Discovery of a Family of Isopolyoxotungstates
\([\text{H}_4\text{W}_{19}\text{O}_{62}]^{6-}\) Encapsulating a \{WO_6\} Moiety within a \{W_{18}\} Dawson-like Cluster Cage**

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Polyoxotungstates are continuing to attract attention because of their appealing electronic and molecular properties that give rise to many applications in, for example, catalysis\(^{[1]}\) and materials science.\(^{[2]}\) Since their materials properties are intricately linked to their structural features, the creation of novel polyoxotungstate structural types remains a pressing challenge. However, the development of new structures has thus far mostly involved the integration of heteroanions or heterometalsthat support the tungstate-based frameworks.\(^{[3]}\) Only a few examples of basic types of isopolyoxotungstates are known, including \([\text{HW}_5\text{O}_{19}]^{12-}\)^{[4]} and \([\text{W}_6\text{O}_{19}]^{12-}\)^{[5]}

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[H₆W₁₉O₆₀]⁵⁻ [W₉O₂₄]⁴⁻ [W₁₀O₆₆]⁴⁻ [H₂W₁₈O₅₄(PO₄)₂]⁶⁻ [H₂W₁₈O₅₄(SO₄)₂]⁶⁻. The synthesis of fundamentally new isopolyoxotungstates, which may subsequently be used as building blocks in constructing larger architectures or networks, therefore requires new strategies that exploit supramolecular interactions during the construction of the cluster architecture. In this context we recently explored the use of larger, flexible organic cations that allowed us to isolate new cluster structures, for example, the isopolyoxomolybdate [H₅Mo₆O₃₃]³⁺⁻ using protonated hexamethylenetetramine, which encapsulates this unit in solution, thereby limiting its reorganization to simpler structure types. We extended this strategy to tungstate-based systems by using protonated triethanolamine (TEAH⁺) as cations at around pH 2 and isolated the isopolyoxotungstate [H₆W₁₈O₅₄]⁴⁻, which can be thought of as an inorganic “crown ether”.[12] Notably, the same reaction system at lower pH values (around 1) yields a fundamentally new type of isopolyoxotungstate [H₄W₁₉O₆₂]⁶⁻ (1a), which was isolated as its salt (TEAH)₆[H₄W₁₉O₆₂] (4).

Compound 1 forms after refluxing a solution of sodium tungstate and TEAH⁺ at pH 0.8 for more than three days, during which time the solution gradually changes from colorless to pale green. In the absence of the bulky organic TEAH⁺ cations, under otherwise identical reaction conditions, only the well-known [W₉O₃₃]⁴⁺ cluster compound forms, which implies the existence of a crucial cation effect.[13] Although crystals of 1 were of poor quality, which meant that the cluster oxido positions and the TEAH⁺ cations could not be well resolved because of disorder,[14] the metal skeleton of 19 W centers is clearly resolved and resembles that of a Dawson-type [W₁₈] cage (realized for instance as [W₁₈O₅₄(PO₄)₂]⁶⁻) featuring an additional W center located in the center of the cluster and the absence of the two heteroatoms typically associated with Dawson-type clusters.

Analysis of 1 by ¹⁸⁷W NMR spectroscopy in aqueous solution shows three groups of W centers, which correspond to a single tungsten center and two types of tungsten centers typically found in a Dawson-type cluster sphere (consisting of six “cap” and twelve “belt” W atoms). Furthermore, recrystallization of 1 in water yields a new crystal form 1’,[14] which has cubic morphology and composition (TEAH)₆[H₄W₁₉O₆₂]·6H₂O. The vastly improved crystal quality led to a better resolved structure with minimal disorder of the central WO₆ environment and the positions of the capping W centers.[14] Thus, [H₂W₁₈O₅₄]⁶⁻ represents the first example of an isopolyanion adopting a Dawson-type heteropolyanion framework structure.[15,16]

