

Assembly of Tungsten-Oxide-Based Pentagonal Motifs in Solution Leads to Nanoscale $\{W_{48}\}$, $\{W_{56}\}$, and $\{W_{92}\}$ Polyoxometalate Clusters

Cai-Hong Zhan, Ross S. Winter, Qi Zheng, Jun Yan, Jamie M. Cameron, De-Liang Long,* and Leroy Cronin*

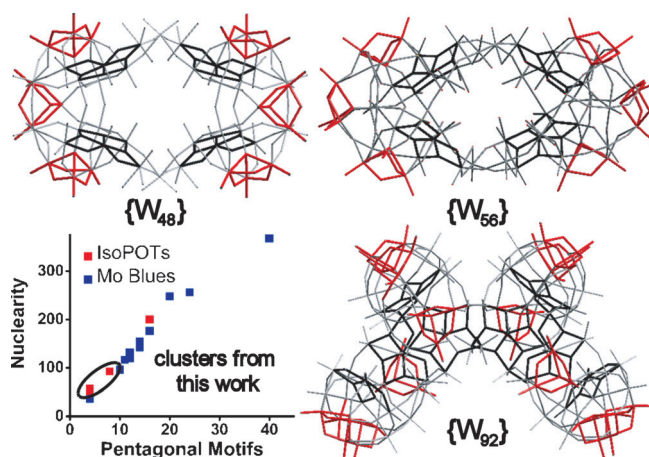
Abstract: We report an approach to synthesize molecular tungsten-oxide-based pentagonal building blocks, in a new $\{W_{21}O_{72}\}$ unit, and show how this leads to a family of gigantic molecular architectures including $[H_{12}W_{48}O_{164}]^{28-}$ $\{W_{48}\}$, $[H_{20}W_{56}O_{190}]^{24-}$ $\{W_{56}\}$, and $[H_{12}W_{92}O_{311}]^{58-}$ $\{W_{92}\}$. The $\{W_{48}\}$ and $\{W_{56}\}$ clusters are both dimeric species incorporating two $\{W_{21}\}$ units and the $\{W_{56}\}$ species is the first example of a molecular metal oxide cluster containing a chiral “double-stranded” motif which is stable in solution as confirmed by mass spectrometry. The $\{W_{92}\}$ anion having four $\{W_{21}\}$ units is one of the largest transition metal substituted isopolyoxotungstates known.

The design and synthesis of gigantic molecular structures remains a fantastic challenge in the assembly of nanoscale molecules since the structures often need to be assembled under “combinatorial” conditions as a step by step strategy is not generally feasible.^[1] Control of the geometry of the building blocks allows the structures to be directed as can be seen in complex topological supramolecular compounds,^[2] frameworks,^[3] and bioinspired systems.^[4] In polyoxometalate chemistry, this is not usually possible due to the lack of direct geometrical control and subsequent combinatorial explosion. The use of reducing agent appears to give some control, see Scheme 1, via the assembly of pentagonal units,^[5] and these in turn lead to a family of gigantic (> 3 nm) spherical and ring-shaped clusters, although this seems limited to molybdenum oxides to date.

In the case of tungsten, isopolyoxotungstates (isoPOTs) represent a growing subset of polyoxometalates (POMs).^[6] IsoPOT species are particularly rare and only a handful of examples are known.^[6–11] Within isoPOTs a recurring unit is $\{W_3O_{13}\}$ which is more generally found as a capping “triad” in traditional Dawson and Keggin^[8] architectures. In our previous research we have explored approaches to isolate new POM cluster architectures and we have discovered many new isoPOTs, for example, the S-shaped $[H_4W_{22}O_{76}]^{12-}$, the §-shaped $[H_{10}W_{34}O_{116}]^{18-}$ clusters,^[12] the triangular^[13]

$[H_{12}W_{36}O_{120}]^{12-}$, $[H_4W_{18}O_{56}(WO_6)]^{6-}$ (a Wells–Dawson-like species)^[14] as well as the gigantic $[H_{64}W_{200}O_{684}]^{104-}$ cluster.^[15] However, although these compounds are interesting, they represent “synthetic one-offs” and a general synthetic approach to create larger structures appears elusive.

