Communications

Isopolyoxotungstates

Structural Evolution of "S"-Shaped $[H_4W_{22}O_{74}]^{12-}$ and "§"-Shaped $[H_{10}W_{34}O_{116}]^{18-}$ Isopolyoxotungstate Clusters**

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The formation of polyoxometalates (POMs), which are anionic oxide clusters of the early transition metals,[1] are a vast class of inorganic materials with a virtually unmatched range of properties.[2,3] As POM clusters are constructed using {MO_x} building blocks (where M = Mo, W; x = 4–7) that can be condensed at low pH, the number of possible structure types,[4] especially in the isopolyoxometalate (*iso*-POM) area can be incredibly large. For example, on acidification of an aqueous tungstate solution, addition and condensation reactions occur, triggering the self-assembly of polynuclear isopolytungstate ions.[5] These species can serve as structural components of large polyoxometalates formed by conservative self-organizing processes.[6,7] However, the most recent development in the discovery of new POM structures (the subject of > 5000 research papers during the last decade) to date has mainly involved the integration of heteroanions or heterometals that support the molybdate- or tungstate-based frameworks.[8] In this context, we recently explored approaches to isolate new cluster structures, for example, $[H_2Mo_{16}O_{52}]^{10-}$[9] using protonated hexamethylenetetramine, and $[H_{12}W_{36}O_{120}]^{12-}$, which can be considered as an inorganic crown.[10] Furthermore, the same reaction system at lower pH values (ca. 0.8) yields a fundamentally new type of isopolyoxotungstate, $[H_4W_{18}O_{56}(WO_6)]^{6-}$, which was isolated as triethanolammonium (TEAH$^+$) salt $(TEAH)_6[H_4W_{19}O_{62}]$.[11] In POM chemistry, the number of polyoxotungstates being reported is rising at an incredibly rapid rate,[4,6,12] but isopolyoxotungstates are extremely rare, with only a handful of examples, such as, $[HW_5O_{19}]^{7-}$,[13] $[W_6O_{19}]^{2-}$,[14] $[H_3W_6O_{22}]^{5-}$,[15] $[W_7O_{24}]^{6-}$,[16] $[W_{10}O_{32}]^{4-}$,[17] $[H_4W_{11}O_{38}]^{6-}$,[18] $[H_2W_{12}O_{40}]^{6-}$,[19] $[H_2W_{12}O_{42}]^{10-}$,[20] and $[W_{24}O_{84}]^{24-}$.[21] There are also clear indications that the nature of the inorganic cation and the pH has a strong influence on the reaction pathways in solution.[22] Unlike the polyoxomolybdates,[23] the influence of the inorganic counterion on the assembly of polyoxotungstates has not been explicitly studied.

Herein we aimed to extend the family of isopolyoxotungstates using a combination of pH and anion control to unravel the influence of these factors on the self assembly of anionic isopolyoxotungstates. We demonstrate that it is possible to discover radically new cluster architectures in the isopolyoxotungstate family by simply acidifying solutions of sodium tungstate, whereby it is possible to isolate and crystallize a "S"-shaped $[H_4W_{22}O_{74}]^{12-}$ cluster at pH 3.4 to give compound **1** as $Na_{12}[H_4W_{22}O_{74}]\cdot31H_2O$. On lowering the pH to 2.4, a related "§"-shaped $[H_{10}W_{34}O_{116}]^{18-}$ cluster is isolated as $Na_{18}[H_{10}W_{34}O_{116}]\cdot47H_2O$ (**2**). Moreover, both compounds can only be isolated in good yield if Na_2SO_3 is used, and this is verified by using a series of anion control experiments. Both compounds were characterized by chemical analysis, X-ray crystallography, spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In addition, studies using electrospray mass spectrometry show that both the {W_{22}} and {W_{34}} clusters can be observed in the gas phase, with envelopes centered at $m/z = 1814$ for {W_{22}} and $m/z = 2077$ for {W_{34}}, which demonstrate that the clusters are present in solution.
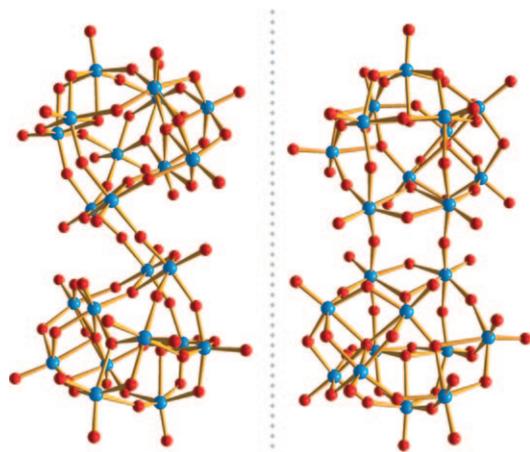
During the synthesis of **1**, the pH was adjusted to about 3.4 by the addition of hydrochloric acid upon stirring. The pale yellow solution was heated, filtered, and the filtrate left to stand for three days. During this period of time, pale creamy, almost colorless hexagonal crystals of **1** gradually appeared in good yield (see the Experimental Section). The compound can also be synthesized over a wider pH range (3.0–3.7), with the optimum yield being at pH of 3.4. X-ray crystallographic analysis of **1** shows that the new *iso*-POM $[H_4W_{22}O_{74}]^{12-}$ in **1**, $Na_{12}[H_4W_{22}O_{74}]\cdot31H_2O$,[24] has a unique S-shaped topology (1.8 nm in length and 0.9 nm wide) and that the {W_{22}} cluster is built from two {W_{11}} subunits linked by two μ_2-oxo bridges in *trans* fashion (Figure 1).

