely unexplored, so potential uses are yet to be established; we note polyoxomolybdates have many applications as catalysts, as analytical reagents, as sensors and as biologically active compounds, so their antimony analogues may be equally versatile.

#### Acknowledgements.

We thank Cody Wright for synthesis of the aryl stibonic acids and for mass spectral studies as part of his MSc studies, and we are very grateful to Tania Groutso (University of Auckland), Shane Telfer and Geoff Jameson (Massey University) for assistance with the X-ray crystallography, which is far from routine because of the high levels of solvation and ready loss of crystallinity.

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