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What Can Electrospray Mass Spectrometry of Paratungstates in An Equilibrating Mixture Tell us?

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Abstract

An acidified aqueous solution of Na_2WO_4 at nearly neutral conditions, in which paratungstates A ($[W_7O_{24}]^{6-}$) and B ($[H_2W_{12}O_{42}]^{10-}$) were coexistent in an equilibrating mixture, was firstly investigated by a combination of ESI-MS, ^{183}W NMR and Raman spectroscopy. $[W_7O_{24}]^{6-}$ was proved to be the main species in the equilibrating mixtures at pH ≤ 7 by NMR and Raman spectroscopies, however, it failed to be detected by ESI-MS due to its limited stability in the gas phase. The distinctive composition of the precipitate from its precipitating solution suggests that the product isolated in crystalline form may not necessarily be the one with the highest abundance in solution. This is the first representative example to demonstrate non-compliant structures derived from ESI-MS and NMR studies, illustrative of the limitation of ESI-MS analysis for labile POMs, and to show different speciation in solid and its corresponding solution.

Key words: ESI mass spectrometry, Paratungstate anions, Solution and precipitate characterizations, ^{183}W NMR and Raman spectroscopies

Introduction

Polyoxometalates (POMs) are a vast class of anionic oxide clusters of the early transition metals which have been extensively studied due to tunable structures and virtually unmatched range of physical properties [1]. A family of isopolyoxotungstates, e.g. $[W_6O_{19}]^{2-}$ [2], $[W_6O_{22}]^{8-}$ [3], $[W_7O_{24}]^{6-}$ [4], $[W_{10}O_{32}]^{4-}$ [5], $[H_2W_{12}O_{40}]^{6-}$ [6], $[H_2W_{12}O_{42}]^{10-}$ [7], $[H_4W_{19}O_{62}]^{6-}$ [8], $[H_4W_{22}O_{74}]^{12-}$ [9], $[H_{10}W_{34}O_{116}]^{18-}$ [9], $[H_{12}W_{36}O_{120}]^{12-}$ [10], has been synthesized using routine "one-pot" reaction by acidification of an aqueous tungstate solution to different pH. However, the complex solution speciation processes behind the simple method arising from multiple equilibria are still not completely understood.

Electrospray ionisation mass spectrometry (ESI-MS) has been used to analyze a range of polyoxoanions, as well as complex mixtures of oxoanions [11-12]. The approach has recently been extended to directly probe the reaction solution, thereby simplifying the conventional crystallization-based procedure to cluster discovery [13-15]. However, people seldom scrutinize this method. There are cases to show failure on detection of intact POMs by ESI-MS [16] and subtle speciation changes due to ESI-induced reactions [17-20].

It is known that paratungstate A ($[W_7O_{24}]^{6-}$) is rapidly formed when sodium tungstate is acidified to nearly neutral pH. It will then convert to thermodynamically stable paratungstate B ($[H_2W_{12}O_{42}]^{10-}$) slowly. The kinetics to establish the equilibrium between the two is quite slow [21, 22]. Usually the salt based on $[H_2W_{12}O_{42}]^{10-}$, not $[W_7O_{24}]^{6-}$, crystallizes upon standing of the equilibrating solution [23] unless special measures (i.e., the use of organic amine or transition-metal-complex cations [4d, 24-28]) were taken. The difficulty in the crystallization of heptatungstate is still a great challenge in POM synthesis. Yamase and coworkers [29] characterized a pH 6.8 Na_2WO_4 solution by ^{183}W NMR spectroscopy in which three peaks (δ = 268.3, -178.0 and -91.8 ppm) with an intensity ratio of 1:2:4 can be assigned to paratungstate A anion as a main species. This result tells us the equilibrium between $[W_7O_{24}]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$ is largely shifted to $[W_7O_{24}]^{6-}$ at the pH. Our recent work on the MS of an unusual compound $Na[Cu(en)_2]_2[HW_7O_{24}]\cdot 5H_2O$ (en = ethanediamine) [4d] indicated that the main species is $[W_6O_{19}]^{2-}$ (**W_6**), not $[W_7O_{24}]^{6-}$ (**W_7**). The contradictory result from NMR and MS measurements based on the same system begs a question: Is the **W_7** anion itself not stable in solution or it is simply not survival the ionization process?

Herein we report a complete investigation on the speciation of an aqueous $NaWO_4$ solution at nearly neutral pH by a combination of ESI-MS, ^{183}W NMR and Raman spectroscopy. This work is highlighted by the characterization of paratungstates in an equilibrating mixture in solution and solid phases. The validity of ESI-MS method is also addressed by taking this system as a test case.

Experimental

Sample preparation: $Na_2WO_4 \cdot 2H_2O$ and formic acid were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd and used without further purification. The measurements of MS, NMR and Raman spectroscopy were conducted in triplicate for each sample. A Hanna HI 8521 pH meter (Hanna Instruments, Italy) was used to measure pH values. All aqueous solutions of tungstate for MS analysis were prepared with a concentration of 10^{-3} M using HPLC-grade water. After adjusting the pH to about 6, 7 and 8 with formic acid, the solutions were allowed to equilibrate for different lengths of time, which were then analyzed. The precipitate from the aqueous solution of tungstate was obtained by adding aqueous solution of tetrabutylammonium bromide with stirring. The resultant precipitates were filtered and washed with water and dried under the ambient environment. The tungstate solutions used for Raman spectroscopy were prepared with concentrations of 0.1 M, 0.5 M, 1 M, 4 M, respectively. $TBA_2W_6O_{19}$ and $Na[Cu(en)_2]_2[HW_7O_{24}] \cdot 5H_2O$ were prepared according to Refs. [2] and [4d]. The solutions used for ^{183}W NMR were prepared by adjusting pH values of the 0.6 M Na_2WO_4 (1 g Na_2WO_4 dissolved in 5 mL of 1:1 H_2O:D_2O) to 5.8, 6.8, 7.8 with H_2SO_4 (33 wt.%).