The two {W_{11}} subunits (analogous to the framework of the $[H_4W_{11}O_{38}]^{6-}$)[18] can be described as a fishing net, in which two fused half cubanes share one edge with another half cubane, and two corner-shared dimeric tungsten-species bridge them together. A direct comparison with the uncapped Keggin structure (to draw comparisons between the isopoly and heteropoly anions) reveals a similar framework, in which a dimeric unit has been replaced by a set of the aforementioned fused double-half cubane unit introducing asymmetry to the {W_{11}} synthon along with disorder of the WO_6 octahedra (Figure 2). One of the two edge-shared dimeric units consists of dioxo tungsten metal centers, and the other unit brings the two {W_{11}} units together through a μ_2-oxo bridge. This is in contrast to the $[H_4W_{11}O_{38}]^{6-}$ compound, in which both the dimeric units incorporate two terminal oxo groups. This is important, as the {W_{22}} architecture has two accessible lacunary-like positions and potentially can be used as a building block in an effort to further extend the structural
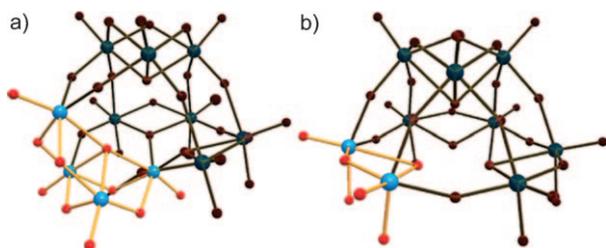
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Figure 1. Representations of the framework found in the structures of compound **1**. Left: the S-shaped structure; right: a view of the two μ_2-bridges in the plane. W blue, O red.
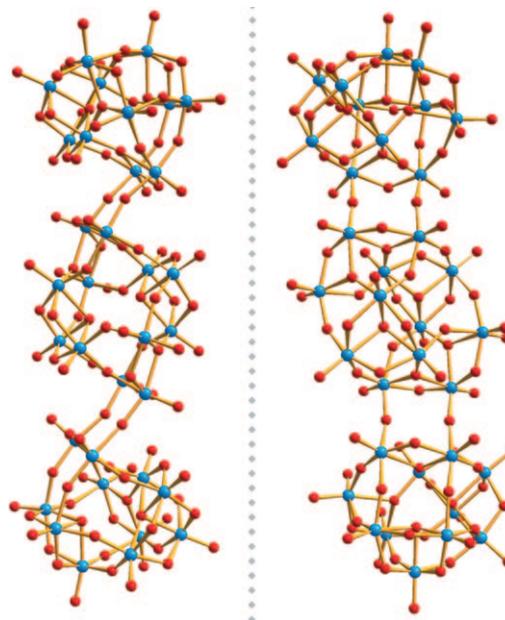

Figure 2. Ball and stick representation of a) the $\{W_{11}\}$ adduct, and b) the uncapped $\{W_9\}$ trivacant lacunary Keggin anion (the heteroanion is omitted for clarity). The different parts of the two structures are highlighted to make a comparison between the isopoly and hetero-polyanion.