Herein, we present the discovery of three very large and structurally diverse tungsten-based metal oxide anions (isoPOTs) with the formulae: $[H_{12}W_{48}O_{164}]^{28-}$ $\{W_{48}\}$ (**1a**), $[H_{20}W_{56}O_{190}]^{24-}$ $\{W_{56}\}$ (**2a**), and $[H_{12}W_{92}O_{311}]^{58-}$ $\{W_{92}\}$ (**3a**). These discoveries are important since they reveal the existence of the building block $\{W_{21}O_{72}\}$ which appears to be a new versatile building unit, combining $\{W_3\}$ triads typical of isoPOTs with the pentagonal bipyramidal $\{MO_7\}$ units generally associated with Mo Blues (see Scheme 1). We



Scheme 1. Showing the importance of pentagons in isoPOM chemistry and highlighting the pentagonal and triad motifs in clusters 1–3.

postulate that $\{W_{21}O_{72}\}$ should be considered a new isoPOT building block which facilitates the formation of increasingly large architectures with chiral features, a rare and much sought after structural property in POMs.^[16] The $\{W_{21}O_{72}\}$ motif consists of three $\{W_3O_{13}\}$ triads linked via four $\{WO_6\}$ to two $\{WO_7\}$ units that form the center of dilacurary $\{W(W)_3\}$ pentagons. The extension of these defect pentagons at specific sites facilitates the formation of the larger IsoPOTs reported herein (see Figure 1 a).

Compound **1**, $\{W_{48}\}$, obtained as $Na_{19}(C_2H_8N)_9 \cdot 1a \cdot 30H_2O$ at pH 1.7 from a solution containing $Na_2WO_4 \cdot 2H_2O$ and dimethylamine hydrochloride, initially reduced to a dark blue solution by addition of sodium dithionite. The solution was initially stored in a fridge at 4 °C and the tungsten centers

[*] C. Zhan,^[‡] Dr. R. S. Winter,^[‡] Q. Zheng, Dr. J. Yan, Dr. J. M. Cameron, Dr. D.-L. Long, Prof. Dr. L. Cronin
WestCHEM, School of Chemistry, The University of Glasgow
Glasgow G12 8QQ (UK)
E-mail: Deliang.Long@glasgow.ac.uk
Lee.Cronin@glasgow.ac.uk
Homepage: <http://www.croninlab.com>

[‡] These authors contributed equally to this work.

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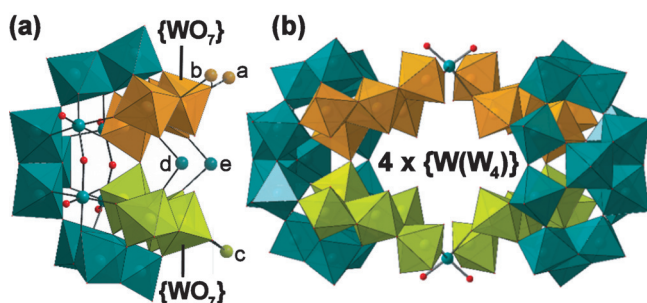


Figure 1. a) Representation of the $\{W_{21}\}$ building block showing the $\{W_3\}$ triads in teal polyhedrons and the $\{WO_7\}$ centered lacunary pentagons are shown in orange and green. The sites where the cluster extends are labelled a–e. b) Representation of anion **1a**. Each $\{W_{21}\}$ has sites a and c occupied to form two $\{W(W_4)\}$ units which connect to the adjacent building block via an additional two $\{W_1\}$ units along the molecular C_2 axis. Color scheme: W (teal), O (red).

gradually oxidized back to W^{6+} , as signified by decoloring of the solution, then crystallized at 18 °C. In this instance, the chemical reduction step appears necessary to induce and promote the formation of the pentagonal motifs, as confirmed by control experiments.^[17] A similar pre-reduction followed by oxidation phenomenon has been reported recently.^[18]