Methods: Mass spectra were recorded on an Agilent 6520 Q-TOF LC/MS in the negative ion mode. Each scan or data point on the total ion chromatogram is an average of 5000 transients, producing a scan every 500 ms. Spectra were created by averaging the scans across each peak. The dual-spray electrospray ionization source conditions: Vcap: 3500 V; skimmer: 65 V; OCT R_fV: 750 V; nebulizer: 30 psi; drying gas flow: 10 L/min; drying gas temperature: 300 °C; fragmentor: 80 V; scan range 100 – 3000 *m/z*. Sample solutions were made to approximately 10^{-3} M in water (solutions) or in acetonitrile (precipitates) and analyzed by direct injection using an automatic sampler with a flow rate of 0.2 mL/min. CID experiments were performed using N2 as the target gas. Collisional energy voltage was 40 V for $[W_6O_{19}]^{2-}$ precursors. ^{183}W NMR spectra of the Na_2WO_4 solution (in $H_2O:D_2O$ = 1:1) in nearly neutral condition at 20 °C were obtained on a 400 MHz JEOL ECX NMR system (equipped with 10 mm multinuclear probe head) at 12.5 MHz using external Na_2WO_4 (2.0 mol.L^{-1} in D_2O) as reference. The spectra were recorded over the region between -300 and 500 ppm. Raman spectra were recorded on a RM (Renishaw) spectrophotometer equipped with a liquid-nitrogen-cooled CCD detector. The argon line at 514.5 nm was used for excitation. The measurements were carried out at room temperature (25 ± 3 °C) three times for each sample solution after preparation. The spectra were recorded over the region between 500 and 1500 cm^{-1}. The grating grooves were 1800 l/mm and the exposure time was 30 s.

Results and discussion

Analyses of the acidified solutions of Na_2WO_4 at nearly neutral condition (pH = 5.8, 6.8) by ^{183}W NMR spectroscopy (Fig. 1) show three groups of W centers, which correspond to a single tungsten center (a) and two types of tungsten centers (consisting of four "cap" (b) and two "belt" (c) W atoms) typically found in a paratungstate A anion $[W_7O_{24}]^{6-}$, related to three peaks at δ = 270.7, -90.6, -177.5 ppm with an intensity ratio of 1:4:2, respectively. This result suggests that paratungstate A anion $[W_7O_{24}]^{6-}$ is a main species in the solutions (pH = 5.8, 6.8), consistent with that of pH 6.8 reported in the literature [29]. However, this anion starts a noticeable dissociation (into $[WO_4]^{2-}$) at pH 7.8, indicated by the abundant peak of $[WO_4]^{2-}$ in Fig. 1(c).

Raman spectra of the Na_2WO_4 solutions show the characteristic peaks for $[W_7O_{24}]^{6-}$ at 962 and 903 cm^{-1} and for $[WO_4]^{2-}$ at 931 cm^{-1}, respectively, indicating that $[W_7O_{24}]^{6-}$ is the dominant species at pH values of 5.8 and 6.8 except for 7.8 in which $[WO_4]^{2-}$ is prevalent (Fig. 2). The characteristic Raman frequencies of isopolytungstates determined to be 931 cm^{-1} (intense) for $[WO_4]^{2-}$, 962 cm^{-1} (intense) for $[W_7O_{24}]^{6-}$, and 996 cm^{-1} (intense) for $[W_6O_{19}]^{2-}$ (Fig. S1 in the supporting information), respectively, via using a few compounds with known structures (e.g. an aqueous solution of $NaWO_4$ with adjusted and unadjusted pH, $Na[Cu(en)_2]_2[HW_7O_{24}]\cdot 5H_2O$ and $TBA_2[W_6O_{19}]$ in DMF) were in excellent agreement with those reported in the literature [30-31]. Also, it was found that the relative abundances of $[W_7O_{24}]^{6-}$ were in direct proportion to its concentrations in solution (Fig. S2 in the supporting information).

