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Unravelling the Complexities of Polyoxometalates in Solution Using Mass Spectrometry: Protonation versus Heteroatom Inclusion

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Polyoxometalate (POM) chemistry is one of the most diverse and rapidly expanding areas in inorganic chemistry today,[1−3] and the ongoing interest in the field is highlighted by the large number of new iso- and heteropolyoxometalate clusters which have been discovered in recent years.[2,3] One of the most important properties of these clusters is their ability to act as solid acids, a feature highly desired for industrial applications and green chemistry.[4] Despite the ever increasing interest in this class of materials,[1−3] accurate determination of the formula and structure still represents a great challenge[5] important for understanding the clusters and their exploitation. For instance, the well-known Keggin $\{M_{12}O_{40}X_1\}^{x-}$ and Dawson $\{M_{18}O_{62}X_2\}^{y-}$ (X = S, P, etc.) clusters still inspire an enormous amount of new research (>4000 papers during the last 4 years alone) owing to their intriguing range of applications in catalysis and materials, yet even the formulation of these compounds can often be debated.[5] Although several studies have investigated the solid-state protonation of different clusters,[5−9] the complex equilibria between different protonation states in solution have not yet been fully understood. Further problems in the analysis of heteropolyoxometalates arise when one of the heteroatoms is "missing" or when a heteroatom is disordered over several sites, thus creating a structural vacancy. This means that the exact number of heteroatoms per cluster, and hence the resulting protonation, cannot be determined by structural studies alone. Overcoming these challenges is a vital step towards understanding POM clusters and extended cluster formation *via* building blocks in solution.[1]

Herein we demonstrate that a combination of cation exchange and electrospray-ionization mass spectrometry (ESI-MS) can be used as a versatile tool in various complex systems to investigate the cluster species in solution, allowing the unambiguous determination of both the number of heteroanions and the degree of protonation, as well as determining the relative proportions of the cluster species present in solution. The study of polyoxometalate systems by means of mass spectrometry can be dated back to the 1980s.[10] Since then, several papers reported the observation of small clusters like $\{M_{12}\}$-Keggin type anions by MS methods.[11−13] Thus far, the use of comparatively hard ionization techniques and the complex isotopic envelopes given by W and Mo has not allowed mass spectroscopy to become an established analytical technique for complex problems in polyoxometalate chemistry. However, it has recently been demonstrated that larger cluster assemblies can, in principle, be observed using ESI-MS methods.[14]

We reasoned that polyoxometalate clusters should be ideal candidates to be examined using high-resolution mass spectrometry since they are intrinsically charged and have characteristic isotopic envelopes which can be precisely fitted to determine the exact formula. In particular, the use of soft ionization techniques such as ESI in combination with a high-resolution detector system allows the elucidation of the complete cluster formula including all protons. This has thus far been a major drawback of standard crystallographic XRD studies which often do not provide direct information on the protonation state of the cluster anions. Therefore, nondestructive mass spectrometry of polyoxometalates has the potential to become a standard analysis technique for complex cluster systems since it provides vital complementary information of the cluster composition in solution which cannot be deduced from crystallographic studies. Furthermore, MS studies enable us to elucidate the overall protonation as a function of the heteroatom type and number included within the cluster shell. For instance, although the Dawson-like clusters $[H_mW_{18}O_{60}X_n]^{y-}$ (where X = As, Sb, Bi)[6−8] have been known for three decades, along with their approximate formulation of $n = 1$, their composition could not be confirmed unambiguously due to disorder of the heteroatoms over two positions in a single cluster. Furthermore, analysis of the bulk sample cannot provide unambiguous evidence to support the molecular composition of the cluster to be W:X = 18:1 since the isolated material could contain a mixture of $\{W_{18}X_2\}$ and "empty" $\{W_{18}\}$ clusters.[15] In the course of extending our work using pyramidal anions as templates in constructing Dawson-like POM clusters,[16] we have obtained the new compound $Na_7[H_mSb_nW_{18}O_{60}]\cdot32H_2O$, **1**$\cdot(Na_7)\cdot32H_2O$, which represents a new D_{3d} symmetric isomer of the antimonite-based heteropolyoxotungstate $[H_mSb_nW_{18}O_{60}]^{y-}$.[8] Crystallographic studies of **1**$\cdot(Na_7)\cdot32H_2O$ showed that the asymmetric unit contains nine W centers and one Sb with three Sb−O bonds (average Sb−O distance = 2.00 Å). Extension of the asymmetric unit reveals the full cluster of 18 tungsten centers which are arranged on a Dawson-like shell of D_{3d} symmetry and "peanut-like" shape (Figure 1, left); two Sb atoms can be seen within the cluster framework with a Sb···Sb distance of 2.18 Å, although our initial elemental analysis and crystallographic refinement of the cluster points to n being equal to 1.

