Heteropolyoxometalates (HPOMs) are molecular metal oxide cages of the general composition (MO3)X. This class of HPOM cluster was first structurally characterized fifty years ago and since then the subject of many hundreds of papers.[2–7] We are interested in the design of new fundamental types of isopolyoxometalates[8,9] as well as non-conventional HPOM clusters[10] that incorporate two pyramidal anions[11] similar to the Dawson archetype, as such clusters may exhibit unprecedented properties arising from the intramolecular electronic interactions between the encapsulated anions, thus providing a novel route to manipulate the physical properties of the [M18] Dawson-type clusters.

In an attempt to develop internally switchable molecular clusters based on polyoxometalates, we have recently discovered the sulfite-based Dawson-type polyoxomolybdates α- and β-[MoVII3O9(SO4)2]4– (1a and 1b, respectively). They incorporate two adjacent sulfite anions in a configuration causing a short, yet non-bonding intramolecular S–S interaction between the sulfite anions and exhibit unusual reversible thermochromic properties over the temperature range 77 to 500 K.[10] In an extension of this work we succeeded in synthesizing the first two examples of polyoxotungstate clusters incorporating the sulfite anion,[12] [WVI18O56(SO3)2(H2O)2]8– (2a), the isostructural tungstate analogue to 1a, and [WVI18O56(SO3)2(H2O)2]6– (3a; see Figure 1). They were isolated as (Bu4N)6[WVI18O56(SO3)2]2 (2) and K2Na2[WVI18O56(SO3)2(H2O)2]20H2O (3) and characterized by single crystal X-ray structure analysis,[13] elemental analysis, IR and UV-Vis spectroscopy, bond valence sum (BVS) and DFT calculations.[14]

Interestingly, 3a has a curious structure including two terminal water ligands which is unknown for closed-shell HPOM clusters of any type.[15] Moreover, 3a also demonstrates unprecedented electronic properties: the cluster anion [WVI18O56(SO3)(H2O)2]6– undergoes a unique electron-transfer reaction when heated, in which a structural re-arrangement allows the two embedded pyramidal sulfite (SO42–) anions to release up to four electrons (analogous to the “soldiers” hidden inside the “Trojan Horse”) to the surface of the cluster generating the sulfate-based, deep blue, mixed-valence cluster [WVI18O56(SO3)2]6–. Although electron-transfer reactions and structural rearrangements are very well known for HPOMs,[15] this is the first example of a coupled structural-rearrangement and electron-transfer process, whereby the electrons are “released” from the core of the cluster. It is also the first example of a fully characterized unimolecular reaction involving an HPOM.

To fully explore and understand these properties we must consider the structural differences between the cluster anions 2a and 3a. The structures of both clusters consist of two [WVI18O56(SO3)]2 halves which contain six equatorial and three capping metal positions. The two halves are joined by linking each of the six equatorial metal atoms of each half together through six bridging oxo ligands (Figure 1 and Figure 2). The key structural differences between these two cluster families are primarily based on the relative orientation of their two sulfite groups (Figure 2) whereby the base of the pyramid...
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formed by the trigonal-pyramidal SO₃ group in 2a is centrally aligned and binds to all nine metal centers of each [W₆(SO₃)]⁻ fragment, whereas in compound 3a the SO₃ pyramids are tilted so that only seven of the nine metal centers of each [W₆(SO₃)]⁻ fragment are connected.

This arrangement leaves four neighboring equatorial tungsten positions in 3a uncoordinated to the templating sulfite groups and thereby reduces the overall molecular symmetry from D₉h (1a and 2a) to C₅, with the loss of a number of mirror planes and the C₃ axis for 3a. The significantly different orientations of the sulfite ions in 3a compared to 1a and 2a is also reflected by the S···S distance of 3.61(2) Å in 3a which is significantly longer than the distance of 3.19(1) Å in 2a and 3.27(1) Å in 1a.

The second major structural difference between 2a and 3a lies in the number of terminal oxo ligands present in each cluster type. All of the metal atoms present in 2a (as well as in 1a) only support one terminal oxo ligand that is not shared by other metal atoms, however cluster 3a contains four tungsten units (labeled as W* in Figures 1 and 2), each with two terminal ligands. This situation arises because these four tungsten units are not bonded to the embedded sulfite groups. The two terminal ligands and four bridging µ₂-oxo (O⁻) ligands per W* center complete a slightly distorted octahedral coordination geometry. Structural analysis (including bond valence sum analysis) reveals that while two of the four unique W* centers each have two terminal oxo ligands (W=O ca. 1.7 Å), the other two W* centers each have one terminal oxo ligand and one terminal water ligand (W=O ca. 1.7 Å and W−OH₂ ca. 2.2 Å). There is a slight disorder but the presence of two water ligands and two oxo ligands is confirmed by the average bond valence sums as well as chemical and thermal analysis. Furthermore the bridging oxo group (O2 in Figure 2) between the two W* positions of a [W₆(SO₃)]⁻ half is now folded into the cluster and points towards the vacant site of the SO₃ pyramid with a O2−S distance of 2.96(2) Å, whereas the equivalent position in 1a and 2a points outwards.

