

Oscillatory Template Exchange in Polyoxometalate Capsules: A Ligand-Triggered, Redox-Powered, Chemically Damped Oscillation

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S Supporting Information

ABSTRACT: The redox-controlled driven oscillatory template exchange between phosphate (P) and vanadate (V) anions enclosed in an $\{X_2M_{18}\}$ cluster is reported. Extensive investigations using a range of techniques, including correlated ESI-MS, EPR, and UV-vis as a function of reaction time, showed that six complete oscillations interconverting the capsule species present in solution from $\{P_2M_{18}\}$ to $\{V_2M_{18}\}$ were possible, provided that a sufficient concentration of the TEA reducing agent was present in solution.

Polyoxometalates (POMs) are anionic metal oxides constructed from transition metals (usually vanadium, molybdenum, tungsten or niobium) in their higher oxidation states and are formed through a self-assembled condensation process.¹ Polyoxometalates have attracted the attention of researchers because of their aesthetically appealing and complex architectures.² In addition, they have also attracted interest because of their nanoscale size ranging from 1 to 6 nm (the size of small proteins)³ as well as their diverse electronic properties with applications in the field of catalysis, medicine, and electronics.⁴ Recently many advances in the understanding and control of the self-assembly processes that govern the architectures of POM-based chemical systems have been made utilizing X-ray diffraction and high-resolution electrospray ionization (ESI) and cryospray ionization (CSI) mass spectrometry (MS).⁵ Consequently, this has allowed a more sophisticated synthetic approach and designed synthetic procedures⁶ to be employed, which have given rise to the discovery of unprecedented archetypes and the emergence of novel functionalities.^{6,7}

Herein we describe a redox-driven oscillatory template exchange that causes the exchange of the two XO_4^{3-} heteroatom guests (denoted as “P” and “V” for $X = P^V$ and V^V , respectively) contained within the $\{M_{18}O_{54}(XO_4)_2\}^{6-}$ capsule for two complete oscillation cycles ($P_2 \rightarrow V_2 \rightarrow P_2 \rightarrow V_2 \rightarrow P_2$) before being “chemically” damped. We also show that the oscillations can be restarted by “resetting” the process, allowing up to four further complete cycles as shown by preliminary in situ UV-vis spectroscopy experiments. We postulate that the process proceeds via opening and closing of the cluster capsule and show that this process is driven by a competition between reductive and oxidative processes. The

discovery was made by the combined use of electron paramagnetic resonance (EPR) spectroscopy and MS. In addition, the MS studies allowed us to follow the whole process in real time by stopping and sampling the system at given time intervals, giving preliminary mechanistic information regarding the intermediate molecular fragments that take part in the process.

The diphosphate molybdenum Dawson capsule $[Mo_{18}O_{54}(PO_4)_2]^{6-} = \{P_2Mo_{18}\}$ has been known for decades⁸ and used as a secondary building unit for the construction of larger architectures, while numerous studies have revealed its use as a redox-active material and catalyst because of its acidic properties.⁹ It is well-established that the $\{P_2Mo_{18}\}$ capsule retains its integrity in an acidic environment while it can store electrons with minimum structural rearrangement.¹⁰ Furthermore, we recently reported examples of polyoxometalate cluster cages where transition metals can be trapped within the metallic cage under specific experimental conditions, such as the encapsulation of $\{WO_6\}$ octahedra within $\{W_{18}\}$ cages¹¹ and $\{VO_4\}$ tetrahedra within $\{M_{18}\}$ ($M = Mo, W$) cages (Figure 1).¹² On the basis of the above observations, we envisaged the possibility of preferential inclusion or exchange of the template by another transition metal with the appropriate geometry within the $\{P_2Mo_{18}\}$ Dawson capsule and of observing this by ESI-MS (Figure 1).

