Polyoxoanions functionalized by diorganotin groups: the tetrameric, chiral tungstoarsenate(III), [{Sn(CH$_3$)$_2$(H$_2$O)}$_2${Sn(CH$_3$)$_2$}As$_3$(α-AsW$_9$O$_{33}$)$_4$]$^{21-}$

Firasat Hussain and Ulrich Kortz*

The tetrameric, hybrid organic–inorganic tungstoarsenate(III) [{Sn(CH$_3$)$_2$(H$_2$O)}$_2${Sn(CH$_3$)$_2$}As$_3$(α-AsW$_9$O$_{33}$)$_4$]$^{21-}$ (**1**) is composed of four (B-α-AsW$_9$O$_{33}$) fragments that are linked by three dimethyltin groups and three As(III) atoms resulting in an unprecedented, chiral polyoxoanion assembly with C_1 symmetry.

Polyoxometalates are discrete metal–oxygen clusters with an enormous structural variety combined with a multitude of interesting properties.[1–6] This class of compounds has been known since the time of Berzelius,[7,8] but the rate of discovery of novel species is currently faster than ever before. There have been increasing efforts worldwide to prepare functionalized polyoxometalates *via* incorporation or coordination of organometallic or organic moieties.[9,10] Predominantly the groups of Knoth, Liu and Pope have investigated the reactivity of monoorganotin species (*e.g.* C$_6$H$_5$SnCl$_3$) with lacunary polyoxotungstate precursors.[11–13] The size of tetravalent tin fits well into the lacunary sites of Keggin- or Dawson-based polyoxotungstates and furthermore the Sn–C bond is hydrolytically and oxidatively stable. This allows to foresee applications of this class of polyanions in medicine (*e.g.* antiviral).[14] Recently Hasenknopf *et al.* used the same methodology to introduce peptide functions in monolacunary Wells–Dawson derivatives [*x*-P$_2$W$_{17}$O$_{61}$]$^{10-}$ (*x* = α$_1$, α$_2$).[15] Very recently Pope *et al.* reported on similar species of the Keggin type.[16]

We decided to investigate the reactivity of diorganotin precursors with lacunary polyoxotungstates in order to introduce additional organic functionalities. Recently we reported on the first examples of dimethyltin-substituted polyanions which are monomeric in solution, but form a 2D lattice in the solid state.[17]

Here we report on the tetrameric tungstoarsenate(III) [{Sn(CH$_3$)$_2$(H$_2$O)}$_2${Sn(CH$_3$)$_2$}As$_3$(α-AsW$_9$O$_{33}$)$_4$]$^{21-}$ (**1**). Single crystal X-ray analysis on K$_7$(NH$_4$)$_{14}$[(Sn(CH$_3$)$_2$)$_3$(H$_2$O)$_2$As$_3$(α-AsW$_9$O$_{33}$)$_4$]·26H$_2$O (**1a**) revealed that the title polyanion **1** is composed of four (B-α-AsW$_9$O$_{33}$) fragments that are linked by three dimethyltin groups and three As(III) atoms resulting in an unprecedented, chiral cage-like assembly with C_1 symmetry (Fig. 1, left).† Polyanion **1** can also be described as a trimeric assembly of [{Sn(CH$_3$)$_2$(H$_2$O)}$_2${Sn(CH$_3$)$_2$}(α-AsW$_9$O$_{33}$)$_3$]$^{21-}$ (Fig. 1, right) which is capped by a fourth (α-AsW$_9$O$_{33}$) Keggin fragment *via* three trigonal pyramidal As(III) linkers (Fig. 2). Interestingly, the [As$_3$(α-AsW$_9$O$_{33}$)] capping unit is formally neutral. The three As(III) linkers are coordinated by two oxygens of a Keggin unit

from the triangular assembly and by one oxygen of the unique Keggin unit. As a result, only three of the six belt tungsten atoms of the unique (AsW$_9$O$_{33}$) unit are involved in the bonding to adjacent Keggin building blocks in an alternating fashion. The orientation of this unique Keggin unit with respect to the triangular tri-Keggin fragment is the reason why **1** is chiral (Fig. 1, left).