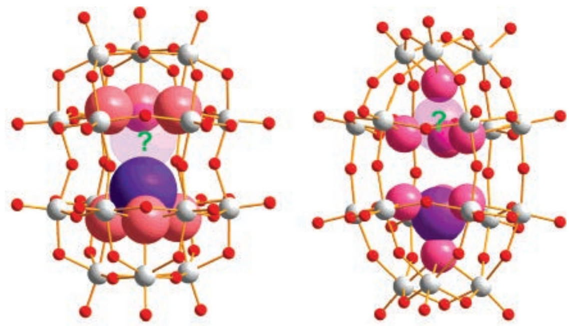

Figure 1. Representation of the structures of $[H_mSb_nW_{18}O_{60}]^{y-}$ (**1**) and $[H_mP_nW_{18}O_{62}]^{y-}$ (**2**). Color scheme: W gray, O red, Sb and P purple.

This situation can be compared to the discovery of $[H_mP_nW_{18}O_{62}]^{y-}$ which was recently reported with the formula $K_7[H_4P_1W_{18}O_{62}]\cdot18H_2O$, **2**$\cdot(K_7)\cdot18H_2O$; that is, also with $n = 1$; see Figure 1.[17,18] Both clusters **1** and **2** appear to include only one heteroatom; in addition, **1** is templated by a pyramidal SbO_3^{3-} anion, whereas **2** contains one tetrahedral PO_4^{3-} anion. This is in contrast to the traditional and well-known idea that all Dawson clusters are

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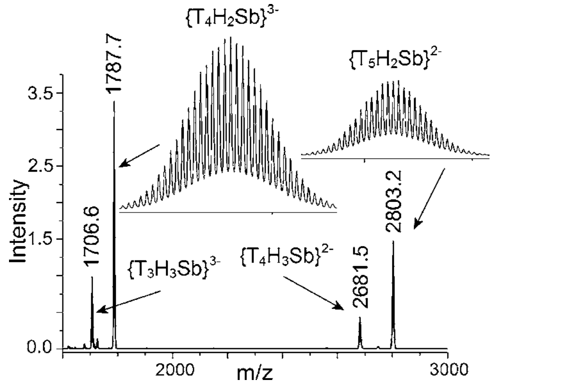

Figure 2. The negative ion mass spectrum of the TBA$^+$ salt of **1** showing the series of tri- and tetraprotonated forms of $(TBA)_y[H_xSb_1W_{18}O_{62}]^{(9-(x+y))-}$ in solution. T ≡ TBA$^+$, Sb ≡ $Sb_1W_{18}O_{60}$ (intensity $\times 10^4$).

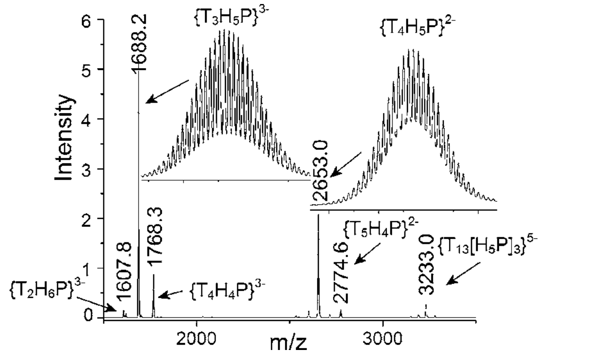

Figure 3. The negative ion mass spectrum of the TBA$^+$ salt of **2** showing the series of tetra-, penta-, and hexaprotonated forms of $(TBA)_y[H_xP_1W_{18}O_{62}]^{(11-(x+y))-}$ in solution. T ≡ TBA$^+$, P ≡ $P_1W_{18}O_{62}$ (intensity $\times 10^4$).

templated by two tetrahedral heteroanions. However, exchanging the K$^+$ cations in the K$^+$ salt of **2** with TBA$^+$ (=$(n\text{-}C_4H_9)_4N^+$) yields a TBA$^+$ salt of **2** with only six TBA$^+$ counterions and an α-Dawson cluster $[P_2W_{18}O_{62}]^{6-}$ found by crystallographic analysis thus implying the formula of the TBA$^+$ salt of **2** could even be given as $(TBA)_6[P_2W_{18}O_{62}]$ even though the thermal parameters for the P atoms appear to be unreasonable.[18]

Using the electrospray[14b,19] ionization approach, coupled with a high-resolution TOF detector, allowed us to establish the composition of clusters **1** and **2** in acetonitrile solution after ion-exchange to TBA$^+$ (see Figures 2 and 3).