Experimentally, the procedure allowing the template-guest exchange involves heating an aqueous solution of $\{P_2Mo_{18}\}$ in the presence of ammonium vanadate and triethanolamine (TEA) under acidic conditions in air. The mixture was monitored in real time utilizing ESI-MS by collecting and measuring aliquots from the reaction mixture at specific time intervals. The aliquots were collected and treated by ion exchange in an identical manner, thereby aiding the rapid and accurate assignment of the species present in the reaction aliquots. The same acetonitrile solutions prepared as described above [see the Supporting Information (SI) for details] were studied by ESI-MS and EPR spectroscopy. Initially, the ESI-MS studies revealed that after the solution was heated for 0.5 h, the oscillation was initiated with guest exchange where the two PO_4^{3-} anion templates were replaced by two VO_4^{3-} units, and the color of the mixture changed from yellow to green.

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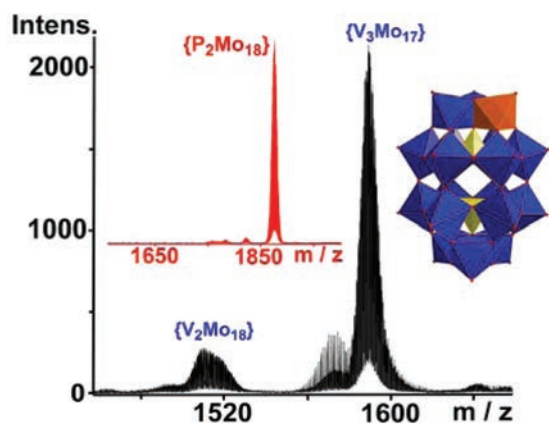


Figure 1. Negative-ion mass spectrum of the reaction mixture at $t = 0.5$ h in acetonitrile after counterion exchange with TBABr, showing the typical species $[\text{Mo}_{14}^{\text{VI}}\text{Mo}_4^{\text{V}}(\text{VO}_4)_2\text{O}_{54}(\text{TBA})_7(\text{H}_2\text{O})]^{3-} = \{\text{V}_2\text{Mo}_{18}\}$ and $[\text{H}_2\text{V}^{\text{IV}}\text{Mo}_{13}^{\text{VI}}\text{Mo}_4^{\text{V}}(\text{VO}_4)_2\text{O}_{54}(\text{TBA})_7(\text{TEA})_2]^{3-} = \{\text{V}_3\text{Mo}_{17}\}$ at m/z 1511.96 and 1591.04, respectively. Left inset: negative ion mass spectrum of the parent molecule $\{\text{P}_2\text{Mo}_{18}\text{O}_{62}(\text{TBA})_4\}^{2-} = \{\text{P}_2\text{Mo}_{18}\}$ with its envelope centered at m/z 1875.53. Right inset: polyhedral representation of the parent POM-based capsule $[\text{Mo}_{18}\text{O}_{54}(\text{XO}_4)_2]^{6-}$ ($\text{Mo} = \text{blue polyhedra}$), which interconverts between $\{\text{P}_2\text{Mo}_{18}\}$ ($\text{Mo} = \text{orange polyhedron}$, $\text{PO}_4 = \text{yellow polyhedra}$) and $\{\text{V}_3\text{Mo}_{17}\}$ (framework $\text{V}^{\text{IV}} = \text{orange polyhedron}$, $\text{VO}_4 = \text{yellow polyhedra}$).

Assignment of species detected by ESI-MS showed that two similar molybdenum-based capsules were present: $[\text{Mo}_{18}\text{O}_{54}(\text{VO}_4)_2]^{6-} = \{\text{V}_2\text{Mo}_{18}\}$ and $[\text{H}_2\text{V}^{\text{IV}}\text{Mo}_{17}\text{O}_{54}(\text{VO}_4)_2]^{6-} = \{\text{V}_3\text{Mo}_{17}\}$ respectively (Figure 1).

On the basis of the fact that the $\{\text{V}_3\text{Mo}_{17}\}$ cluster capsule, which oscillates in a parallel fashion with the parent molecule $\{\text{P}_2\text{Mo}_{18}\}$, carries a reduced vanadium center on the cluster cage, we decided to utilize EPR spectroscopy in conjunction with the ESI-MS studies to follow the oscillatory guest exchange process. The series of samples isolated from the reaction mixture for the ESI-MS studies were transferred directly, and their EPR spectra were recorded at 298 K. The only species detected was $\{\text{V}_3\text{Mo}_{17}\}$. Quantitative analysis of the spectral intensity (per unit mass) as a function of reaction time (see the SI) followed an oscillatory pattern that was in excellent agreement with the ESI-MS studies, providing the opportunity to follow the formation of the $\{\text{V}_3\text{Mo}_{17}\}$ capsule with time. The bottom panel of Figure 2 clearly shows that the spectral intensity increased and reached a maximum during the first hour of the experiment and then decreased before reaching a second maximum value after the mixture was heated for 8 h.

