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

De-Liang Long, Carsten Streb, Yu-Fei Song, Scott Mitchell, and Leroy Cronin*

WestCHEM, Department of Chemistry, The University of Glasgow, Glasgow, G12 8QO, U.K.

Received August 7, 2007; Revised Manuscript Received December 1, 2007; E-mail: lcronin@chem.gla.ac.uk

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.4,5 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.6 Despite the ever increasing interest in this class of materials,1-3 accurate determination of the formula of the compound still represents a great challenge important for understanding the clusters and their exploitation. For instance, the well-known Keggin \([\{\text{M}_12\text{O}_{40}\}]^{-}\) and Dawson \([\{\text{M}_8\text{O}_{19}\text{X}_2\}]^{-}\) (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, even if 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.9

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 heteroatoms 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 \([\{\text{M}_{12}\}\text{-Keggin type anions by MS methods.}^{11-13}\) 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 \([\{\text{H}_m\text{W}_{18}\text{O}_{60}\}]^{-}\) (where X = As, Sb, Bi)\(\text{m}^{+}\) 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 \(\text{W}:\text{X} = 18:1\) since the isolated material could contain a mixture of \([\text{W}_{18}\text{X}_2]\) and “empty” \([\text{W}_{18}\text{]}\) 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 \([\text{Na}_7\{\text{H}_m\text{Sb}_n\text{W}_{18}\text{O}_{60}\}]^\text{32}\text{H}_2\text{O}\) that has 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 \(\text{W}:\text{X} = 18:1\) since the isolated material could contain a mixture of \([\text{W}_{18}\text{X}_2]\) and “empty” \([\text{W}_{18}\text{]}\) clusters.15

Figure 1. Representation of the structures of \([\{\text{H}_m\text{Sb}_n\text{W}_{18}\text{O}_{60}\}]^{-}\) (1) and \([\{\text{H}_m\text{P}_n\text{W}_{18}\text{O}_{60}\}]^{-}\) (2). Color scheme: W gray, O red, Sb and P purple.

This situation can be compared to the discovery of \([\text{H}_m\text{P}_n\text{W}_{18}\text{O}_{60}\}]^{-}\) which was recently reported with the formula \([\text{K}_7\{\text{H}_4\text{P}_1\text{W}_{18}\text{O}_{62}\}]^{-}\) \(18\text{H}_2\text{O}\), \(2\{\text{K}_7\}\cdot18\text{H}_2\text{O}\); 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 \(\text{SbO}_3\)\(^{3+}\) anion, whereas 2 contains one tetrahedral \(\text{PO}_4\)\(^{3-}\) anion. This is in contrast to the traditional and well-known idea that all Dawson clusters are...
templated by two tetrahedral heteroanions. However, exchanging the K⁺ cations in the K⁺ salt of 2 with TBA⁺ (=([n-C₄H₉])₄N⁺) yields a TBA⁺ salt of 2 with only six TBA⁺ counterions and an α-Dawson cluster [P₂W₁₈O₆₂]⁻ found by crystallographic analysis thus implying the formula of the TBA⁺ salt of 2 could even be given as (TBA)₆[P₂W₁₈O₆₂] even though the thermal parameters for the P atoms appear to be unreasonable.¹⁸

Using the electrospray 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 aggregated, or converting into other species which is typically seen in acetonitrile solution after ion-exchange to TBA⁺ (see Figures 2 and 3).

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⁺(H₂O)ₖ 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 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)₆[H₂Sb₁W₁₈O₆₀] (1·(TBA)₆) and (TBA)₆[H₃P₁W₁₈O₆₂] (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 [H₂Sb₁W₁₈O₆₀]⁻ and [H₃P₁W₁₈O₆₂]⁻, respectively.¹⁶,¹⁷

The unambiguous assignment of one heteroatom per cluster unit also allows clarification of the crystallographic studies since each [W₁₈] 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)₁₆[P₂W₁₈O₆₂] (3·(TBA)₁₆), 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)₁₆ in acetonitrile. All peaks are related to [P₂W₁₈O₆₂] with no protons attached to the cluster framework. Furthermore, this study shows that 3 contains a pure phase without contamination of [H₃PW₁₈O₆₂].

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)₁₆[P₂W₁₈O₆₂], 3·(TBA)₁₆ with the monophosphate (TBA)₁₆[H₃P₁W₁₈O₆₂], 2·(TBA)₁₆ 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 6).
confirmed that precisely one Sb "template" is included within the observed using electrospray mass spectrometry. In addition, we have heteroanions included within the cluster, and this was directly the protonation of a heteropolyacid as a function of the number of resolution, soft ionization mass spectrometry to accurately reveal the nature of the POM cluster species in solution.

Acknowledgment. This work was supported by the EPSRC, The University of Glasgow, and Bruker Daltonics.

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.

References


JA075940Z

Figure 5. The negative ion mass spectrum of the TBA$^+$ salt of 3 showing the series of charged forms of $\{\text{TBA}_6\{P_2W_{18}O_{62}\}\}$ in solution. T $\equiv$ TBA$^+$, P$_2$ $\equiv$ P$_2$W$_{18}$O$_{62}$ (intensity $\times 10^6$).

Figure 6. Positive ion mass spectra (+m/z range 3120–3170) of 2 and 3 (3138 for $[\text{TBA}_6\{\text{H}_2\text{P}_2\text{W}_{18}\text{O}_{62}\}]^{12+}$ and 3152 for $[\text{TBA}_6\{\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}\}]^{13+}$). Solution A: 0.007 mmol L$^{-1}$ (TBA)$_6$H$_2$P$_2$W$_{18}$O$_{62}$ in CH$_3$CN. Solution B: 0.028 mmol L$^{-1}$ (TBA)$_6$H$_5$P$_2$W$_{18}$O$_{62}$ in CH$_3$CN. (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 7. X-ray crystallographic diagram of 2 showing the ion-exchanged form with TBA$^+$.