Crystal structure determination of compound **1** shows that $[H_{12}W_{48}O_{164}]^{28-}$ comprises two $\{W_{21}O_{72}\}$ building blocks linked in a parallel double-stranded fashion. Each $\{W_{21}\}$ is extended by two $\{W_1\}$ units to form two $\{W(W_4)\}$ motifs that are opposite each other so that each building block retains its plane of symmetry. The $\{W(W_4)\}$ units of neighboring building blocks connect via two additional $\{W_1\}$ units such that equivalent $\{W(W_4)\}$ units on each building block are adjacent to one another (see Figure 1b). Overall the cluster has C_{2h} symmetry with the C_2 axis passing through the $\{W_1\}$ units that connect the defect pentagonal motifs. The cluster is 4.3 nm long and 1.4 nm wide.

In a similar reaction to **1** but at the higher pH of 2.0 and in the presence of $Te(OH)_6$, the expanded cluster $[H_{20}W_{56}O_{190}]^{24-}$ $\{W_{56}\}$ (**2a**) was isolated as $(C_2H_8N)_{18}Na_6 \cdot 2a \cdot 25H_2O$, alongside the major product of $\{W_{18}O_{56-}(TeO_6)\}$ —the TeO_6 -centred Wells–Dawson-like cluster.^[19] Repeated elemental analysis showed that **2** was free of Te, but paradoxically *only* in the presence of Te did **2** form as confirmed by control experiments.^[20] X-ray single-crystal determination reveals that **2** has a double stranded topology with dimensions of 2.7 nm in length and 1.4 nm in width (Figure 2a). Cluster **2** is similar to **1** in respect to it containing two $\{W_{21}\}$ building blocks (hence four pentagonal motifs) connected by additional $\{W_1\}$ units, however there are significant differences between **1** and **2**.

In **2a** each building block is extended by filling all possible extension sites (as shown in Figure 1a) to create one $\{W(W_4)\}$ and one $\{W(W_5)\}$ motif per unit with two $\{W_1\}$ units bridging the pentagonal motifs on each building block. This has the consequence of breaking the symmetry of the building block. The two building blocks do not connect as straightforwardly as in **1a**. Adjacent building blocks are connected via two $\{W_1\}$ units. One $\{W_1\}$ unit corner shares oxygen with two W atoms

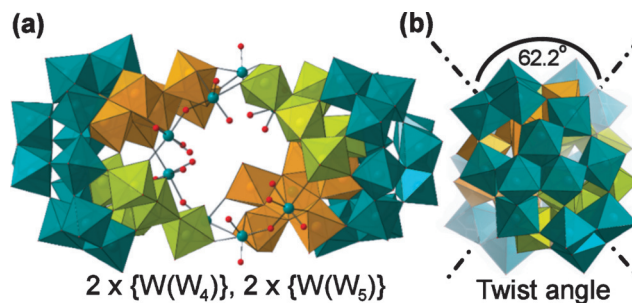


Figure 2. Representation of anion $\{W_{56}\}$ (**2a**). Two $\{W_{21}\}$ building units are extended to create $2 \times \{W(W_5)\}$ (orange) and $2 \times \{W(W_4)\}$ (green) connected in a twisted fashion via a central double helix motif. Color scheme: W (teal), O (red).

from the $\{W(W_5)\}$ motif of one building block and edge shares with one W atom on the $\{W(W_4)\}$ motif of the adjacent building block. The other $\{W_1\}$ corner shares oxygen with one W atom on the $\{W(W_4)\}$ motif of one building block and edge shares with one W atom from the $\{W(W_5)\}$ motif on the adjacent building block. This complicated coordination pattern forces the $\{W_{21}\}$ building blocks to be twisted at an angle of 62.2° and creates a central double-stranded motif, a first for metal oxide and POM architectures. Despite the molecular cluster displaying chiral D_2 symmetry the cluster crystallizes as a racemate in $P\bar{1}$ space group and could not be resolved.