Insert Figs. 1 & 2

The ESI-MS mass spectra of the Na_2WO_4 solutions at pH 5.8, 6.8 and 7.8 after equilibrating for 4 hour were shown in Fig. 3, where the major species changes noticeably with the pH. At pH values of 5.8 and 6.8, $[W_6O_{19}]^{2-}$ exist as main species which were assigned on the basis of the exact mass and isotopic distribution of the clusters. At a slightly basic pH (7.8), however, $[W_6O_{19}]^{2-}$ was barely detectable and $[HWO_4]^{-}$ became the dominant species. The reason leading to the conflicting results between NMR, Raman and MS is the stability of $[W_7O_{24}]^{6-}$. Two points should be addressed with regard to the limited stability of $[W_7O_{24}]^{6-}$: 1) $[W_7O_{24}]^{6-}$ has a lower symmetry in the structure than the Lindqvist analogue $[W_6O_{19}]^{2-}$; 2) it is very difficult to crystallize heptatungstate from solution because paratungstates A and B are formed simultaneously during the acidification of $[WO_4]^{2-}$ at pH 6 - 8 and establishment of the equilibrium is very slow. To date, only five crystals based on $[W_7O_{24}]^{6-}$ have been successfully isolated, $Na_6[W_7O_{24}]\cdot 21H_2O$ [4a], $(C_5H_{10}NH_3)_6[W_7O_{24}]$ [4b], $[(t\text{-}C_4H_9)NH_3]_6[W_7O_{24}]\cdot 2H_2O$ [4c], $Na[Cu(en)_2]_2[HW_7O_{24}]\cdot 5H_2O$ (en = ethanediamine) [4d], and $[Co(en)_3]_2[H_2W_7O_{24}]\cdot 8H_2O$ [4e]. The limited stability of $[W_7O_{24}]^{6-}$ during ESI process was firstly reported by our group for the compound of $Na[Cu(en)_2]_2[HW_7O_{24}]\cdot 5H_2O$ [4d], in which the quasi-molecular ion, $[H_5W_7O_{24}]^{-}$ (*m/z* 1675.8376, 67%) partially dissociates into $[W_6O_{19}]^{2-}$ (*m/z* 703.8175, 100%). The subsequent CID experiments on $[W_6O_{19}]^{2-}$ generated from two precursors (Fig. 4), one is $TBA_2[W_6O_{19}]$ (dissolved in pure CH_3CN) and the other is an aqueous Na_2WO_4 solution at pH 6.8, confirms the $[W_6O_{19}]^{2-}$ anions generated from different sources have the same Lindqvist structure based on the identical CID spectra.

The complete absence vs. partial presence of intact molecular ion $[W_7O_{24}]^{6-}$ in the mass spectra of aqueous solutions of Na_2WO_4 at pH 6.8 and $Na[Cu(en)_2]_2[HW_7O_{24}]\cdot 5H_2O$ may be attributed to the nature of cations. It was mentioned by many studies that cations affect the solution chemistry and also the gas-phase dissociation chemistry of polyoxoanions [32-34]. That the copper-complex cation ($Cu(en)_2^{2+}$) stabilizes $[W_7O_{24}]^{6-}$ to a greater extent than Na^+ does allows a lot more portion of intact molecular ion to be detected in presence of $Cu(en)_2^{2+}$. As for the same alkali metal cations, Li^+ has a stronger stabilizing effect on the polyanion than Na^+. Howarth et al [35, 36] studied aqueous $LiWO_4$ solution at pH ca. 6.0 and showed by ESI-MS and ^{183}W NMR spectroscopy to be very largely paratungstate B ($[H_2W_{12}O_{42}]^{10-}$). This result states that the equilibrium between paratungstates A and B is substantially dependent on the cations. The Li^+ cation, having the least ionic radius, can effectively shift the balance from paratungstate A to paratungstate B.

Insert Figs. 3 & 4

The MS analyses of $NaWO_4$ and $Na[Cu(en)_2]_2[HW_7O_{24}]\cdot 5H_2O$ in aqueous solutions suggest that the heptatungstate anion can hardly retain its structural integrity in the gas phase, which can be explained by the following reasons. First, the intrinsic structural weakness of the asymmetric anion $[W_7O_{24}]^{6-}$. Second, it was reported by a few papers [17-20] that the electrospray ionization process can induce a series of reactions including protonation/desolvation and fragmentation, which make the species in solution more or less different from those detected in the mass spectrum. The ESI-induced dissociation of $[W_7O_{24}]^{6-}$ might result from collisions between the analyte and nitrogen gas during the desolvation of electrospray ionization process. This is a special case of non-compliant structures derived from solution and gas phases for the same system. By monitoring the whole equilibrium process of an aqueous Na_2WO_4 solution at pH 6.8, we found out that the $\mathbf{W_6}$ cluster started to be generated in large quantity at 1 hour and kept in growth for longer equilibrium time. No abundant polymerization products other than $\mathbf{W_6}$ clusters were detected during the whole equilibrium period (Fig. S3 in the supporting information).

Finally, we tempted to analyze the constitution of the precipitate isolated from the aqueous Na_2WO_4 solution by adding tetrabutylammonium bromide (TBABr) into the solution at final equilibrating time (48 h). The resultant precipitate was redissolved in CH_3CN for ESI-MS analysis after filtration and a few washings with water. By comparing the mass spectrum of the precipitate with that of the corresponding pH 5.8 aqueous solution of Na_2WO_4 (Fig. 5), it can be seen that a range of $\mathbf{W_{12}}$ species appeared in addition to $\mathbf{W_6}$ clusters, e.g., $[TBANa_xH_{8-x}\mathbf{W_{12}}O_{42}]^{3-}$ (x = 1 and 2, *m/z* 1049.8479 and 1057.1756, 30% and 77%), $[TBA_2Na_4H_3\mathbf{W_{12}}O_{42}]^{3-}$ (*m/z* 1152.5854, 54%), $[TBANa_xH_{9-x}\mathbf{W_{12}}O_{42}]^{2-}$ (x = 2 and 3, *m/z* 1586.2871 and 1597.2804, 19% and 23%), $[TBA_2Na_xH_{8-x}\mathbf{W_{12}}O_{42}]^{2-}$ (x = 4 and 5, *m/z* 1729.3899 and 1740.3744, 13% and 25%) $[TBA_3Na_6\mathbf{W_{12}}O_{42}]^{2-}$ (*m/z* 1871.9984, 12%) and $[H_4\mathbf{W_{12}}O_{40}]^{4-}$ (*m/z* 712.3118, 100%), $[Na_3H\mathbf{W_{12}}O_{40}]^{4-}$ (*m/z* 728.7865, 91%), $[Na_xH_{5-x}\mathbf{W_{12}}O_{40}]^{3-}$ (x = 0 - 4, *m/z*