The disorder pattern found in the structures of 1 (and 1’) implies that different isomers of 1a cocrystallize in 1 (and 1’) which cannot be resolved in the presence of water as a solvent and TEAH⁺ cations. To explore the [Wₙ] cluster type fully, cation exchange and transformation of the clusters into organic solvent were performed by redissolving 1 in water and precipitating the [W₉] cluster with n-tetrapropylammonium (Pr₄N⁺) and recrystallizing the resulting precipitate from acetonitrile. Two isomers (Pr₄N⁺)[H₆W₁₈O₅₄]·6CH₃CN (2) and (Pr₄N⁺)[H₆W₁₈O₅₄]·3CH₃CN (3) were successfully obtained as crystalline solids and were fully characterized by single-crystal X-ray diffraction.[14] Compound 2 crystallizes in a monoclinic system (space group C2) with two crystallographically independent cluster halves in the asymmetric unit, where both complete clusters consist of a Dawson-type [W₁₈] cage and an additional central W site that lies on crystallographic C₂ axes. Figure 1 shows one of the two complete clusters (2a), defined as the D₃₀-symmetric α isomer of the new isopolyoxotungstate [H₆W₁₈O₅₄]⁶⁻ family. Cluster 2a consists of the [W₁₈O₅₄] cage framework and interior oxido ligands of the conventional Dawson cluster anion α-[W₁₈O₅₄(PO₄)₂]⁶⁻ (X = P, S).[9] But, in contrast to the classical Dawson structure, the two tetrahedral XO₆⁻ heteroanions are replaced by a trigonal-prismatic WO₆⁻ anion and two µ₃-oxido ligands (partially protonated, see below), each of which bridges the capping [W₁₈] triangle from the inside of the cluster with an average W–O bond length of 2.23(3) Å. To the best of our knowledge, this is the first observation in polynuclear tungstates of a [WO₄] unit in which the W center adopts a trigonal-prismatic coordination environment with all W–O bond lengths virtually identical (1.96(3) Å) – in all previous examples the [WO₄] units typically display octahedral geometries.
with one or two short terminal W=O bonds and some longer W-(µ-O) bonds. Two tetrahedral “voids” exist in 2a at the positions that are typically occupied by the heteroatoms in conventional Dawson cluster anions α-[W₁₈O₄₆(XO₄)₉]⁻. Two of the four oxido ions that define each tetrahedral “void” are protonated and form H-bonds with the other two ions, which is similar to the corresponding situations inside the Keggin cluster [H₃W₁₁O₃₉]⁻.[17] and the semivacant Dawson polyoxotungstate [Ce[P(H)W₁₇O₆₁]₉]⁻.[18] This protonation assignment is supported by ¹H NMR measurements, elemental analyses, bond valence sum analysis, and crystal structure determinations, which showed only six Pr₃⁺ counterions per cluster in 2. Interestingly, 2a bears some resemblance to the [WO₆]-type cluster α-[H₂W₄NaO₇F]⁻ previously reported by Baker and co-workers[19] in which the central template [NaF₆]⁻ also displays a trigonal prismatic configuration with six Na–F bond lengths in the range from 2.17 to 2.32 Å, which are significantly longer than those of the corresponding W–O bond lengths of the central [WO₆]⁻ unit in 2a. The F–W bonds (ca. 2.22 Å) are much shorter than the corresponding O–W bonds (ca. 2.42 Å) in 2a. Bearing the geometric similarity of these two structures in mind, we have carefully checked the position of the central W atom in 2a. However, all evidence from structure refinement, spectra, and chemical analyses unambiguously confirmed the central position as a tungsten center. In addition we have measured the cold-spray mass spectra of an acetonitrile solution of 2 and 3, which clearly showed the intact cluster in the gas phase: [(Pr₄N)₂–2a]⁻ and [(Pr₄N)–3a]⁻ were observed at m/z 5420 and could be unambiguously assigned by comparison to the expected isotopic envelope.

