Polyoxometalates (POMs) are fascinating metal oxide cluster compounds with applications in many fields, from medicine to nanotechnology.\cite{1-8} In POM chemistry, countless new structural types have been synthesized and characterized,\cite{14-15} but there is a need to develop new synthetic routes to allow the development of tunable and functional cluster systems.\cite{11,12} We have been targeting cluster cage template systems whereby new guest species, such as $\text{WO}_6^{6-}$ and $\text{IO}_6^{5-}$, are inserted into a $\{\text{M}_{18}\text{O}_{54}\}$ cage.\cite{13} The $\{\text{M}_{18}\text{O}_{54}\}$ cluster cage ($\text{M}=\text{Mo}$ or $\text{W}$) has many versatile features, such as electronic configurability or use as a synthetic platform, which should allow the design of novel functional nano-objects. Although the crystallization-based approach to cluster discovery has transformed the field, the direct unambiguous discovery of new clusters in a given reaction system is difficult. This difficulty arises because of the need to correlate the synthetic parameters with the cluster structure, requiring cycles of synthesis, crystallization, and structural characterization.

Herein we present a new approach to the discovery of cage-template nanoclusters, which utilizes cryospray mass spectrometry (CSI-MS)\cite{14} to directly probe the reaction solution, thereby allowing the process to be accomplished much more quickly and facilitating the discovery of new guests inside nanocluster cage architectures (Scheme 1).

We targeted the encapsulation of $\{\text{TeO}_6\}^{6-}$ units within $\{\text{W}_{18}\text{O}_{54}\}$ cluster shells to give the tellurate-based Dawson-like anion because, although this process should be straightforward according to our previous work,\cite{13} we found that it was not possible to synthesize these new clusters using the conventional approach. However, by probing the reaction mixture with CSI-MS, we were able to screen different cation systems. Of the cations screened, dimethylammonium (DMAH)$^+$ and tetrabutylammonium (TBA)$^+$ were successful, yielding $[\text{H}_3\text{W}_{18}\text{O}_{56}(\text{TeO}_6)]^{-}$ (1a; Figure 1) as Na-DMAH$_{\text{2e}}$$[\text{H}_3\text{W}_{18}\text{O}_{56}(\text{TeO}_6)]^{-}\cdot 14\text{H}_2\text{O}$ and (TBA)$_{\text{2e}}$$[\text{H}_3\text{W}_{18}\text{O}_{56}(\text{TeO}_6)]^{-}\cdot \text{4CH}_3\text{CN}$ 1',\cite{15} respectively. Furthermore, the activation of the cluster cage by the Te heteroanion is demonstrated by the reduction of the tellurate $\{\text{TeO}_6\}^{-}$ within 1a to tellurite $[\text{TeO}_6^{3-}]$, thereby transforming 1a to $[\text{H}_3\text{W}_{18}\text{O}_{56}(\text{TeO}_6)]^{-}$ (2a; Figure 1) without decomposition of the cluster cage. Cluster 2a has also been isolated in the solid state as (TBA)$_{\text{2e}}$$[\text{H}_3\text{W}_{18}\text{O}_{56}(\text{TeO}_6)]^{-}\cdot \text{35H}_2\text{O}$ 2, in which the pyramidal tellurite anion $[\text{TeO}_6^{3-}]$ acts as a template supporting the $\{\text{W}_{18}\text{O}_{54}\}$ cage. This redox reaction, which transforms 1a into 2a, can be monitored in situ by use of CSI-MS. Finally, the inclusion of the Te-based heteroanion activates the surface of the $\{\text{W}_{18}\text{O}_{54}\}$ cluster cage, facilitating the assembly of the cluster to nanoscale structures without the introduction of other transition metal electrophiles, with two $[\text{W}_3\text{Te}_5\text{V}]^{2-}$ units linked together by two $[\text{W}_3\text{Te}_5\text{V}]^{2-}$ units to give $\text{Na}_8$$[\text{H}_3\text{Te}_5\text{W}_{38}\text{O}_{198}]^{26-}$ 3a, which was isolated as Na$_8$$[\text{H}_3\text{Te}_5\text{W}_{38}\text{O}_{198}]^{26-}\cdot 35\text{H}_2\text{O}$ 3 in the solid state. Compounds 1–3 were fully characterized by use of elemental analysis and single-crystal structure determination, and compounds 1 and 2 were detected by use of CSI-MS.