Even though the vanadium-templated capsules were the major product in the reaction mixture, low-intensity envelopes of species with smaller m/z values were detected and assigned mainly to the half part of the Dawson architecture (e.g., $\{\text{M}_9\text{X}\}$) along with some smaller fragments. A series of low-intensity envelopes were assigned to the $\{\text{PMo}_5\text{O}_{18}\}^-$, $\{\text{PMo}_5\text{O}_{20}\text{H}_4\}^-$, $\{\text{V}_2\text{Mo}_7\text{O}_{31}\text{TBA}_4(\text{H}_2\text{O})\text{H}_5\}^{2-}$, $\{\text{Mo}_8\text{O}_{26}\text{TBAH}_2\}^-$, $\{\text{V}_2\text{Mo}_7\text{O}_{32}\text{TEA}(\text{H}_2\text{O})_7\text{H}_{11}\}^-$, $\{\text{V}_2\text{Mo}_7\text{O}_{29}\text{TBA}_5(\text{H}_2\text{O})_3\text{H}\}^-$, and $\{\text{Mo}_6\text{O}_{24}\text{TBA}_4\text{TEA}(\text{H}_2\text{O})\text{H}_6\}^-$, indicating that the template exchange reaction occurs via capsule opening or dissociation into $\{\text{M}_9\text{X}\}$ -type units. Thus, upon heating, the pale-yellow suspension turned green, indicating the presence of reduced vanadium centers. Reduction of the vanadium centers in the presence of TEA upon heating triggered the “opening” of the Dawson capsule

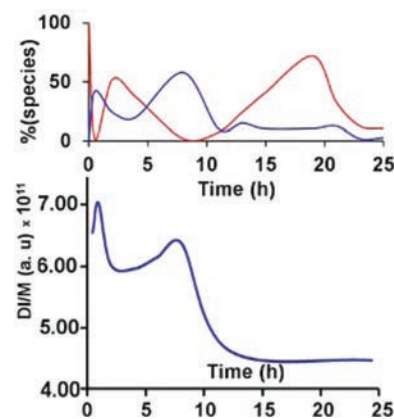


Figure 2. Top: Representation of the amounts of the $\{\text{P}_2\text{Mo}_{18}\}$ (red line) and $\{\text{V}_3\text{Mo}_{17}\}$ (blue line) capsules in the reaction mixture as a function of the time, based on their relevant observed intensities. Bottom: Double integral (DI) of the EPR spectrum weighted by the sample mass for the sample series isolated from the reaction mixture at different time intervals. The samples were recorded at 0.5, 1, 2, 4, 6, 8, 18, and 24 h.

with a minimum amount of fragmentation. It is worth noting that the template exchange process did not occur in the absence of a reducing environment following similar experimental conditions (i.e., in the absence of TEA). The final step involved the exchange of the phosphates by vanadates followed by the reorganization of the two lobes to form the V-templated Dawson-like cluster.

Further time-dependent measurements showed that as the reaction continued, reoxidation of the reduced species occurred after 3 h, and the solution turned from green to pale-yellowish-green. After 8 h of heating, the solution turned green again because of the abundance of reducing agent in solution. On the basis of the above observations we followed the reaction using ESI-MS to identify the species in solution during the redox process. Interestingly, we discovered that after 2–4 h of heating, the vanadium-templated cluster capsule reopened, expelled the vanadium centers, and captured the phosphate anions again, consequently reforming the parent molecule. The whole process took place all over again from the beginning, provided that we supplied the system with small amount of TEA to initiate the oscillation again (Figure 3). When the amount of TEA was not sufficient, the exchange process gradually stopped (see Figure S3 in the SI), no matter how long we kept heating the solution. Plotting the relevant intensities of the detected species obtained from the ESI-MS studies clearly showed the oscillatory guest exchange process that occurs. Here the intensity of the parent molecule $\{\text{P}_2\text{Mo}_{18}\}$ decreased rapidly at the beginning, while at the same time the formation of the $\{\text{V}_3\text{Mo}_{17}\}$ capsule was observed.