950.0780, 957.4084 and 964.7362, 972.1154 and 979.3961, 17%, 24%, 33%, 3% and 16%); $[\mathbf{W_6}O_{19}]^{2-}$ (*m*/*z* 703.8073, 12%). This result manifest a fact that most often the product isolated in crystalline form may not necessarily be the one with highest abundance in solution, suggesting that the crystallisation process itself may cause the selective formation of a particular product out of vast library of candidates available in solution. At this end, it is summarized that $[\mathbf{W_7}O_{24}]^{6-}$ is the main species in the aqueous Na_2WO_4 solution at pH 5.8 and 6.8, however, this anion can not be isolated from solutions unless special measures were taken. Usually $[\mathbf{W_{12}}O_{42}]^{12-}$ (mostly in a high degree of cationized and/or dehydrated form due to the instability of highly charged polyoxoanions) is the solid form isolated from the solution. The results in the study are summarized in Scheme 1.

Insert Fig. 5

In summary, this study highlights a combined use of ESI-MS, ^{183}W NMR and Raman spectroscopy to address the speciation in an aqueous solution of Na_2WO_4 at nearly neutral conditions. In general, $[\mathbf{W_7}O_{24}]^{6-}$ is proved to be the main species in an equilibrating mixture at pH ≤ 7 by NMR and Raman spectroscopies. This fragile anion, however, fails to be detected due to its ESI-induced dissociation into Lindqvist $[W_6O_{19}]^{2-}$. The distinctive composition of the precipitate from its precipitating solution suggests that the product isolated in crystalline form may not necessarily be the one with the highest abundance in solution. This study also shows that ESI-MS is applicable mostly to stable polyanions. $[\mathbf{W_7}O_{24}]^{6-}$ polyanion is a representative of unstable polyanions whose structures are labile, cautions must be taken when correlating the MS data with the solution speciation in this case.

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Figure captions

Fig.1 ^{183}W NMR spectra of Na_2WO_4 solution (in 1:1 H_2O:D_2O) as a function of pH (equilibrating time = 4 h): A, pH 5.8; B, pH 6.8; C, pH 7.8.

Fig.2 Raman spectra of Na_2WO_4 solution as a function of pH (equilibrating time = 4 h): A, pH 5.8; B, pH 6.8; C, pH 7.8.

Fig.3 Negative-ion ESI mass spectra of Na_2WO_4 solution as a function of pH (equilibrating time = 4 h): A, pH 5.8; B, pH 6.8; C, pH 7.8.

Fig.4 CID mass spectra of $[W_6O_{19}]^{2-}$ generated from different precursors: (A) $TBA_2W_6O_{19}$ in CH_3CN; (B) Na_2WO_4 solution at pH 6.8 (equilibrating time = 4 h). Collision energy = 40 eV, Isolation width = 4. The parent ion (denoted by a diamond) is shown in a blue square box in each spectrum.

Fig.5 Comparison of negative-ion ESI-MS mass spectra of (A) Na_2WO_4 solution at pH 5.8 (equilibrating time = 48 h); (B) precipitate isolated from (A).

Scheme 1 The equilibrium between paratungstates A and B in an aqueous solution of Na_2WO_4 at pH $\approx$ 7 and the actual species detected by ESI-MS.