The cation exchange process was used first because the TBA$^+$ cations have a much higher mass than Na$^+$ or K$^+$ and give a large separation between signals corresponding to differently charged or protonated cluster states. Second, the TBA$^+$ cations have a lower affinity than Na$^+$ or K$^+$ for the cluster anions and solvent molecules. Third, the use of acetonitrile can prevent clusters from decomposing, aggregating, or converting into other species which is typically seen in aqueous solution.

The Na$^+$ or K$^+$ salts of **1** and **2** are only soluble in water and give complex mass spectra due to the side reactions listed above and also due to association of the terminal oxo groups of the anionic clusters with $M^+(H_2O)_n$ units (see Figure 4). However, as shown in Figures 2 and 3, the TBA$^+$ salts of **1** and **2** in acetonitrile give well-defined spectra with limited speciation related to the accessible protonation states of the clusters in solution.[17,20] Furthermore, each species can be observed at different *m*/*z* values due to the formation of ion pairs with variable numbers of TBA$^+$ cations. In contrast to the spectra observed in organic solvent, aqueous samples of **1** give extremely complex mass spectra showing the presence of many

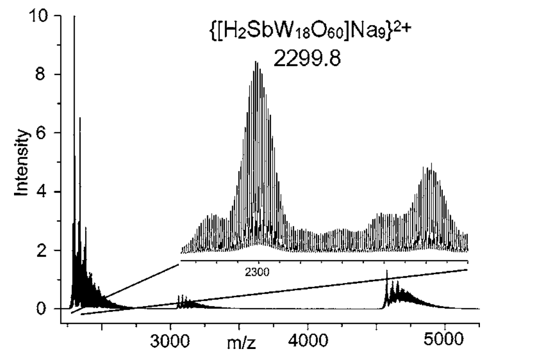

Figure 4. The positive ion mass spectrum of **1**·(Na_7) in water showing the complex spectrum and speciation in aqueous solution (intensity $\times 10^3$).

species resulting from the rapid speciation of the clusters in aqueous solution and the ability to form complex adducts with sodium cations and water ligands (see Figure 4). This demonstrates the utility of the ion-exchange phase transfer to organic solvent approach.

The cation exchange of inorganic salts of **1** and **2** with TBA$^+$ quantitatively yielded the compounds as $(TBA)_7[H_2Sb_1W_{18}O_{60}]$ (**1**·$(TBA)_6$) and $(TBA)_6[H_5P_1W_{18}O_{62}]$ (**2**·$(TBA)_6$) as confirmed by the combination of structural analysis, elemental analysis, and ESI-MS studies in acetonitrile. Exhaustive analysis of the ESI-MS data shows that **1** and **2** can be unambiguously identified in both positive and negative ion mode and **1** speciates in solution to give the di- and triprotonated forms (Figure 2), whereas **2** can be observed as the hexa-, penta-, and tetraprotonated forms (Figure 3).

This result shows that heteropolyoxometalate clusters exist in solution in a range of accessible protonation states which can often not be identified by bulk analytical methods. For both compounds **1** and **2**, respectively, the most intense single ion signal or base peak was observed for the di- and pentaprotonated species (see Figures 2 and 3). Further, the analysis of **1** gave no evidence for the presence of a bisantimony-containing species. Similarly, the mass spectrometric analysis of **2** did not show evidence of the bisphosphorus-containing species. These findings fully confirm our formula assignments of the anions **1** and **2** as $[H_2Sb_1W_{18}O_{60}]^{7-}$ and $[H_5P_1W_{18}O_{62}]^{6-}$, respectively.[16,17]

The unambiguous assignment of one heteroatom per cluster unit also allows clarification of the crystallographic studies since each $\{W_{18}\}$ cluster contains one heteroatom disordered over two sites. The accuracy of the mass spectrometry study of compound **2** can be confirmed by the analysis of the well-known bisphosphate Dawson cluster $(TBA)_6[P_2W_{18}O_{62}]$ (**3**·TBA_6), which was deliberately synthesized as a potassium salt using a previously reported strategy, and subsequently, the cations were exchanged to TBA$^+$. This approach mimics the experiments conducted with clusters **1** and **2** and allows utilization of **3** as a reference sample for the objective comparison of the MS datasets. Figure 5 shows the mass spectrum of **3**·$(TBA)_6$ in acetonitrile. All peaks are related to $[P_2W_{18}O_{62}]$ with no protons attached to the cluster framework. Furthermore, this study shows that **3** contains a pure phase without contamination of $[H_nPW_{18}O_{62}]$.