Compound 3 crystallizes in an orthorhombic system (space group Pcen)[16] and contains the [H₃W₁₈O₄₆]⁻–cluster 3a as the centrosymmetric γ⁺ isomer with D₁₈h symmetry (Figure 1). Cluster 3a is based on the geometry of the [W₉O₄₃]⁻ cage framework and interior oxido ligands as found in the conventional Dawson cluster anion γ⁺-[W₁₈O₄₆(SO₄)₉]⁻.[20] Again, an additional W site is located at the center of the cluster and coordinates to six oxido ligands to form a central [WO₆] centrooctahedral template of octahedral geometry. As in 2a, two further µ₃-oxido ligands inside the cluster each bridge one of the capping [W₃] triangles with an average W–O bond length of 2.28(1) Å. All W–O bond lengths in the [WO₆] central template of 3a are nearly identical (1.95(5) Å), and such a [WO₆] octahedral geometry is also the first observation of this kind in polynuclear clusters. Two tetrahedral “voids” similar to those in 2a are occupied by two protons each and this is confirmed by ¹H NMR results. Unlike the chemical shift values found in the ¹H NMR spectrum of the Keggin cluster [H₂W₁₁O₃₉]⁻, which only shows one peak at around 6.0 ppm because of the inner regular tetrahedral O⁻ environment (with O–O distances of approximately 2.90 Å), several peaks corresponding to the four protons present within the clusters 2 and 3 are found in the range 4.7–8.1 ppm (and all these peaks integrate to about 4 protons per cluster). This observation can be explained by the trigonal pyramidal (nontetrahedral) environment. In 2, the average base length (O–O) of the pyramid is 2.61(5) Å, while the side length is 2.85(2) Å. In 3, these two values are 2.73(3) and 2.96(2) Å. Strong hydrogen bonding (indicated by short O···O separations in 2 and 3) means that the protons will be observed at lower chemical shifts (e.g. δ = 4.7 ppm), and, since the local symmetry is lowered, the four protons are not equivalent. In the ¹H NMR spectrum of 1 in D₂O, only aliphatic protons (-CH₂- in TEAH⁺) are resolved as the protons present in the clusters were not observed owing to rapid exchange with solvent, which is similar to the case in semivacant Dawson polyoxotungstate [Ce[P(H)W₁₇O₆₁]₉]⁻.[18] However, we were able to measure a ¹H NMR spectrum of 1 in DMSO which shows several peaks at δ = 8.01, 7.23, 5.74, 5.27, 4.66, 4.45, and 4.00 ppm. As 1 is not soluble in CD₃CN, any comparison of ¹H NMR spectra for 1, 2, and 3 is purely qualitative; this is because of the possibility of several protonation sites and uncertainty about the population at a given site. However, it is notable that the same types of proton environment associated with pure isomers 2 and 3 all have corresponding shifts found in 1, which contains the isomers found in 2 and 3.

The difference between the [W₁₈] isomers 2a and 3a concerns the [W₉O₄₃]⁻ cage and central template [WO₆]⁻ geometries. Topological analysis indicates that, besides 2a and 3a, other isomers are possible: the [H₃W₁₈O₄₆]⁻ family consists of six isomers that are also observed for the conventional Dawson anions [W₉O₄₆(XO₄)₉]⁻ (X = P, S, etc.),[15,20] that is, the same [W₉O₄₆]⁻ cage variations and interior bridging oxido group orientations are present; we therefore adopt the same isomer designations (α, α*, β, β*, γ, γ*). The α, β, and γ isomers all contain the trivalent prismatic [WO₆]⁻ central unit (D₃h), whereas the α*, β*, and γ* isomers contain a centrosymmetric octahedral [WO₆]⁻ central unit (D₃d), α, β*, and γ isomers all form a D₁₈h-symmetric [W₁₈] cage whereas the α⁺, β, and γ⁺ isomers all form a D₃d-symmetric [W₁₈] cage. As the point groups of the [W₁₈] cages and the [WO₆]⁻ central units match, the complete α and γ cluster isomers adopt D₁₈h symmetry, whereas the α⁺ and γ⁺ cluster isomers adopt D₃d symmetry. The symmetry mismatch for the [W₁₈] cages and central [WO₆]⁻ units in both β and β⁺ isomers reduces their overall symmetry to C₃v. Therefore, the comparison between the [W₁₈] Dawson and the [W₁₈] structure types is strengthened not only by their framework topology, but also by the fact that the 18 tungsten centers of the [W₁₈] caged of the corresponding α and γ isomers occupy exactly the same positions in both structure types within an error margin of 0.2 Å. Planar projections (Schlegel diagrams) were constructed to understand the connectivity of the Dawson-type [W₁₈] and our [W₁₈] frameworks better and to examine the similarity between the two.[21] Schlegel diagrams can be used for the Dawson-like clusters to describe the [W₁₈] cage frameworks in which each link represents a bridging oxido ligand between W atoms. Therefore in the D₁₈h-symmetric systems (Figure 2a), the edges of the outmost and innermost triangles (capping [W₃] groups) are parallel, whereas in the D₃d-symmetric systems (Figure 2b), these two triangles are inverted with respect to each other. These two configurations, combined with the orientations and geometries of the central [WO₆]⁻ units as described above, produce planar projections of all six isomers. Figure 2 demonstrates the α isomer 2a and γ⁺ isomer
Figure 2. Schlegel diagrams of the \{WO₆\}_n anion template. The central WO₆ units shown as eclipsed (trigonal prismatic) and staggered lines (octahedral). a) \(\alpha\) isomer and b) \(\gamma^*\) isomer. Other isomers can be deduced in the following ways: \(\beta\) isomer: the \{WO₆\}_n cage in (b) plus WO₆ unit in (a); \(\gamma\) isomer: \(\alpha\) isomer in (a) with the WO₆ unit turned by 60° along the main C₃ axis; \(\alpha^*\) isomer: \(\gamma^*\) isomer in (b) with the WO₆ unit turned by 60° along the main C₃ axis; \(\beta^*\) isomer: the cage in (a) plus WO₆ unit in (b).