The structure of 3a is already pre-arranged for an internal reorganization and a concurrent internal redox reaction, in which the encapsulated sulfite anions act as embedded reducing agents, and are oxidized to sulfate when heated to over 400°C. In the course of this reaction a maximum of four electrons could be transferred to the metal oxide framework, causing the color change from colorless ([WVI⁴⁺,W⁵⁺]) to blue ([WVI³⁺,W⁶⁺]). The overall reaction is accompanied by the release of the two coordinated water ligands from the W* centers. Because the reduction of the metal oxide shell by four electrons is balanced by the internal oxidation of the two sulfite anions (to sulfate groups), the overall charge of the cluster remains identical to give [WVI⁴⁺,W⁵⁺O₆(SO₄)₂]⁶⁺ (4a). The reaction can be summarized as shown in Equation (1).

\[
\text{[WVI}^{4+},\text{W}^{5+}\text{O}_6(\text{SO}_4)_2]^{6+} \rightarrow \alpha\text{[WVI}^{4+},\text{W}^{5+}\text{O}_6(\text{SO}_4)_2]^{6+} + 2\text{H}_2\text{O}
\]

This reaction mechanism is confirmed by a variety of experiments which includes the observation of the loss of two water molecules at 400°C, indicated in the IR spectrum and quantified by thermogravimetric analysis (TGA). The formation of the two sulfate moieties is shown by the IR and Raman spectra (emergence of an additional band at 650 cm⁻¹, attributed to sulfate) and in differential scanning calorimetry (DSC) traces, a sharp exothermic process associated with the onset of the internal redox reaction and the formation of sulfate at ca. 400°C (Figure 3).

Analysis of compound 4 (K₉Na[W₁₈O₅₄(SO₄)₂]) also confirms its formula, and the four-electron reduced polyoxotungstate shell which is also indicated by the transformation of colorless 3 into deep blue 4. This data also confirms that 4a is not protonated, which is confirmed by the loss of the H₂O signal in solid-state ¹H magic angle spinning (MAS) NMR spectrum. Given the unambiguous analytical data for the formation of 4 it is unfortunate that crystals suitable for single-crystal X-ray diffraction could not be obtained and that it is exceptionally reactive, but 4 is stable for many weeks if sealed in an evacuated glass tube. However, we are able to confidently suggest that the mixed-valence framework of the
product $\alpha$-[W$_{18}$O$_{44}$(SO$_4$)$_2$]$^{8-}$ (4a) is equivalent to the fully oxidized framework of the conventional sulfate-based Dawson cluster $\alpha$-[W$_{18}$O$_{44}$(SO$_4$)$_2$]$^{4-}$ (5a), which can be synthesized by the reaction of tungstate in the presence of sulfate anions.[16] This structural hypothesis follows from a comparison of the structure of the cluster anion 5a with that of the starting species 3a. Overlaying the two structures reveals that the positions of all the tungsten and sulfur centers are identical to within 0.30(2) Å. We therefore hypothesize that the frameworks of the reduced product 4a and oxidized 5a are virtually isostructural; this idea is also supported by the fact that almost all other $\{\text{M}_{18}\}$ clusters with tetrahedral templates (over 80 are reported) display the same metal oxide framework geometry and may only differ in the relative orientation of the capping $\{\text{M}_3\}$ units giving several isomeric possibilities.

To examine this hypothesis, the preliminary energetic features of a pathway for the reaction in Equation (1) can be established from ab initio density functional theory (DFT) calculations.[14] Owing to the complexity of the system, the complete energy hyper-surface cannot be obtained and we thus used an approximate transition state. This transition-state geometry was obtained from geometrical arguments by interpolation between the atomic coordinates in 3a and 5a. Although the results can only be interpreted semi-quantitatively, they agree with the existence of a substantial activation barrier requiring heating and a subsequent exothermic step.

The energy difference between 3a and the transition state (plus two water molecules), that is, the reaction state representing the thermodynamic barrier, is approximately 200 kJ mol$^{-1}$, while the step from the transition state to the final state is characterized by an energy gain of approximately 450 kJ mol$^{-1}$, rendering the final state ($4a + 2\text{H}_2\text{O}$) around 250 kJ mol$^{-1}$ more stable than 3a. The energy release during the exothermic process at 400°C (when 3 transforms to 4) measured using DSC (288 kJ mol$^{-1}$) coincides within 15% with the theoretical result. This comparison therefore provides a striking link between theory and experiment.[17] The initial step of the reaction in Equation (1) requires movement of some of the terminal and bridging oxygen ligands of the W1 and W2 centers (Figure 4). First, the O1, O2 (both blue) and the O3, O4 (orange) positions shown in Figure 4A and 4B rotate clockwise about the central tungsten atoms through the transition state (Figure 4A, center) until the terminal O1 (bound to W1) position is within bonding distance of W2 and...
the bridging O2 center moving towards the sulfur atom reaches bonding distance with this center.