motif and discover new members of isopolyoxotungstate family. However, these building blocks are not templated by heteroanions, which means that the structures are potentially a lot more flexible and diverse. The remainder of the metal centers incorporate one terminal oxo group, which is located at an average bond distance of 1.72(2) Å (W=O_t), whilst the bridging has an average bond distance of 1.90(15) Å (W−O) from the metal centers. The W···W separations are between 3.10(1) and 3.90(2) Å, with the longer separations located between the metal centers at the bridging point of the two $\{W_{11}\}$ units. All the tungsten atoms have distorted octahedral geometry and the bond-valence sum (BVS) model[25] clearly indicates that all the tungsten atoms are in the +6 oxidation state. Inside the cluster, there is a distorted tetrahedral vacancy in each $\{W_{11}\}$ unit occupied by one proton (BVS for this site is 1.1), whereas two additional protons appear to be located on the outer shell of the architecture (from the BVS analysis). The $\{W_{22}\}$ unit can thus be considered to be formed by the condensation of two $\{W_{11}\}$ units.

During the synthesis of **2**, the pH was adjusted to about 2.4 by the addition of hydrochloric acid upon stirring. The pale yellow solution was heated, filtered, and the filtrate left to stand at room temperature for 5 days. Rod-shaped crystals of **2** appeared in good yield. X-ray crystallographic analysis of **2**

indicates that the new *iso*-POM $[H_{10}W_{34}O_{116}]^{18-}$ in **2**, $Na_{18}[H_{10}W_{34}O_{116}]\cdot47H_2O$,[24] has a unique §-shaped topology (2.8 nm in length and 1.0 nm wide), and that the $\{W_{34}\}$ cluster consists of two identical $\{W_{11}\}$ subunits as described above (Figure 2a). These $\{W_{11}\}$ subunits are linked in a *trans* fashion by a $[H_2W_{12}O_{42}]^{10-}$ $\{W_{12}\}$ unit[20] through two μ_2-oxo bridges to give an expanded §-like architecture (Figure 3). All the

Figure 3. Representations of the framework found in the structure of compound **2**. Left: the §-shaped structure; right: a view of both sets of W−O−W linkages in the plane. W blue, O red.

tungsten atoms are in a distorted octahedral geometry and BVS[25] clearly show that all the tungsten atoms are in the +6 oxidation state. One of the two edge-shared dimeric blocks of $\{W_{11}\}$ subunits consists of dioxo tungsten metal centers, whereas the rest incorporate one terminal oxo group O_t. The latter group is located at an average distance of 1.72(2) Å (W=O_t), whereas the bridging groups are at 1.99(14) Å (W−O). The W···W separations are between 3.2405(1) and 3.8824(1) Å with the longer separation located between the W(4) and W(5) metal centers within the $\{W_{12}\}$ bridging unit. This $\{W_{12}\}$ unit is compressed from the tetrahedral geometry to a flatter species (Figure 3).
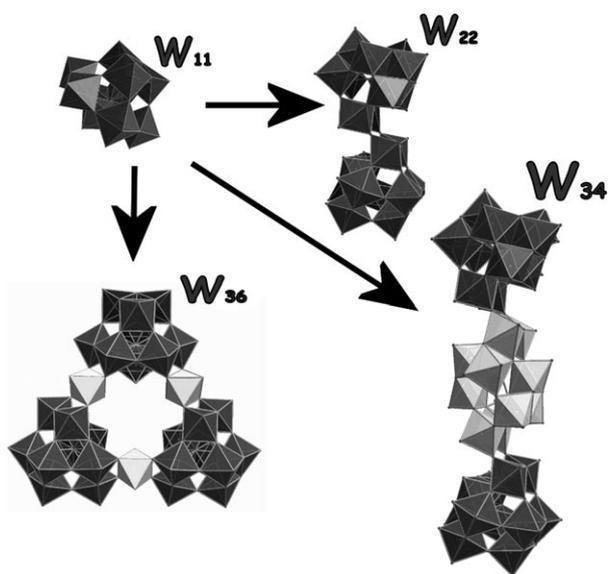
Both the $\{W_{22}\}$- and the $\{W_{34}\}$-based clusters have related architectures, which are unexpected, with divergent topologies based upon the linkage of $\{W_{11}\}$ building blocks. For instance, it is possible to convergently combine three $\{W_{11}\}$ building blocks to give a triangular-shaped $[H_{12}W_{36}O_{120}]^{12-}$ cluster.[10] The $\{W_{36}\}$ unit consists of three "*cis* edge-shared" $\{W_{11}\}$ units linked by three $\{W_1\}$ groups. The $\{W_1\}$ groups act as spaces to facilitate the *cis* linkage of the three $\{W_{11}\}$ units, whereas it is not sterically possible to connect the three $\{W_{11}\}$ units together in an analogous manner to the $\{W_{22}\}$ unit, through two μ_2-oxo bridges between each pair of the clusters.