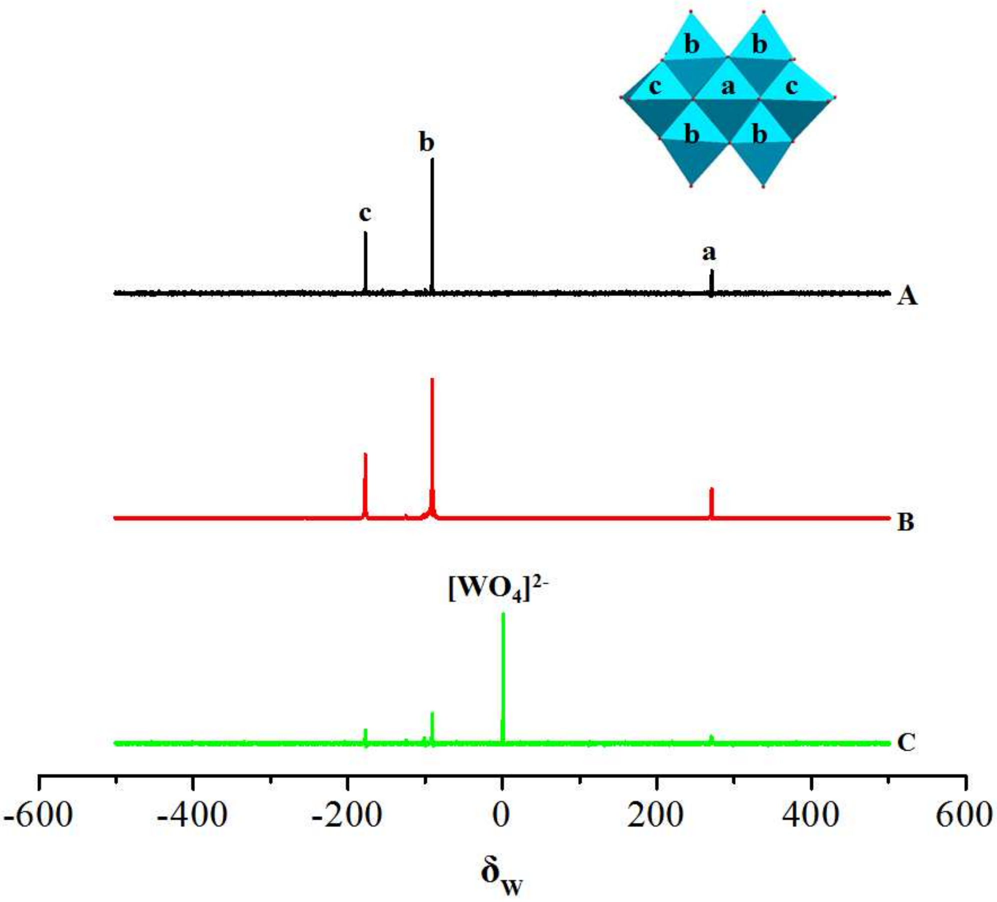


Fig. 1 ^{183}W NMR spectra of Na_2WO_4 solution (in 1:1 H_2O:D_2O) as a function of pH (equilibrating time = 4 h): A, pH 5.8; B, pH 6.8; C, pH 7.8.

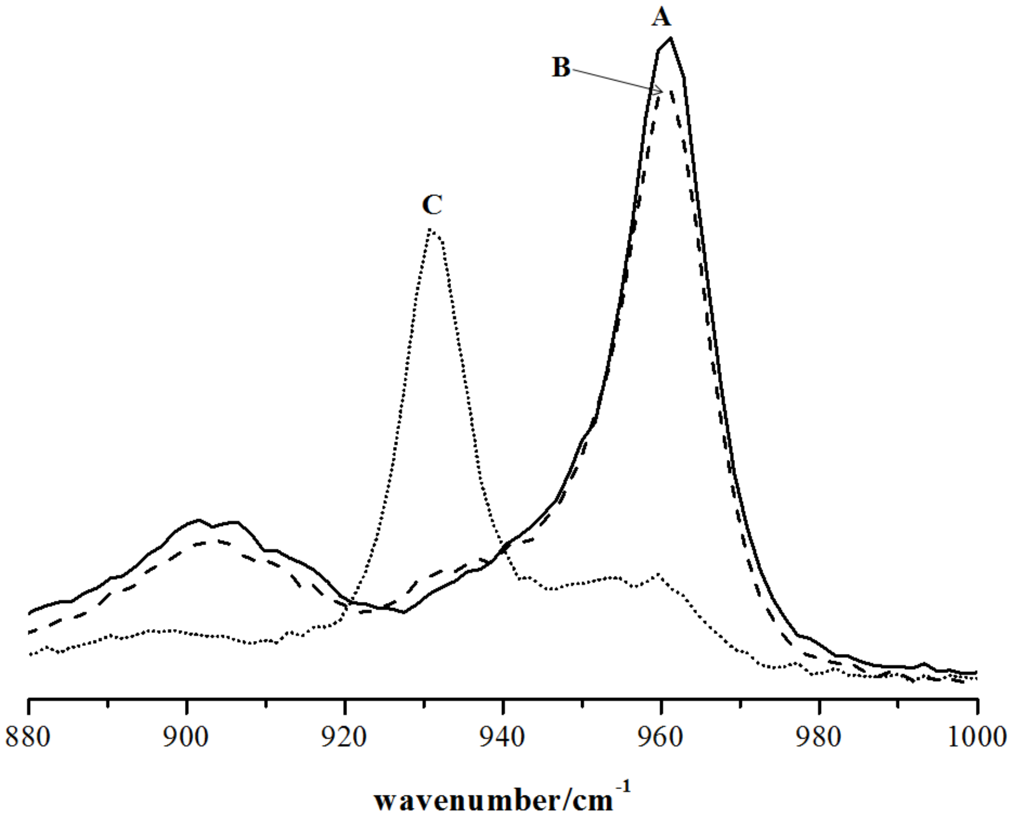


Fig. 2 Raman spectra of Na_2WO_4 solution as a function of pH (equilibrating time = 4 h): A, pH 5.8; B, pH 6.8; C, pH 7.8.