As can be seen in Figure 4A and 4B, the oxygen trajectories during the transformation are extremely (O1 $\Delta = 1.8 \AA$; 66%), (O2 $\Delta = 1.5 \AA$; 37%), (O3 $\Delta = 1.2 \AA$; 30%), (O4 $\Delta = 1.2 \AA$; 37%). Finally, as the bond is being made between O1 and W2 the trans-positioned water ligand on W2 is cleaved off (an animation of this transformation, generated by the interpolation of the coordinates between 3a and 5a, is present in the Supporting Information).

In conclusion, the enclosure of sulfite anions with a “correct” orientation in an HPMC cluster shell transforms these anions from “innocent” structural templates to electronically reactive, functional units. The sulfite ions can now release electrons to the cluster shell upon activation by heat (the sulfite groups in cluster 3a are “activated” whereas those in 2a are not). Therefore this new class of “activated” metal oxide cluster shows promise for the development of novel functional metal oxides, and 3a is the first characterized inorganic cluster to undergo a concerted reaction in which a unimolecular process is characterized by a coupled structural and electronic rearrangement. Although the transformation of 3 to 4 does not appear reversible we will seek to extend this system, for example, by the replacement of the water groups for other ligands.

**Experimental Section**

2: Na3W2O7·2H2O (6.6 g, 20 mmol) and Na2SO4 (2.4 g, 19 mmol) were dissolved in water (25 mL). Hydrochloric acid (37%, 5 mL) was added to the stirred solution and the pH value of the solution was adjusted to 1.9 using diluted hydrochloric acid. The solution was then added to the stirred solution and the pH value of the solution was dissolved in water (25 mL). Hydrochloric acid (37%, 5 mL) was added to the stirred solution and the pH value of the solution was adjusted to 1.9 using diluted hydrochloric acid. The solution was then heated under reflux for 72 h. After cooling, the solution was added to a solution of Bu4NBr (6.0 g, 18.6 mmol) in water (200 mL). A white precipitate was collected by centrifuging, washed with water and ethanol, and dried in vacuum. Recrystallization of the solid in acetonitrile afforded cream yellow crystals of 2 (yield 2.3 g, 39%). IR (KBr disk): ν = 3434, 2961, 2873, 1625, 1482, 1379, 1151, 1105, 993, 915, 877, 779 cm$^{-1}$; elemental analysis (%) calc. for C6H14N4O6S3W18: C 14.5, H 2.7, N 1.1, W 62.4; found: C 14.2, H 2.6, N 1.2, W 63.0.

3: Compound 3 was produced in the same procedure as 2 except that in the final step solid KCl (5.0 g, 67 mmol) was added to the reaction mixture instead of a Bu4NBr solution and the mixture was stirred for 2 h to yield a white precipitate, which was collected and then recrystallized in minimum water (ca. 140 mL) with the addition of KCl (2 g) and drops of diluted hydrochloric acid to keep the pH value at 2.0. After the solution was concentrated to about 100 mL (by evaporation in air), the colorless crystals of 3 were collected (yield 2.3 g, 41%). IR (KBr disk): ν = 3434, 2961, 2873, 1625, 1482, 1379, 1151, 1105, 993, 915, 877, 779 cm$^{-1}$; elemental analysis (%) calc. for C6H14N4O6S3W18: C 14.5, H 2.7, N 1.1, W 62.4; found: C 14.2, H 2.6, N 1.2, W 63.0.

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hybrid B3-LYP exchange-correlation functionals to converge. All structures ($C_1$ symmetry) were allowed to briefly equilibrate until a small, consistent mean energy gradient $|\partial E/\partial xyz|$ was reached. The mean shift for each atomic position generated by the free geometric equilibration amounted to 0.007 Å. Initial structures for the starting and the final reagent were obtained from crystallographic data for 3 and 5, respectively, with two water molecules added to the final geometry.

[15] This is, to our knowledge, the first example of a non-lacunary HPOM which includes tungsten centers with more than one terminal ligand.


[17] Other characteristic electronic properties support the suggested reaction pathway as well: A gradual transfer of charge density from the sulfite groups in the initial state 3a to the tungsten positions in the final state is reflected by a continuous decrease in the HOMO–LUMO energy gap and a gradual decrease of the tungsten partial atomic net charges. In the final product, the four electrons are delocalized over all 18 tungsten positions, resulting in nearly uniform Löwdin partial charges (with standard deviations of 2%). Throughout the series, the Löwdin charges of the sulfur positions successively increase from 0.173 (3a) to 0.186 (transition state) to 0.198 (final product), a pattern corresponding to the oxidation of the sulfite groups.