During the real-time monitoring of the reaction mixture, the major “intermediate” species prevailing in solution were detected and identified. Analysis of the MS data showed that the reaction solution had a high concentration of the half-Dawson fragments implicated in the reaction mechanism, which were templated either by phosphorus or vanadium atoms. As such the MS data gave an indication that the exchange process proceeds via a redox-promoted opening of the capsule with minimum additional fragmentation.¹³ Another interesting observation is that the template exchange process seems to be much faster than the “closing” process of the molecular capsule, since only cages encapsulating the same type

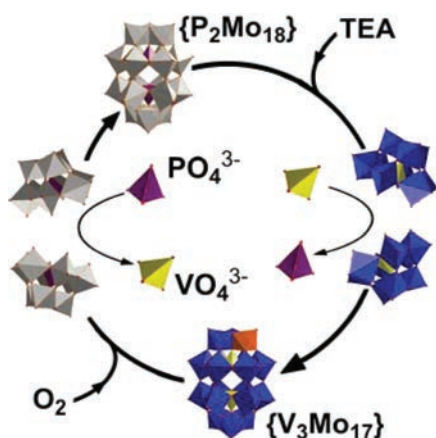


Figure 3. The reaction cycle described here, showing the redox-driven guest exchange reaction. Color scheme: PO_4^{3-} templated cluster, gray; VO_4^{3-} templated cluster, blue; PO_4^{3-} purple; VO_4^{3-} template, yellow; reduced V, orange. The data point to the dissociation of the $\{\text{M}_{18}\text{X}_2\}$ cluster into two $\{\text{M}_9\text{X}\}$ halves.

of template were detected (this means that each exchange process, driven by the redox state of the components, can proceed fully to completion). If it had been the case that the above rates were comparable, we should have detected a statistical mixture of capsules encapsulating either PO_4^{3-} , VO_4^{3-} , or both of the anions within the Dawson-type capsules at the same time.

Although the oscillation could be “reset” and oscillate for longer than two cycles (Figure 3), the system did become damped in the end, presumably because of the formation of the Keggin ion. Therefore, to suppress the formation of the Keggin ion, we tried to reset the reaction not only by adding extra TEA reducing agent but also by temporally increasing the pH through the addition of ammonia (see the SI), and we employed in situ UV–vis measurements using a dip probe to follow the yellow \leftrightarrow green (low \leftrightarrow high absorbance at 650 nm) oscillation associated with the switch between the P_2 and V_2 clusters. To our surprise, the system oscillated for a further four cycles (Figure 4), highlighting this system as a redox-powered dynamically oscillating host–guest system.

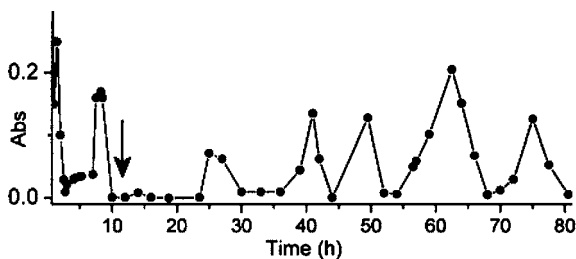


Figure 4. Time-dependent UV–vis monitoring at 650 nm for 80 h showing oscillations in the absorbance mirroring those observed by ESI-MS and EPR spectroscopy in the 0–20 h period. The reaction was reset after ca. 10 h (arrow) by adding ammonia to reset the pH and also by supplying more TEA reducing agent. The absorbance values approaching 0.1–0.15 signal a change in the solution color from yellow to green, indicating the presence of the $\{\text{V}_2\}$ -centered Dawson capsule. The period of the oscillations is erratic, ranging from 6.75 to 16 h in length. ESI-MS measurements after 80 h confirmed the presence of the oscillating clusters in the proportions indicated by the UV–vis data.