The participation of tellurate and tellurite as heteroanions in POM chemistry is reasonably well known: tellurate is employed in the formation of the Anderson-type cluster $[\text{TeO}_6\text{M}_6]^{2-} (\text{M}=\text{Mo}$ or $\text{W})$\cite{16,17} and tellurite in the $[\text{TeO}_6\text{W}_3]$...
building blocks that form a variety of metal complexes, such as [Te₆WO₄CuO₂(M₆OH)]⁰−¹⁰, [Fe₃(Η₂O)₆(TeWO₄)₃]³⁺, and [M₃(H₂O)(WO₄)(TeWO₄)₃]⁻ (M = V⁹⁺, Co⁶⁺, Zn⁶⁺, or Ni⁷⁺) [18,19]. However, to our knowledge, compounds 1, 1', 2, and 3 represent the first examples of tellurate and tellurite embedded within the Dawson-type [W₁₈O₅₄]₆⁻ matrix, and thus offer the potential to develop new chemical and physical properties derived from the well-known conventional Dawson cluster structure type.

Cluster 1 was discovered in a reaction system containing Na₂WO₄ and Te(OH)₆ at pH 0.8 in the presence of DMA. The presence of DMA is crucial since its absence leads exclusively to the formation of the Anderson-type cluster [Te₆WO₄]⁴⁻, which reiterates the pivotal effect of employing organic cations for the assembly of new POMs [11,12]. X-ray crystallographic structure analysis of 1 revealed a Dawson-type D₆ᵥ-symmetric [W₁₈O₅₄]₆⁻ cluster shell enclosing a D₆ᵥ-symmetric [TeO₆]₆⁻ unit with an average Te–O distance of 1.98 (2) Å and an average Te–O–W distance of 2.34 (2) Å. The two additional interior oxygen positions each bear one of the capping [W₆] groups of the clusters, with an average W–O distance of 2.24 (2) Å. The cluster represents a γ*-isomer in the family of [W₆] Dawson-type structures (Figure 1) [13].

The structure of the cluster γ*-[H₄W₆O₁₉(TeV₂O₅)]⁻ 1a is similar to that of the β*-,[H₄W₆O₁₉(TeV₂O₅)]⁻ with Te or I located at the cluster centers (Figure 1). For conventional Dawson heteropolyanions, each of the two tetrahedral cavities are normally occupied by a heteroatom, but in the [W₆X]₅ systems, wherein there is only one central heteroatom, structural and bond valence sum analyses suggest that these tetrahedral positions are occupied instead by protons [15]. The Te-containing structure (Figure 1) adopts a γ* conformation, whereas the I-containing structure has a β* conformation. One major difference between the two isomers is the orientation of the three capping W metal centers, and in the β* isomer the [W₆O₃]₆⁻ cluster shell is D₆ᵥ-symmetric [15]. In this work we were only able to discover the correct synthetic route to the Te-[W₆O₃]₆⁻ compound type by use of CSI-MS, which then allowed isolation and crystallographic analysis of the pure compound. This analysis was important also because the heteroatom was located on a crystallographic threefold axis, and the CSI-MS data allowed us to rule out the possibility that the central template could be [WO₆]⁻, which would have implied the cluster could be formulated as [H₄W₆O₁₉(TeV₂O₅)H₄]⁻ [20–22]. CSI mass spectra of compound 1' showed four characteristic peaks at m/z 2822.5 ([H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻), 2701.4 ([H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻), 3065.4 ([H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻), and 3186.0 ([H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻). In contrast, the mass spectrum of the TBA salt of the [H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻ anion showed quite different peaks at m/z 2729.9 ([H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻) and 2850.6 ([H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻).