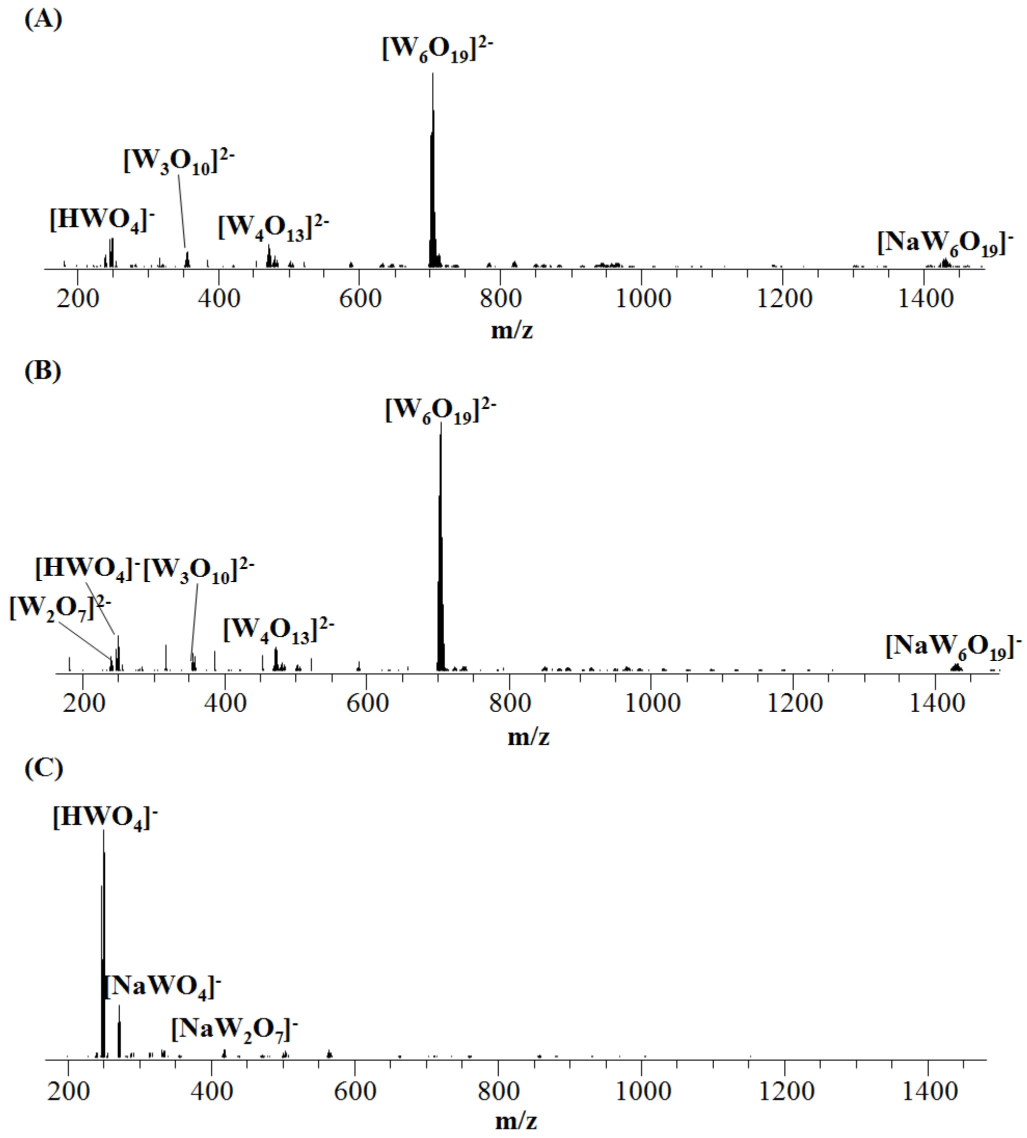


Fig. 3 Negative-ion ESI mass spectra of Na_2WO_4 solution as a function of pH (equilibrating time = 4 h): A, pH 5.8; B, pH 6.8; C, pH 7.8.