To further assess the role of cations in the system and to try to obtain even larger structures we employed transition metal ions, specifically Cu^{2+} as counterions. Ethylenediamine was added to partially chelate to some of the available Cu^{2+} coordination sites to promote the formation of soluble molecular species instead of infinite frameworks. This approach yielded an even larger anion $[H_{12}W_{92}O_{311}]^{58-}$ (**3a**). The composition of **3** was revealed by chemical analysis and single-crystal X-ray diffraction as $Na_{26-}(C_2H_8N_2)_4Cu_{16} \cdot 3a \cdot 80H_2O$. Remarkably this $\{W_{92}\}$ cluster has four principal $\{W_{21}\}$ building units which are connected in a helical chain-like fashion (see Figure 3). The cluster is the first known example of an inorganic architecture that includes three types of pentagonal units: complete and incomplete, $\{W(W_5)\}$, $\{W(W_4)\}$ and $\{W(W_3)\}$.

The cluster anion contains a C_2 -symmetry axis which runs through the single W–O–W bridging oxygen that serves as a corner sharing oxygen between the two complete $\{W(W_5)\}$ motifs present in the architecture. Consequently this “tetrameric” chain of **3** can be described by each half of the cluster molecule which forms the crystallographic asymmetric unit found for **3**. Each half has one terminal and one central $\{W_{21}\}$ unit as shown in Figure 4. The terminal unit possesses one $\{W(W_3)\}$ motif and one $\{W(W_4)\}$ motif. The $\{W(W_4)\}$ species shares a $\{W_1\}$ unit with a second $\{W(W_4)\}$ species on the central unit and this serves as the main connection between the two building blocks. This overall $\{W_9\}$ moiety is a rare example of pentagonal $\{WO_7\}$ centers edge sharing the same $\{W_1\}$ species. Such a phenomena has not been observed in Mo Blue species, but has been observed in a $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ architecture.^[21] The central unit also contains a complete

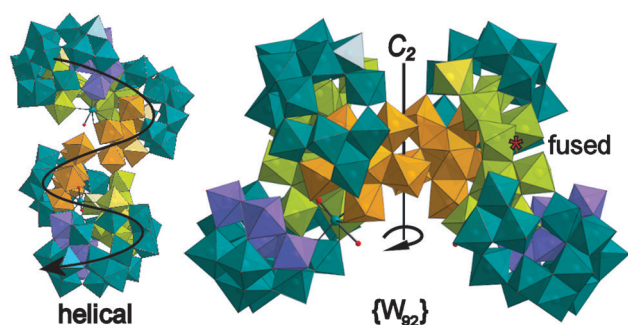


Figure 3. Representation of the W-only framework of anion **3a**, possessing {W(W₅)} (orange), {W(W₄)} (green), and {W(W₃)} (purple) pentagonal centered motifs. The helical nature of the cluster is emphasized to the left. The cluster comprises two identical halves mapped onto each other via a C₂ axis between the {W(W₅)} units. Color scheme: W (teal), O (red).

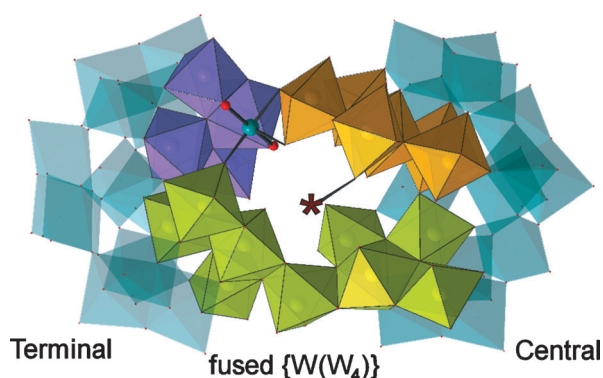


Figure 4. Representation of the asymmetric unit of **3a** showing the connectivity between the terminal and central building blocks. Color scheme as for Figure 4. (* shows connection to other half of cluster).

{W(W₅)} motif, which connects to the other half of the cluster (shown by * in Figure 4). An additional {W₁} unit connects the two building blocks by corner sharing with the {W(W₃)} and {W(W₄)} units of the terminal unit and edge sharing with the {W(W₅)} unit of the central unit. The bridging between the terminal and central units creates a twist angle of 57.1° between the two building blocks.