The dimethyltin groups are coordinated to two oxygens of each of the adjacent Keggin units and two methyl groups which are in *trans*-positions, as had been observed previously by Kortz *et al.* for [{Sn(CH$_3$)$_2$}$_3$(H$_2$O)$_4$(β-XW$_9$O$_{33}$)]$^{3-}$ (X = As^{III}, Sb^{III}).[17] However, the coordination number and geometry of the three tin centers in **1** is not equivalent. One of the tin atoms (Sn1) is six-coordinated (octahedral) whereas the other two tin atoms (Sn2, Sn3) are seven-coordinated (pentagonal bipyramidal) due to an additional terminal water ligand in the equatorial plane (Sn2–OH$_2$ 2.285(19), Sn3–OH$_2$ 2.49(4) Å). The Sn1–O(W) bonding can be described as two short bonds (2.091, 2.095(17) Å) and two very
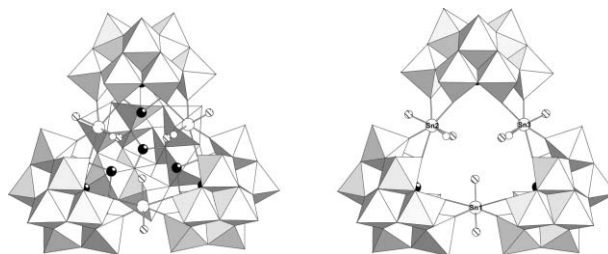

Fig. 1 Top view of [{Sn(CH$_3$)$_2$(H$_2$O)}$_2${Sn(CH$_3$)$_2$}As$_3$(α-AsW$_9$O$_{33}$)$_4$]$^{21-}$ (**1**). In the right figure the unique (AsW$_9$O$_{33}$) fragment and its three associated As(III) linkers are not shown for clarity. The octahedra represent WO$_6$ and the balls are tin (large white), arsenic (black), carbon (hatched) and oxygen (small white). Hydrogen atoms are omitted for clarity.
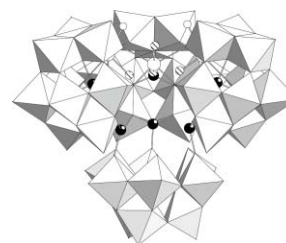

Fig. 2 Side view of [{Sn(CH$_3$)$_2$(H$_2$O)}$_2${Sn(CH$_3$)$_2$}As$_3$(α-AsW$_9$O$_{33}$)$_4$]$^{21-}$ (**1**). The color code is the same as in Fig. 1.

*u.kortz@iu-bremen.de

long bonds (2.400, 2.457(17) Å). On the other hand, the Sn2–O(W) bond lengths (2.300, 2.354, 2.372, 2.478(17) Å) and the Sn3–O(W) bond lengths (2.220, 2.282, 2.308, 2.462(17) Å) indicate three long bonds and one very long bond around the tin centers. The structural inequivalence between Sn1 on one side and Sn2 and Sn3 on the other side is further reflected by the C–Sn–C angles. Specifically, the C–Sn1–C angle (159.7(10)°) is significantly smaller than the C–Sn2–C (169.0(9)°) and C–Sn3–C (172.4(11)°) angles, respectively.

Polyanion **1** was synthesized in a simple one-pot procedure in aqueous, acidic medium by reaction of $(CH_3)_2SnCl_2$ with $K_{14}[As_2W_{19}O_{67}H_2O]$.[18] We have also tried to prepare **1** by a more rational procedure (*e.g.* 3 $(CH_3)_2SnCl_2$ + 4 $Na_9[AsW_9O_{33}]$ + 1.5 As_2O_3), but without success.

Bond valence sum calculations indicate that the water molecules attached to Sn2 and Sn3 represent the only protonation sites in **1**.[19] All potassium ions in **1a** could be identified crystallographically, but some of them are disordered resulting in partial (0.5) occupancy. They are located all around **1** and are coordinated to bridging and terminal oxygens of the polyanion.