We examined the reduction of cluster 1a, to test whether we could access a Te²⁺-based species [23]. On addition of solid Na₂S₂O₇ to the acidic solution of compound 1, the solution initially turned blue, owing to the reduction of the [W₆]₆⁻ based cluster shell, and then became pale yellow within seconds. We postulated that the central Te was reduced in this process from Te⁵⁺ to Te⁴⁺. This reduction was confirmed by isolation of 2a, by precipitation with TBA⁻, and this material was subsequently crystalized from acetone trflate to yield 2. Single-crystal X-ray diffraction analysis of 2 revealed that the Te⁴⁺ center had shifted by 1.10 Å towards one end of the cluster to form a pyramidal tellurite ion. Upon formal two-electron reduction, the central octahedral [TeO₆]₆⁻ unit was transformed into a pyramidal [TeO₆]₆⁻ unit with the breaking of three W–O bonds. The two interior “capping” oxo ligands were also lost in this reduction process. The resulting cluster that contained the Te⁴⁺ center hadpseudo D₆ᵥ symmetry, with the sole Te atom disordered over two possible positions, approximately 2.20 Å apart, an average Te–O distance of 1.90 Å, and an average Te–O–W distance of 2.31 Å (Figure 1). Cluster 2a had a similar structure to its Sb analogue [H₄W₆O₁₉(SbIVO₆₀)]⁻ [23].

The composition of cluster 2a, was confirmed by use of high-resolution CSI-MS experiments, which gave rise to peaks corresponding to the cluster [W₆TeIVO₆]⁻: m/z (expected values and anion composition in parentheses): 2573.9 (2574.3; [Na(TBA)₃H₂W₁₈TeIVO₆₀]⁻), 2563.0 (2563.3; [H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻), 2438.3 (2438.7; [H₂(TBA)₃H₂W₁₈TeIVO₆₀]⁻), 2684.5 (2684.4; [H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻), 1708.6 (1708.5; [H₄(TBA)₃H₂W₁₈TeIVO₆₀]⁻).

Further investigation of the tungstate–tellurate reaction-parameter space revealed that, by adjusting the solution to approximately pH 2, it was possible to form a nanosized crown-like tetrameric heteropolytungstate cluster 3a, approximately 1.9 × 2.9 nm in size, which was isolated as a crystalline product. Single-crystal X-ray diffraction analysis of 3 shows the cluster is composed of two [TeW₆O₃]₆⁻ and two [W₆O₃]₆⁻ subunits that are linked together by corner-sharing W₆ octahedra (Figure 2).

The structure of the [W₁₈O₅₄]⁻ unit in 3a is similar to the known cluster [H₄W₆O₁₉(TeV₂O₅)]⁻ and the [W₆]₁ building blocks found in the isopolyoxotungstate clusters [H₄W₆O₃]₁²⁻ and [H₃W₆O₉]₁⁰⁻. To allow the linkage from the [W₆]₁ unit, two adjacent belt W centers on each of the [W₆]₆⁻ clusters are shifted towards the outside of the cluster from normal positions found in a conventional “closed” Dawson-type [W₁₈O₅₄]⁻ cage, whereby the belt W–O–W bridge is missing and the Dawson-type clusters are pried apart (i.e. the W–O–W bond is broken) and distorted to give a window (Figure 2). The two metal centers across the window are 5.1 Å apart, which is much longer than the normal belt W–O–W distance of 3.4 Å in the normal W₆ cage. The heteroanion TeO₆⁻ remains at the center of the distorted [W₆] cage in a non-ideal octahedral geometry with Te–O distances in the range 1.90–2.00 Å. Compound 3a represents a rare, if not the first ever nonlacunary polyoxotungstate to be linked without the need for additional electrophilic linkers, which has great potential for the future design and assembly of large POM nanostructures.