To probe the nature of the species present in solution, we conducted a range of mixed-cluster ESI-MS experiments as a function of concentration to examine if it was possible to quantify the transmitted ion intensity directly with the concentration of the cluster species in solution. By comparison of the bisphosphate Dawson cluster $(TBA)_6[P_2W_{18}O_{62}]$, **3**·$(TBA)_6$ with the monophosphate $(TBA)_6[H_5P_1W_{18}O_{62}]$, **2**·$(TBA)_6$ described here, we found a linear correlation between the relative ion intensity and the ratio of the concentration of the above two compounds in solution (see

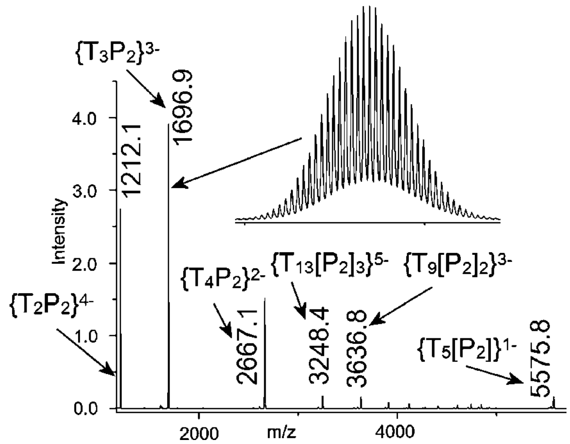

Figure 5. The negative ion mass spectrum of the TBA$^+$ salt of **3** showing the series of charged forms of $(TBA)_y[P_2W_{18}O_{62}]^{(6-y)-}$ in solution. T $\equiv$ TBA$^+$, $P_2 \equiv P_2W_{18}O_{62}$ (intensity $\times 10^4$).

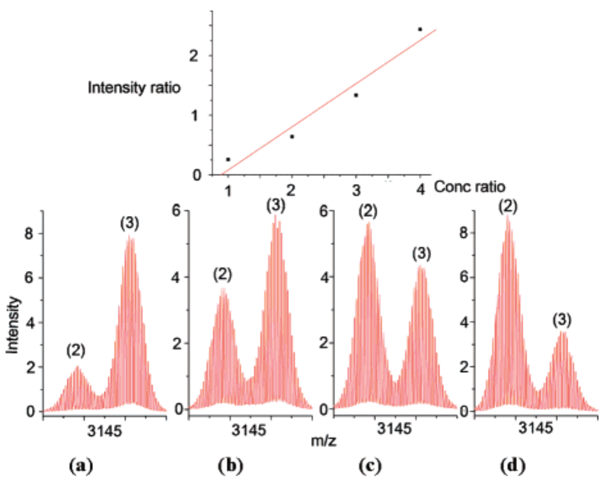

Figure 6. Positive ion mass spectra (+*m*/*z* range 3120−3170) of **2** and **3** (3138 for $\{TBA_8[H_5PW_{18}O_{62}]\}^{2+}$ and 3152 $\{TBA_8[P_2W_{18}O_{62}]\}^{2+}$). **Solution A**: 0.007 mmol·L^{-1} $(TBA)_6[H_5PW_{18}O_{62}]$ in CH_3CN. **Solution B**: 0.028 mmol·L^{-1} $(TBA)_6[P_2W_{18}O_{62}]$ in CH_3CN. (a) 1 mL **A** + 1 mL **B**; (b) 2 mL **A** + 1 mL **B**; (c) 4 mL **A** + 1 mL **B**; (d) 6 mL **A** + 1 mL **B**.

Figure 6). This means that in organic solvents it is possible to use ESI-MS studies to directly probe the solution equilibria.[21] This is an extremely interesting result, opening up a new field in the exploration of POM reaction mechanisms and exploration of the species present in solution under a given set of conditions.[22]

In summary, we have demonstrated that it is possible to control the protonation of a heteropolyacid as a function of the number of heteroanions included within the cluster, and this was directly observed using electrospray mass spectrometry. In addition, we have confirmed that precisely one Sb "template" is included within the cluster, $[H_2Sb_1W_{18}O_{60}]^{7-}$, and established that the majority of the cluster anions **1** are two-fold protonated. This approach was also used to discover that the monophosphate templated cluster, $[H_nPW_{18}O_{62}]^{(11-n)-}$, has a range of protonation states with a maximum of six protons per cluster for the TBA$^+$ ion-exchanged compound of **2**. Finally, it has been demonstrated that ESI-MS can be used to probe the speciation of polyoxometalates by transferring the system into organic solvents using organocations, and it is possible, with a suitable internal standard, to directly relate the transmitted ion intensity with the concentration of the parent species in solution. These observations demonstrate the potential of high-resolution, soft ionization mass spectrometry to accurately reveal the nature of the POM cluster species in solution.

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Supporting Information Available: Experimental details including the synthesis and characterization, X-ray crystallographic (CIF) files. This material is available free of charge via the Internet at http://pubs.acs.org.

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