In conclusion, we have reported the observation of an oscillatory guest exchange process driven by competing redox processes in a POM-based capsule system. Moreover, we have demonstrated the application of EPR spectroscopy and MS to follow the oscillatory template exchange reactions, while the chemical reset and UV–vis experiments highlight the potential of this system as a new type of host–guest chemical oscillator. The findings presented here show the potential of POM cluster capsules for the design of “smart” molecules and responsive materials. In the future, we will investigate whether the oscillation process can be extended toward tens or even hundreds of cycles and use it to explore complex chemical processes involving coupled structural rearrangements driven away from equilibrium using a “redox-metabolism”. In future work, we will explore the damping and activation of the oscillator, including the temporal dynamics of the system, as well as the nature of the “competition” between the capsules for templates and see whether this can be extended to membranes containing these clusters.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, Netherlands, 2001. (b) *Polyoxometalate Chemistry for Nano-Composite Design*; Yamase, T., Pope, M. T., Eds.; Kluwer/Plenum: New York, 2002. (c) *Polyoxometalate Molecular Science*; Borrás-Almenar, J. J., Coronado, E., Müller, A., Pope, M. T., Eds.; NATO Science Series II, Vol. 98; Kluwer: Dordrecht, Netherlands, 2003. (d) Long, D. L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105–121. (e) Kortz, U.; Müller, A.; van Slageren, J.; Schnack, J.; Dalal, N. S.; Dressel, M. *Coord. Chem. Rev.* **2009**, *253*, 2315–2327.
- (2) (a) Müller, A.; Kögerler, P.; Kuhlmann, C. *Chem. Commun.* **1999**, 1347–1358. (b) Miras, H. N.; Cooper, G. J. T.; Long, D.-L.; Bögge, H.; Müller, A.; Streb, C.; Cronin, L. *Science* **2010**, *327*, 72–74. (c) Long, D.-L.; Tsunashima, R.; Cronin, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 1736–1758. (d) Müller, A.; Shah, S. Q. N.; Bögge, H.; Schmidtmann, M. *Nature* **1999**, *397*, 48–50. (e) Bassil, B. S.; Ibrahim, M.; Al-Oweini, R.; Asano, M.; Wang, Z.; van Tol, J.; Dalal, N. S.; Choi, K.-Y.; Biboum, R. N.; Keita, B.; Nadjo, L.; Kortz, U. *Angew. Chem., Int. Ed.* **2011**, *50*, 5961–5964.
- (3) Müller, A.; Beckmann, E.; Bögge, H.; Schmidtmann, M.; Dress, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1162–1167.
- (4) (a) Müller, A.; Luban, M.; Schröder, C.; Modler, R.; Kögerler, P.; Axenovich, M. J.; Schnack, M. J.; Canfield, P.; Budko, S.; Harrison, N. *ChemPhysChem* **2001**, *2*, 517–521. (b) Müller, A.; Kögerler, P.; Dress, A. W. M. *Coord. Chem. Rev.* **2001**, *222*, 193–218. (c) Way, M.; Bond,

A. M.; Wedd, A. G. *Inorg. Chem.* **1997**, *36*, 2826–2833. (d) Thiel, J.; Ritchie, C.; Miras, H. N.; Streb, C.; Mitchell, S. G.; Boyd, T.; Ochoa, M. N. C.; Rosnes, M. H.; McIver, J.; Long, D.-L.; Cronin, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 6984–6988. (e) Ritchie, C.; Ferguson, A.; Nojiri, H.; Miras, H. N.; Song, Y.-F.; Long, D.-L.; Burkholder, E.; Murrice, M.; Kögerler, P.; Brechin, E. K.; Cronin, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 5609–5612. (f) Ibrahim, M.; Lan, Y.; Bassil, B. S.; Xiang, Y.; Suchopar, A.; Powell, A. K.; Kortz, U. *Angew. Chem., Int. Ed.* **2011**, *50*, 4708–4711. (g) Carraro, M.; Nsouli, N. H.; Oelrich, H.; Sartorel, A.; Sorarù, A.; Mal, S. S.; Scorrano, G.; Walder, L.; Kortz, U.; Bonchio, M. *Chem.—Eur. J.* **2011**, *17*, 8371–8378.