After careful scrutiny of the structure of **3**, we found all the extension points unoccupied by tungsten on the {W₂₁} units were filled by Cu²⁺. Thus all defect pentagonal units {W(W₄)} and {W(W₃)} become complete pentagonal {W(CuW₄)} and {W(Cu₂W₃)} moieties (see Figure S1 and S2 in the Supporting Information (SI)). Of all the nine Cu centers found in the asymmetric unit, that is, half of the “tetramer”, only two are not on the {W₂₁} growth positions. Figure S2 (SI) shows all 16 Cu positions together with the ethylenediamine coordination. Some of these copper ions also help to connect the two halves of the cluster. The Cu^{II} centers are well defined in the structure determination, not only in terms of electron density, but also by the distinctive square planar coordination geometry of equatorial M···O distances, as well as the elongated M···O axis which average 2.0 and 2.4 Å. This compound is especially interesting as it

demonstrates the use of transition metal ions to connect the {W₂₁} building units, substituting the positions typically occupied by tungsten. This cluster can thus be viewed as a secondary metal substituted isoPOT.^[15,22] Coincidentally, when we reviewed the previously reported {W₂₀₀} cluster we uncovered that it too contains the {W₂₁} building block (see Figure S7, SI), meaning that all reported cases of {WO₇} pentagonal motifs in isoPOTs contain this building block.

To explore the nature of the clusters in solution, especially to establish if the postulated {W₂₁} building blocks are present, we conducted electrospray ionization mass spectrometry experiments on our clusters. Both clusters **1** and **2** were shown to remain intact in solution. Figure 5 shows the mass

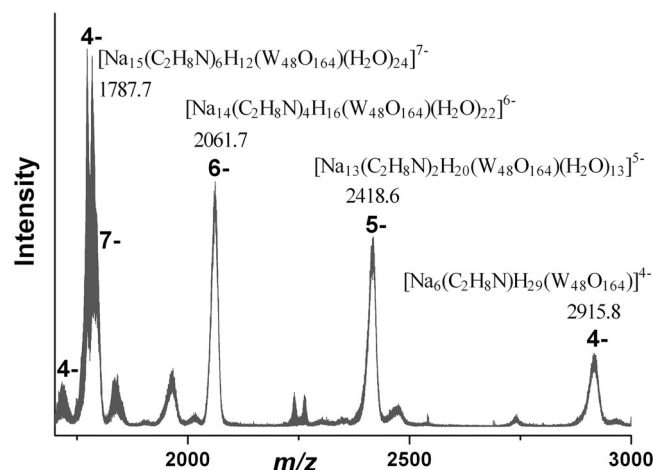


Figure 5. Negative mode mass spectrum of **1** in the *m/z* range of 1700–3000 showing the major envelopes labeled 4– to 7– corresponding to sequentially charged quasi-molecules of {W₄₈O₁₆₄}. The 7– overlaps with other lower mass signals of charge 4–. Representative assignments are provided in the Figure and Table S5 (SI).

spectrum of **1** with the assigned peaks in high mass region (charges –4→–7). Note that these charges are difficult to directly resolve from the spectrum itself but can be deduced from a linear regression of the correlation 1/*P_i* = *z_i*/*m* between peak positions *P_i* and peak charges *z_i* (see SI), which form a regular series as seen in Figure 5. This indicates a solution formula of [Na_{*x*}(DMAH)_{*y*}H_{*n*}(W₄₈O₁₆₄)(H₂O)_{*m*}]^{*z*–} with a mass of ca. 12.0 kDa which contains a single cluster {W₄₈O₁₆₄} of mass 11.5 kDa (and a variable number of cations and solvent molecules of mass around a few hundred Da).

Figure S3 (SI) shows the mass spectrum of **2**, which has similar features of regular peaks of charge 5–, 6– and 7–. The molecular species [Na_{*x*}(DMAH)_{*y*}H_{*n*}(W₅₆O₁₉₀)(H₂O)_{*m*}]^{*z*–} has a mass of ca. 13.5 kDa which contains a single cluster {W₅₆O₁₉₀} of mass 13.3 kDa. The flexible number and type of cation and solvent molecules contribute relatively little to the molecular mass but do give rise to broadening of the peak envelopes defined by the cluster.^[11] As such, even though it is difficult to determine the absolute number and type of cations and solvents in each case, this regular peak pattern strongly suggests the stability of the parent cluster in solution and confirms the cluster remains intact. In both spectra, we

observed several charged peaks (-4) below m/z 1800 with formulae consistent to nuclearities of $\{W_{23}\}$ to $\{W_{25}\}$; this would correspond to the $\{W_{21}O_{92}\}$ building block forming more complete pentagonal units as it extends (see SI).