By utilizing high resolution CSI-MS for the real-time examination of the reactivity of the clusters, we were even able to monitor the transformation process from 1a to 2a, which involves the structural and electronic rearrangement of the Te-base template within the [W₆]₆⁻ based cage, from [TeO₆]₆⁻ in 1a to [TeO₆]₆⁻ in 2a. In this experiment, an acetoniirile solution of compound 1' was infused into the mass
The CSI-MS studies also showed that the cluster \([W_{18}TeV]^{\pm}\) is present as both three- and fourfold protonated forms in acetonitrile solution. Furthermore, this information, when combined with the crystallographic and elemental analysis data, allows us to unambiguously assign the protonation state of the clusters in the solid state; for 3a this is \([H_3W_{18}O_{57}(TeV_06)]^{\pm}\). This state is not unusual and a similar pattern is seen for 2a, which is both two- and threefold protonated in solution, but \([H_3W_{18}O_{57}(TeV_06)]^{\pm}\) is the major solid-state form, as confirmed by elemental and crystallographic analyses. Notably, in the mass spectrum of 1, some shoulder peaks, for example, that at \(m/z\ 2692.9\) (corresponding to \([\text{TBA}]_4[H_3W_{18}O_{57}(TeV_06)]^{\pm}\)) are observed beside the major peaks, for example that at \(m/z\ 2701.4\) (corresponding to \([\text{TBA}]_4[H_3W_{18}O_{57}(TeV_06)]^{\pm}\)). The \(m/z\) difference of nine clearly indicates the loss of one H_2O molecule from the cluster cage. We have detected such behavior before in ESIMS studies for protonated POM clusters, such as \([H_3W_{18}O_{54}]^{\pm}\) and \([H_3W_{18}O_{54}(IO_6)]^{\pm}\).[13,14]

In summary, we have discovered a new type of tungstotellurate compound by use of solution-state CSI-MS, which allowed us to isolate \(\gamma^\text{H} [H_3W_{18}O_{57}(TeV_06)]^{\pm}\), with a tellurate anion embedded within the \([W_{18}O_{54}]^{\pm}\) Dawson-type shell. Selective reduction of the heteroatom yielded \([H_3W_{18}O_{57}(TeV_06)]^{\pm}\), which resulted in both electronic and structural reorganizations of the Te-based ion within the cluster shell. Control of the solution pH allowed us to assemble a nanosized high nuclearity POM heteropolytungstate \([H_3W_{18}O_{57}(TeV_06)]^{\pm}\), based on \([TeV_06]^{\pm}\) cluster cages, without the need to incorporate additional electrophilic linkers. The incorporation of Te gave access to clusters with significantly different chemical and physical properties compared to conventional heteropolyoxometalate clusters, as well as allowing us to monitor, by use of mass spectrometry, a redox reaction involving the transformation of the templating heteroanion from \([TeV_06]^{\pm}\) to \([TeO_6]^{\pm}\). The polarization that results from the movement of the Te atom from the center of cluster 1a closer to one end of cluster 2a gives the cluster an asymmetric charge distribution that is manifested directly in the crystallization of 2, in which 2a is arranged in a polar chiral space group, \(I_4\), which demonstrates potential for use as a polar material. In the future we are looking to develop the cryospray cluster-discovery process further, as well as exploiting the novel properties arising from the incorporation of heteroanions within polyoxometalate nanocages, for the design of nanoscale devices, materials, and new types of redox reagents.

**Experimental Section**

1: Na_2WO_4·2H_2O (20.0 g, 60.6 mmol) and dimethylamine hydrochloride (8.1 g, 100 mmol) were dissolved in water (50 mL) and Te(OH)_6 (1.0 g, 4.35 mmol) was added and dissolved. The pH was adjusted to 0.8 by addition of aqueous 6M HCl. The solution was heated at reflux for 2 h and then allowed to cool to room temperature, before the solvent was allowed to evaporate slowly. Compound 1 appeared as light yellow block crystals within one week (3.8 g, 0.76 mmol, 23.7% based on 1/W). IR (KBr disk): v = 3449, 3143, 2791, 1622, 1464, 1402, 1349, 1265, 1163, 1085, 1019, 973, 850, 794, 760, 718, 670, 640 cm\(^{-1}\).
1019, 949, 799 cm⁻¹. Elemental analysis calcld (%) for Na₂C₇H₇₅N₇W₁₈TeO₆₂: C 1.11, N 1.78, Na 0.49, Te 2.70, W 69.9; found C 1.08, N 1.88, Na 0.56, Te 2.66, W 70.9.