The isopolyoxotungstates found in compounds **1** and **2** (which are isolated from aqueous solutions at pH 3.4 and 2.4

respectively) are interesting as acidification of tungstates has been intensely studied during the last few decades, yet these compounds have evaded detection. However, in polyoxotungstate chemistry, the age of the solution and the total concentration play an important role.[26] It is important to point out that the synthetic procedures for synthesizing compounds **1** and **2** require the presence of the sulfite anion, and control experiments without the presence of sulfite, or only with a catalytic amount of the sulfite, do not allow the isolation of the compounds in high yields. Furthermore, substitution of the sulfite with other anions, such as the sulfate, nitrate, and phosphate, with the same reaction conditions do not result in the formation of compounds **1** or **2** (Supplementary Information). Further attempts to isolate the clusters using different counterions (for example, protonated organic amines) did not allow the clusters **1** and **2** to be isolated.

The evolution of the clusters from $\{W_{11}\}$ to $\{W_{22}\}$ and $\{W_{34}\}$ is intriguing (Figure 1 and 3), as it leads towards a new building block principle for designing new species of this family of compounds. This can be illustrated by the assembly of the $\{W_{22}\}$ and $\{W_{34}\}$ using $\{W_{11}\}$ building blocks, and in the case of the $\{W_{34}\}$, an additional *para* tungstate-B-like unit $[H_2W_{12}O_{42}]^{10-}$[20] is involved linking the two $\{W_{11}\}$ units. Therefore, this structural evolution from $\{W_{22}\}$ leads to the expanded $\{W_{34}\}$ cluster with increased structural complexity compared to the $\{W_{22}\}$ cluster. Comparing the structures of these clusters with the three-fold-symmetric $\{W_{36}\}$ cluster, which comprises three $\{W_{11}\}$ and three $\{W_1\}$ building blocks, establishes the importance of the $\{W_{11}\}$ unit and highlights the possibilities for the assembly of new architectures based on $\{W_{11}\}$ (Figure 4).

In summary, we have demonstrated the isolation and characterization of two isopolyoxotungstate clusters, which adopt an unprecedented structural S-shaped and §-shaped

cluster archetype. The anions $[H_4W_{22}O_{74}]^{12-}$ and $[H_{10}W_{34}O_{116}]^{18-}$ are two new members of the family of isopolyoxotungstates, and the relationship to the previously reported $\{W_{36}\}$ cluster demonstrates that a new building block principle can be generated using pure isopolyoxotungstate-based $\{W_{11}\}$ units. Furthermore, the direct observation of these cluster-based species in the gas phase using electrospray mass spectrometry shows that these systems do have stability in solution, and this is the first time that high nuclearity (>12) of *iso*-POMs have been identified in the gas phase. This means that a whole research area that utilizes pure isopolyoxometalate-based building blocks rather than heteropolyoxotungstates is opened and that the self-assembly of complex polyoxotungstates is now possible using pure isopolyoxotungstates. Although crystallographic and chemical analysis all confirmed that there is no sulfur inside the products, the necessity of sulfite in the reaction is clear from our studies. Further work will be the exploration of the detailed role of the sulfite anion in the formation of the cluster and the possibility of interexchange of different *iso*-POMs using the building-block principle.