3a. Other representations of the remaining four isomers can be derived from these projections. To examine the principal relation of these isomers further, we scaled the stabilities of all six isomers by their relative energies from density functional theory calculations on the cluster anions (Scheme 1).[23] These calculations, performed on geometrically relaxed isolated cluster geometries in the gas phase, suggest that the \(D_{3d}\)-symmetric \(\alpha\) isomer is more stable than the \(D_{3d}\)-symmetric \(\gamma^*\) isomer. The \(\gamma\) and \(\gamma^*\) structures are only separated by 21 kJ mol\(^{-1}\), whereas the \(\alpha\)-to-\(\alpha^*\) energy difference is over three times larger (64 kJ mol\(^{-1}\)). It is important to note that these relative energies only reflect the differing connectivities of the idealized isomer geometries; the actual formation and interconversion of individual isomers is subject to a large set of bulk phase parameters. Having isolated pure \(\alpha\) and \(\gamma^*\) isomers, we investigated the stability of these compounds by using differential scanning calorimetry (DSC). The DSC trace for compound 2 shows a broad endothermic peak starting at 315°C, possibly resulting from the reduction of the cluster by the organic cations, as suggested by the color change to blue observed at this temperature. Compound 3 also shows this feature, as well as a small endothermic peak immediately followed by an exothermic peak (291–298°C). These latter irreversible processes are possibly due to either a rearrangement/decomposition in the cluster shell or associated cations; however, solvent effects have been ruled out.[24]

In summary, we have demonstrated that it is possible to isolate isopolynuclear clusters that are structural analogues of heteropolyacids, in this case, of the Dawson structural archetype. The isolation of two of the six isomers that make up this new family, along with the chemical, thermogravimetric, and theoretical analysis, demonstrates interesting features related to the inclusion of the \{WO₆\}\(^{\text{3-}}\) anion template. Furthermore, the stabilization of the \{WO₆\}\(^{\text{3-}}\) moiety in a trigonal prismatic coordination environment is unprecedented in polyoxotungstate chemistry. Future work will include exploring the potential redox chemistry, photochemistry, and acidic nature of the clusters to compare their physical properties directly with the classical Dawson clusters. In addition, the inclusion of the metal-based octahedra may allow control of the formation of clusters using other \{MO₆\} or \{MX₆\} units as templates.

**Experimental Section**

I: Triethanolamine hydrochloride (14.0 g, 75.4 mmol) and Na₂WO₄·2H₂O (13.0 g, 39.4 mmol) were dissolved in water (80 mL). Hydrochloric acid (6 m) was added with stirring to adjust the pH to 1.2. The solution was then heated at reflux with stirring for 3 days. After the solution was cooled to room temperature, pale green needles crystallized over 2 days; these were then filtered, washed with ethanol, and dried in vacuum (3.8 g, 34% yield, IR (KBr): \(\nu\) = 3434, 1631, 1446, 1400, 1258, 1202, 1091, 1060, 1027, 961, 767, 614 cm\(^{-1}\); elemental analysis (%) calculated for \(\text{C}_{36}\text{H}_{100}\text{N}_{6}\text{O}_{80}\text{W}_{19}: C 8.02, H 1.87, N 2.20\); found: C 8.04, H 1.84, N 2.20). To examine the principal relation of these isomers further, we scaled the stabilities of all six isomers by their relative energies from density functional theory calculations on the cluster anions (Scheme 1).[23] These calculations, performed on geometrically relaxed isolated cluster geometries in the gas phase, suggest that the \(D_{3d}\)-symmetric \(\alpha\) isomer is more stable than the \(D_{3d}\)-symmetric \(\gamma^*\) isomer. The \(\gamma\) and \(\gamma^*\) structures are only separated by 21 kJ mol\(^{-1}\), whereas the \(\alpha\)-to-\(\alpha^*\) energy difference is over three times larger (64 kJ mol\(^{-1}\)). It is important to note that these relative energies only reflect the differing connectivities of the idealized isomer geometries; the actual formation and interconversion of individual isomers is subject to a large set of bulk phase parameters. Having isolated pure \(\alpha\) and \(\gamma^*\) isomers, we investigated the stability of these compounds by using differential scanning calorimetry (DSC). The DSC trace for compound 2 shows a broad endothermic peak starting at 315°C, possibly resulting from the reduction of the cluster by the organic cations, as suggested by the color change to blue observed at this temperature. Compound 3 also shows this feature, as well as a small endothermic peak immediately followed by an exothermic peak (291–298°C). These latter irreversible processes are possibly due to either a rearrangement/decomposition in the cluster shell or associated cations; however, solvent effects have been ruled out.[24]