1. (DMAH)₆Na₂[H₃W₁₈O₅₆(TeVIO₆)] (1.6 g, 0.36 mmol) was dissolved in water (20 mL). Tetrabutylammonium bromide (5.0 g, 20.6 mmol) dissolved in water (20 mL) was added with stirring. The resultant precipitate was centrifuged and washed with water, ethanol, and ether, and dried under reduced pressure. Recrystallization from acetonitrile afforded the pure product P (1.0 g, 0.15 mmol, 49.8% based on W). IR (KBr disk): ν = 3412, 2961, 2933, 2871, 1636, 1483, 1379, 1016, 947.8, 812 cm⁻¹. Elemental analysis calcld (%) for C₈₀H₁₈₅N₅W₁₈TeO₆₀: C 17.12, H 3.29, N 1.25%; found C 17.47, H 3.25, N 1.87, Na 0.56, Te 2.66, W 70.9.

2. (DMAH)₆Na₂[H₃W₁₈O₅₆(TeVIO₆)] (2.0 g, 0.40 mmol) was dissolved in 0.1 M NaCl (8.1 g, 100 mmol) were dissolved in water (50 mL) and the solvent was allowed to evaporate slowly. IR (KBr disk): ν = 3446, 2961, 2932, 2873, 1636, 1483, 1379, 1152, 977, 900, 807 cm⁻¹. Elemental analysis calcld (%) for C₃₃H₆₅N₃Na₂[Na₈H₃W₁₈O₅₆(TeVIO₆)] (7.4 g, 0.15 mmol): Na 8.15, C 21.54, H 4.29, N 1.60; found Na 8.19, C 21.95, H 4.28, N 1.60, Te 1.56, W 70.9%.

Keywords: cluster compounds · mass spectrometry · polyoxometalates · redox chemistry · tungsten


[7] Crystal data and structure refinement: I: C₂₁H₂₅₅N₇W₁₈TeO₆₂: Mᵣ = 4983.70; crystal size 0.23 × 0.19 × 0.11 mm; T = 150(2) K; trigonal; space group R₃₃m; a = 20.7816(5), c = 17.0359(5) Å; V = 6371.7(3) Å³; Z = 3; ρ = 3.896 g cm⁻³; μ(MoKα) = 24.712 mm⁻¹; F(000) = 6588; 1029 reflections measured, 1514 unique reflections (R int = 0.0291); 134 refined parameters; R1 = 0.0223; wR2 = 0.0586. Half of the cluster is well defined in the asymmetric unit, DMAH⁺ cations and a few solvent water sites were refined in the disorder model. P: C₁₅H₇₉N₆NaO₇6Te₁W₁₈: Mᵣ = 6293.35; crystal size 0.20 × 0.15 × 0.04 mm; T = 150(2) K; triclinic; space group P1; a = 15.7634(6), b = 17.8793(9), c = 19.2987(6) Å; a = 106.357(4), β = 103.255(4), γ = 107.717(4)°; V = 4666.9(3) Å³; Z = 1; ρ = 2.239 g cm⁻³; μ(MoKα) = 11.265 mm⁻¹; F(000) = 2944; 60919 reflections measured, 17289 unique reflections (R int = 0.0436); 811 refined parameters; R1 = 0.035; wR2 = 0.091. One cluster is well defined in the asymmetric unit, 7TBA⁺ cations and several CH₃CN sites were refined in the disorder model. 2: C₁₁H₁₅Na₈H₃W₁₈O₆₄Te: Mᵣ = 5653.27; crystal size 0.13 × 0.09 × 0.09 mm; T = 150(2) K; tetragonal; space group I₄₁; a = 15.8445(3) Å; V = 27937.36(5) Å³; Z = 8; ρ = 2.688 g cm⁻³; μ(MoKα) = 15.036 mm⁻¹; F(000) = 20672; 97746 reflections measured; 27014 unique reflections (R int = 0.804); 1224 refined parameters; R1 = 0.0413; wR2 = 0.664. One cluster is well defined in the asymmetric unit, 7TBA⁺ cations and several CH₃CN sites were refined in the disorder model. Crystal data were measured on an Oxford Diffraction Gemini CCD diffractometer using MoKα radiation (λ = 0.71073 Å).

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can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


[26] Controlled fragmentation can be induced by collision-induced dissociation at high energies, enabling us to establish how cluster decomposition would occur. The absence of such peaks, and the clear observation of the transformation of [W_{18}TeVI] to [W_{18}TeIV] is very strong evidence suggesting the cluster remains intact during the reduction process.