(5) (a) Miras, H. N.; Wilson, E. F.; Cronin, L. *Chem. Commun.* **2009**, 1297–1311. (b) Sahureka, F.; Burns, R. C.; von Nagy-Felsobuki, E. I. *J. Am. Soc. Mass Spectrom.* **2001**, *10*, 1136–1143. (c) Ohlin, C. A.; Villa, E. M.; Fetting, J. C.; Casey, W. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 8251–8254. (d) Waters, T.; O’Hair, R. A. J.; Wedd, A. G. *J. Am. Chem. Soc.* **2003**, *125*, 3384–3396. (e) Wang, C.-H.; Huang, M.-W.; Lee, C.-Y.; Chei, H.-L.; Huang, J.-P.; Shiea, J. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 1168–1174. (f) Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955–964. (g) Wilson, E. F.; Miras, H. N.; Rosnes, M. H.; Cronin, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 3720–3724.

(6) (a) Miras, H. N.; Yan, J.; Long, D.-L.; Cronin, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 8420–8423. (b) Miras, H. N.; Stone, D. J.; McInnes, E. J. L.; Raptis, R. G.; Baran, P.; Chilas, G. I.; Sigalas, M. P.; Kabanos, T. A.; Cronin, L. *Chem. Commun.* **2008**, 4703–4705. (c) Miras, H. N.; Ochoa, M. N. C.; Long, D.-L.; Cronin, L. *Chem. Commun.* **2010**, *46*, 8148–8150. (d) Corella-Ochoa, M. N.; Miras, H. N.; Kidd, A.; Long, D.-L.; Cronin, L. *Chem. Commun.* **2011**, *47*, 8799–8801.

(7) (a) Long, D.-L.; Kögerler, P.; Cronin, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1817–1820. (b) Fleming, C.; Long, D.-L.; McMillan, N.; Johnston, J.; Bovet, N.; Dhanak, N. V.; Gadegaard, N.; Kögerler, P.; Cronin, L.; Kadodwala, M. *Nat. Nanotechnol.* **2008**, *3*, 229–233. (c) Long, D.-L.; Abbas, H.; Kögerler, P.; Cronin, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3415–3419.

(8) Wu, X. *J. Biol. Chem.* **1920**, *43*, 189–220.

(9) (a) Liu, J.; Peng, J.; Wang, E.; Bi, L.; Guo, S. *J. Mol. Struct.* **2000**, *525*, 71–77. (b) Liu, D.; Tan, H.-Q.; Chen, W.-L.; Li, Y.-G.; Wang, E.-B. *CrystEngComm* **2010**, *12*, 2044–2046. (c) Wang, X.; Kang, Z.; Wang, E.; Hu, C. *J. Electroanal. Chem.* **2002**, *523*, 142–149.

(10) (a) Belhouari, A.; Keita, B.; Nadjjo, L.; Contant, R. *New J. Chem.* **1998**, *22*, 83–86. (b) Adbeljalil, E.; Keita, B.; Nadjjo, L.; Contant, R. *J. Solid State Electrochem.* **2001**, *5*, 94–106.

(11) Long, D.-L.; Kögerler, P.; Parenty, A. D. C.; Fielden, J.; Cronin, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 4798–4803.

(12) (a) Miras, H. N.; Long, D.-L.; Kögerler, P.; Cronin, L. *Dalton Trans.* **2008**, 214–221. (b) Miras, H. N.; Stone, D.; Long, D.-L.; McInnes, E. J. L.; Kögerler, P.; Cronin, L. *Inorg. Chem.* **2011**, *50*, 8384–8391.

(13) Even though the main detected species exhibited the half-Dawson archetype, other smaller fragments such as $\{\text{Mo}_3\text{O}_{10}\text{TBA}\}^-$, $\{\text{PMo}_5\text{O}_{18}\}^-$, and $\{\text{PMo}_5\text{O}_{20}\text{H}_4\}^-$ were detected in small amounts.