Experimental Section

1: Solid Na_2SO_3 (0.85 g, 6.7 mmol) was added slowly to a stirred boiling aqueous solution of $Na_2WO_4\cdot2H_2O$ (20.0 g, 60.6 mmol in 40 mL of H_2O). Concentrated HCl was then added dropwise up to a pH value of 3.4. In the pH range 4–7, a white precipitate was sometimes formed, which redissolved upon further addition of HCl. The color of the solution changed from colorless to pale yellow. The reaction mixture was heated up to 80°C for 60 min and then filtered. The filtrate was left to crystallize slowly at room temperature in an open Erlenmeyer flask for three days. Hexagonal plate-like colorless crystals were collected by filtation and dried in air. Yield: 5.0 g (29.9%, based on tungsten); elemental analysis calcd (%) for $H_{66}Na_{12}O_{105}W_{22}$ (6067): Na 4.55, W 66.67; found Na 4.22, W 66.39; IR (KBr): $\tilde{v} = 1634$ (δ_{H_2O}), 938 ($\delta_{W=O}$), 874, 843, 802, 715 (v_{W-O-W}); TGA: % weight loss: 9.34 (182.0 °C, assigned to 31 H_2O molecules), 1.03 (up to 1000 °C, assigned to 2 H_2O molecules).

2: Solid Na_2SO_3 (1.70 g, 13.4 mmol) was added slowly to a stirred aqueous solution of $Na_2WO_4\cdot2H_2O$ (40.0 g, 121.2 mmol in 40 mL of H_2O). HCl (4 M) was then added dropwise up to the pH value of 2.4. In the pH range 4–7, a white precipitate sometimes was formed, which redissolved upon further addition of HCl. The color of the solution changed from colorless to yellowish. The reaction mixture was heated up to 80°C for 60 min and then filtered. The filtrate was left to crystallize slowly at room temperature in an open Erlenmeyer flask for 5 days in the fume hood. Rod shaped colorless crystals were filtered and dried in air. Yield: 12.5 g (38%, based on tungsten); elemental analysis calcd (%) for $H_{104}Na_{18}O_{163}W_{34}$ (9377): Na 4.41, W 66.66; found Na 4.25, W 65.76; IR (KBr): $v = 1624$ (δ_{H_2O}), 947 ($\delta_{W=O}$), 888, 841, 808, 678 (v_{W-O-W}); TGA: % weight loss: 9.01 (152.5 °C, assigned to 47 H_2O molecules), 1.52 (up to 1000 °C, assigned to 6 H_2O molecules).

Figure 4. The assembly of the S-shaped $\{W_{22}\}$ and the §-shaped $\{W_{34}\}$ and the trimeric $\{W_{36}\}$ units [10] with the tungsten centers shown as polyhedral representations. The $\{W_{11}\}$ units are shown in dark gray and the $\{W_1\}$ and $\{W_{12}\}$ linkers are shown in light gray.

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[24] Crystallographic data for $Na_{12}[H_4W_{22}O_{74}]\cdot31H_2O$ **1**: $H_{66}Na_{12}O_{105}W_{22}$, $M_r = 6067.11$; hexagonal crystal: $0.18 \times 0.11 \times 0.06$ mm^3; $T = 100(2)$ K. Triclinic, $P\bar{1}$, $a = 11.9813(5)$, $b = 19.7974(8)$, $c = 23.1309(9)$ Å, $\alpha = 73.405(2)$, $\beta = 88.140(2)$, $\gamma = 72.832(2)°$, $V = 5015.7(4)$ Å^3, $Z = 2$, $\rho = 4.02$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 25.282$ mm^{-1}, $F(000) = 5332$, 71959 reflections measured, 18661 unique ($R_{int} = 0.078$), 1199 refined parameters, $R1 = 0.0835$, $wR2 = 0.2186$. $Na_{18}[H_{10}W_{34}O_{116}]\cdot47H_2O$ **2**: $H_{104}Na_{18}O_{163}W_{34}$, $M_r = 9377.55$; block crystal: $0.31 \times 0.23 \times 0.16$ mm^3; $T = 150(2)$ K. Triclinic, $P\bar{1}$, $a = 11.9905(5)$, $b = 13.0962(5)$, $c = 26.0918(8)$ Å, $\alpha = 86.661(3)$, $\beta = 83.342(3)$, $\gamma = 80.998(3)°$, $V = 4016.1(3)$ Å^3, $Z = 1$, $\rho = 3.877$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 24.398$ mm^{-1}, $F(000) = 4122$, 49974 reflections measured, 15675 unique ($R_{int} = 0.037$), 1001 refined parameters, $R1 = 0.0362$, $wR2 = 0.0872$. Crystal data were measured on a Bruker ApexII CCD and Gemini Oxford diffractometers respectively using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-419465 (**1**) and CSD-419466 (**2**).

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