As mentioned previously, the $\{W_{21}O_{72}\}$ building block comprises primarily of $\{W_3O_{13}\}$ triads and pentagonal $\{W_7\}$ centered motifs. Triad units form the basis of classical isoPOTs such as $\{W_{12}O_{42}\}^{9a)}$ and also classical POM architectures like the Keggin and Dawson structures.^[8] Pentagonal building blocks are very rare for isoPOTs, but are very common in Mo Blues—gigantic wheel and ball shaped architectures, known to form quickly.^[5] Tungsten pentagonal units are however prevalent in Keplerate architectures $[\{W(W_5)\}_{12}(\text{linker})_{30}]^{n-}$ (linker = V, Fe, $\{Mo\}_2$, $\{Mo_2S_2\}$), which share a common synthetic strategy of adding the linker solution to a solution of $Na_2WO_4 \cdot 2H_2O$ acidified to pH 4.^[23] In these cases formation of the product is relatively quick, typically <1 week. This indicates that $\{W(W_5)\}$ units are perhaps relatively facile to produce in solution, but need to be trapped quickly. This could be the reason why the relatively kinetically inert tungstate oxoanions have been as yet incapable of forming the same architectures as observed for molybdenum. Combining kinetically reactive Mo with lacunary tungstate precursors to generate $\{W(Mo)_5\}$ moieties has been shown recently by Cadot et al.^[24] without using reducing conditions.

Structurally, the clusters can be broken down into simple monomeric $\{W_1\}$ and dimeric $\{W_2\}$ tungstate units, variable pentagonal based building blocks $\{W_{8-x}\}$ and $\{W_3\}$ triads (see Figure 6). The $\{W_1\}$, $\{W_2\}$ and $\{W_{8-x}\}$ building blocks could

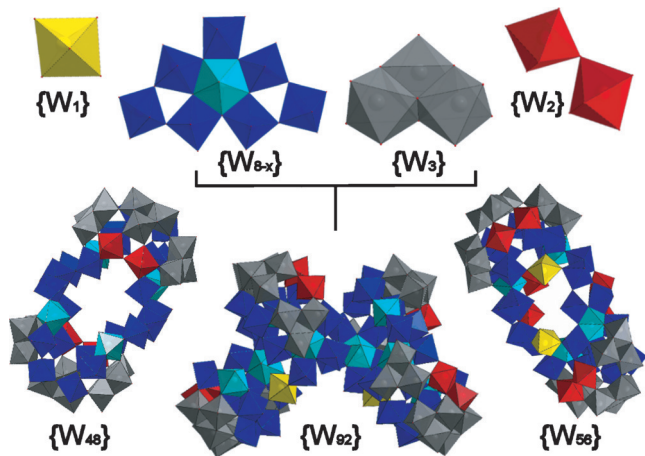


Figure 6. The simplest building blocks that constitute the large isoPOTs reported here.

be viewed as analogous to the building blocks of Molybdenum Blue species,^[5] however there are significant differences. Primarily, the variability in the $\{W_{8-x}\}$ species which show different values of x and different modes of connectivity for these isoPOTs; secondly is that all of the addenda sites in our clusters are fully oxidized W^{VI} and finally is the much lower symmetry of the tungstate clusters, which we attribute to the presence of the “capping” $\{W_3\}$ units which restrict the

expansion of the $\{W_{21}\}$ building blocks in multiple directions. We consider the $[H_{12}W_{48}O_{164}]^{28-}$, $[H_{20}W_{56}O_{190}]^{24-}$ and $[H_{12}W_{92}O_{311}]^{58-}$ clusters presented here as the first members of a growing family large chiral polyoxotungstates that we anticipate will have interesting electronic and physical properties to investigate.

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