We could not identify water molecules or cations in the central cavity of the cage-like **1**. It appears that the hydrophobic nature of the pocket and its small size do not allow for inclusion of the available guests. It is difficult to determine the exact dimensions of the cavity due to the three bridging As(III) centers and their lone pairs of electrons pointing inside the pocket. Nevertheless, we estimate the diameter of the idealized spherical cavity to be around 3.5 Å. Interestingly, the three surface pores of **1** involving the unique Keggin unit are larger than the central cavity (around 5 Å).

We also examined the solution properties of **1** by multinuclear NMR (D_2O, 20 °C). Our ^{119}Sn NMR measurements resulted in 2 singlets (−147.8, −158.4 ppm) with intensity ratios 1 : 2, for ^{13}C NMR we observed a singlet at 7.4 ppm and for ^1H NMR we obtained a singlet at 0.9 ppm. This is in agreement with the solid state structure of **1**, which indicates the presence of two magnetically inequivalent tin atoms. The peak at −158.4 ppm is assigned to the seven-coordinated Sn2 and Sn3, whereas the signal at −147.8 is due to the six-coordinated Sn1. It can be noticed that the magnetically inequivalent Sn2 and Sn3 cannot be distinguished by ^{119}Sn NMR. Apparently the chiral nature of **1**, which is induced by a rotated binding mode of the unique (AsW_9O_{33}) Keggin fragment, does not protrude all the way to the other end of the molecule. Therefore, ^{119}Sn NMR provides only information about the local coordination environment of Sn2 and Sn3. The same conclusions can be drawn based on the ^1H and ^{13}C NMR results for **1**, as all six methyl groups appear as magnetically equivalent. The actual symmetry of **1** in solution could be shown best by ^{183}W NMR, but unfortunately we have not been able to obtain high quality spectra to date. This may be due to the very large number of expected peaks (up to 36).

The title compound **1** represents the first polyanion containing dimethyltin and arsenic(III) linkers at the same time. Furthermore, **1** represents the first member of a novel family of diorganotin–polyanion based cage complexes. The structure of **1** reveals that (a) the dimethyltin unit acts as a linker of two $(B-\alpha-AsW_9O_{33})$ Keggin-type fragments, (b) the linkage is achieved *via* two, coplanar Sn–O(W) bonds between each of the Keggin fragments, (c) the methyl groups of the incorporated dimethyltin units are oriented *trans* to each other, (d) the incorporated dimethyltin units are oriented such that one of the two methyl groups points inside the central polyanion cavity, (e) the tin atoms of the incorporated dimethyltin units can have octahedral as well as pentagonal-bipyramidal coordination geometries, (f) the diamagnetic nature of the dimethyltin unit allows for the use of multinuclear NMR as a structural characterization technique, (g) dimethyltin substituted polyanions tend to form cage-like structures, (h) the dimethyltin unit is an ideal, hydrolytically stable, sterically not too demanding building block/linker for the design of nanomolecular containers, (i) it is possible to prepare discrete, supramolecular host–guest systems with large cavities and a highly porous surface, and finally (j) we have discovered a novel class of polyanions which is of major interest for medicinal applications (*e.g.* antiviral) due to a unique combination of important properties (*e.g.* a discrete, nanomolecular anion, stable at physiological pH, tightly bound organic moieties on the surface, rational modification of steric and electrostatic surface properties).

In summary, the large number of available Keggin- and Dawson-based lacunary polyanion precursors allows for an array of novel diorganotin-based derivatives to be envisioned. In addition, the possibility of studying the mechanism of formation of such compounds accompanied by detailed investigations of applied (*e.g.* medicine) and academic (*e.g.* topology) properties indicate that **1**, as well as the novel family of polyoxometalates it represents, will attract the attention of scientists from many different disciplines.

We have already isolated some other dimethyltin-substituted polyoxometalates with highly interesting shapes and sizes. These compounds are based on different types of Keggin precursors and will be reported elsewhere.

Currently we are also investigating whether the antimony(III) analog of **1** exists.

Firasat Hussain and Ulrich Kortz*
International University Bremen, School of Engineering and Science, PO Box 750 561, 28725 Bremen, Germany. E-mail: u.kortz@iu-bremen.de; Fax: +49 421 200 3229; Tel: +49 421 200 3235

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