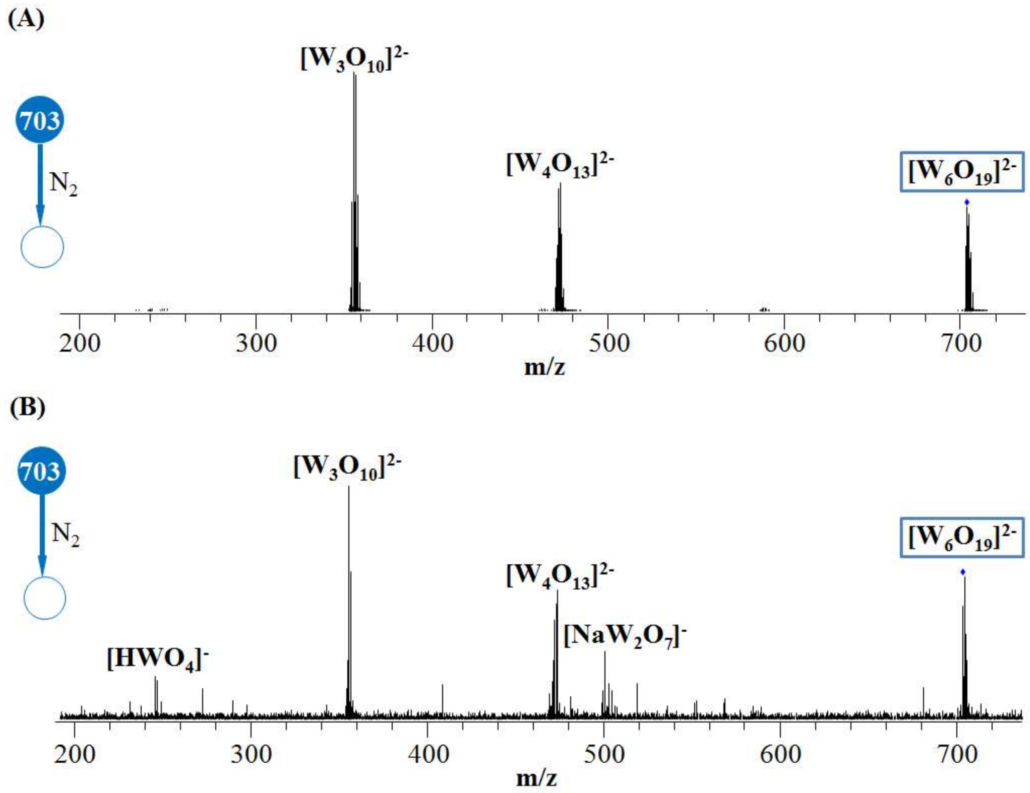


Fig. 4 CID mass spectra of $[W_6O_{19}]^{2-}$ generated from different precursors. (A) $TBA_2W_6O_{19}$ in CH_3CN; (B) Na_2WO_4 solution at pH 6.8 (equilibrating time = 4 h). Collision energy = 40 eV, Isolation width = 4. The parent ion (denoted by a diamond) is shown in a blue square box in each spectrum.