In summary, we have demonstrated that it is possible to isolate isopolynuclear clusters that are structural analogues of heteropolyacids, in this case, of the Dawson structural archetype. The isolation of two of the six isomers that make up this new family, along with the chemical, thermogravimetric, and theoretical analysis, demonstrates interesting features related to the inclusion of the \{WO₆\}\(^{\text{3-}}\) anion template. Furthermore, the stabilization of the \{WO₆\}\(^{\text{3-}}\) moiety in a trigonal prismatic coordination environment is unprecedented in polyoxotungstate chemistry. Future work will include exploring the potential redox chemistry, photochemistry, and acidic nature of the clusters to compare their physical properties directly with the classical Dawson clusters. In addition, the inclusion of the metal-based octahedra may allow control of the formation of clusters using other \{MO₆\} or \{MX₆\} units as templates.
was added and the precipitated product was collected, washed with ethanol, dried in vacuum, and recrystallized from CH$_2$CN (2.8 g, 89% yield, based on W). IR (KBr): v = 2976, 1681, 1629, 1474, 1380, 1325, 1105, 1041, 961, 894, 804, 589 cm$^{-1}$; elemental analysis (%) calculated for Cs$_5$H$_{17}$N$_3$O$_{28}$W$_{11}$: C 19.14, H 7.30, N 2.23, W 58.6; found: C 19.01, H 3.47, N 2.15, W 57.9.

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[13] Crystal data and structure refinements for Pr$_n$Ni$_4$W$_{19}$O$_{60}$: the monoclinic space group C2/c; a = 12.074(4), b = 13.926(4), c = 14.258(4) Å, α = 90°, β = 89.75°, γ = 111.99°, V = 2548.1(8) Å$^3$, Z = 4, ρ = 2.15 g cm$^{-3}$, μ(MoKα) = 7.29 mm$^{-1}$, F(000) = 1648, 3246 reflections measured, 7662 unique (R$_{int}$ = 0.052), 450 refined parameters, R = 0.067, wR = 0.076.

[14] Crystal data and structure refinements for I: Cs$_5$H$_{17}$N$_3$O$_{28}$W$_{11}$: a = 15.991(9) Å, χ = 90°, β = 97.3(2)°, γ = 90°, V = 2694.3(3) Å$^3$, Z = 4, ρ = 7.29 g cm$^{-3}$, μ(MoKα) = 7.29 mm$^{-1}$, F(000) = 1648, 3246 reflections measured, 7662 unique (R$_{int}$ = 0.052), 450 refined parameters, R = 0.067, wR = 0.076.

[15] Crystal data and structure refinements for II: Cs$_5$H$_{17}$N$_3$O$_{28}$W$_{11}$: a = 15.991(9) Å, χ = 90°, β = 97.3(2)°, γ = 90°, V = 2694.3(3) Å$^3$, Z = 4, ρ = 7.29 g cm$^{-3}$, μ(MoKα) = 7.29 mm$^{-1}$, F(000) = 1648, 3246 reflections measured, 7662 unique (R$_{int}$ = 0.052), 450 refined parameters, R = 0.067, wR = 0.076.

[16] Crystal data and structure refinements for III: Cs$_5$H$_{17}$N$_3$O$_{28}$W$_{11}$: a = 15.991(9) Å, χ = 90°, β = 97.3(2)°, γ = 90°, V = 2694.3(3) Å$^3$, Z = 4, ρ = 7.29 g cm$^{-3}$, μ(MoKα) = 7.29 mm$^{-1}$, F(000) = 1648, 3246 reflections measured, 7662 unique (R$_{int}$ = 0.052), 450 refined parameters, R = 0.067, wR = 0.076.
1.1352, β: 0.438, β⁺: 1.034, γ: 0.998, γ⁺: 0.976 debye. For a review on ab initio calculations on polyoxotungstates, see also J. M. Poblet, X. López, C. Bo, Chem. Soc. Rev. 2003, 32, 297.

[24] The two inherently coupled processes have been reproduced for multiple samples on two different DSC instruments. Changes in the heating rate do not change the relative peak positions or integrated energies associated with each of the processes; the process at 291–298°C cannot be due to solvent loss since a simultaneous DSC/TGA experiment demonstrates total solvent loss below 250°C.