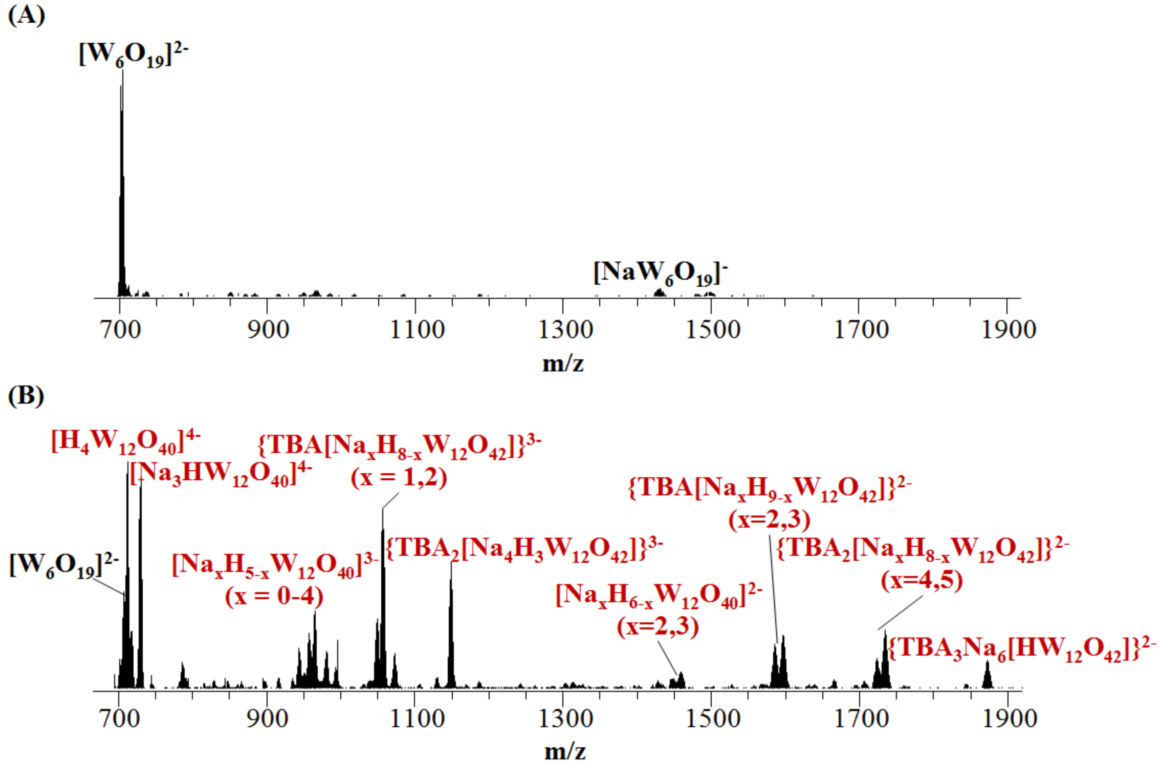
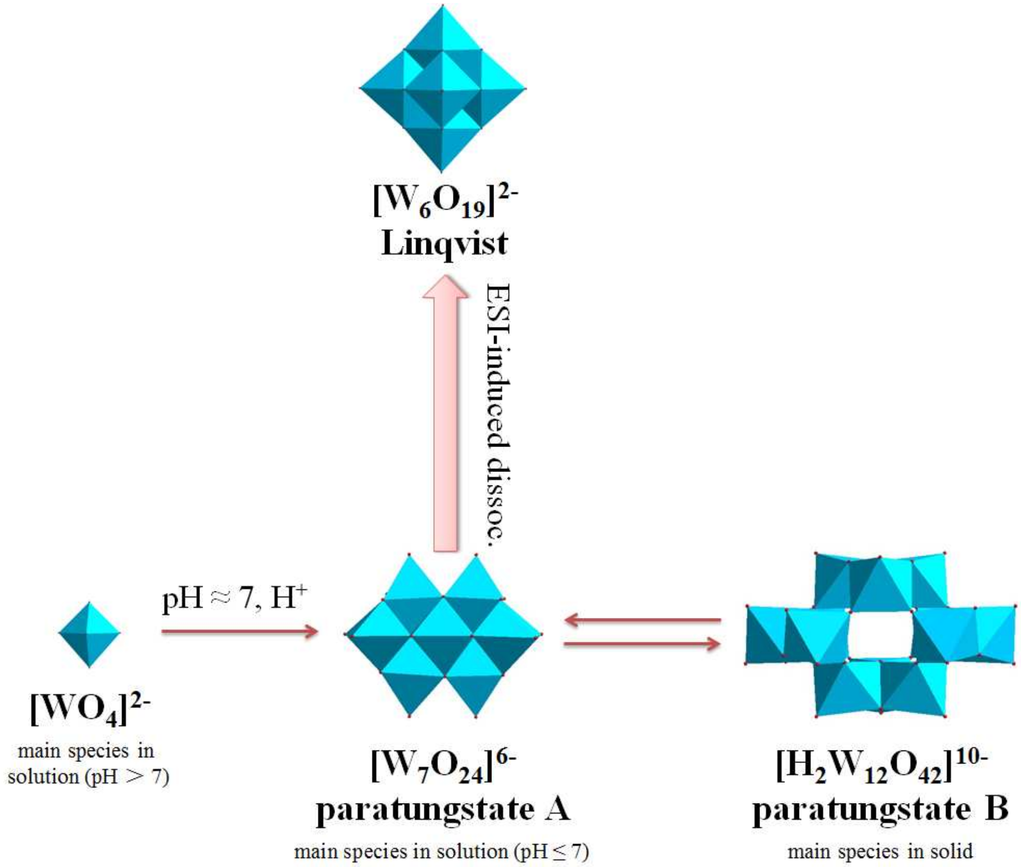
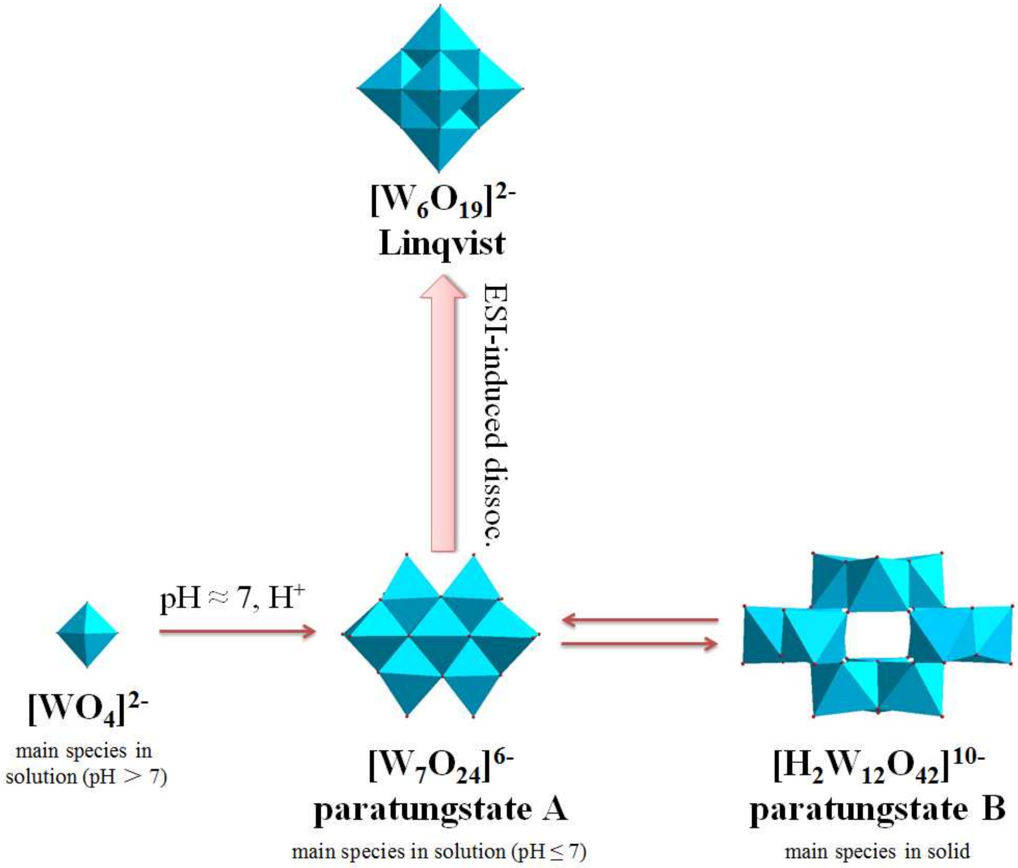


Fig. 5 Comparison of negative-ion ESI-MS mass spectra of (A) Na_2WO_4 solution at pH 5.8 (equilibrating time = 48 h); (B) precipitate isolated from (A).



Scheme 1 The equilibrium between paratungstates A and B in an aqueous solution of Na_2WO_4 at pH ≈ 7 and the actual species detected by ESI-MS.


$[W_6O_{19}]^{2-}$
Linqvist
ESI-induced dissoc.
pH ≈ 7, H$^+$
$[WO_4]^{2-}$
main species in solution (pH > 7)
$[W_7O_{24}]^{6-}$
paratungstate A
main species in solution (pH ≤ 7)
$[H_2W_{12}O_{42}]^{10-}$
paratungstate B
main species in solid

TOC