

# Electrospray Behavior of Lacunary Keggin-Type Polyoxotungstates $[XW_{11}O_{39}]^{p-}$ (X = Si, P): Mass Spectrometric Evidence for a Concentration-Dependent Incorporation of an $MO^{n+}$ (M = $W^{VI}$ , $Mo^{VI}$ , $V^V$ ) Unit into the Polyoxometalate Vacancy

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ESI-MS analysis provides a straightforward tool for the solution characterization of highly charged mono-lacunary Keggin-type polyoxotungstates  $\alpha-[XW_{11}O_{39}]^{p-}$  (X = Si, P;  $p = 8, 7$ ). Doubly and triply charged quasi-molecular ion peaks were identified on the basis of both the theoretical simulation of the isotopic cluster distributions and the fragmentation modes observed with MS/MS technique. This approach allows the characterization of the inorganic polyanions transferred into the gas-phase with associated alkali metal cations ( $Li^+$ ,  $Na^+$ ). Indeed, the ESI-MS spectrum was found to be dependent on the counterion nature and on the initial concen-

tration of the polyoxotungstate. While lithium salts at millimolar concentration represent the best choice for the analytical protocol, upon dilution the inorganic structure rearranges to a saturated Keggin dodecametalate complex. This phenomenon is induced by the electrospray ionization process and was exploited to produce gas-phase ions of monosubstituted species formed through incorporation of molybdenum and vanadium into the polyoxotungstate framework.

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## Introduction

Polyoxometalates (POM), are discrete metal–oxygen clusters of early transition metals in their highest oxidation state.<sup>[1]</sup> Their chemistry, dictated by their remarkable structural and electronic properties, is the subject of an intense interdisciplinary research activity in some major scientific areas, namely catalysis, materials science and medicine.<sup>[1–3]</sup>

An efficient approach to the synthesis of new polyoxometalate architectures is mainly based on lacunary POMs, i.e. species with defect structures.<sup>[1–3]</sup> Due to the presence of a structural “vacancy”, lacunary species possess a reactive nucleophilic polyoxygenated site that can be readily functionalized, and because of this they have been used to provide (i) highly robust, all-inorganic ligands for catalytically active hetero-transition metal nuclei;<sup>[4,5]</sup> (ii) linking building units for the preparation of nanosized aggregates;<sup>[6,7]</sup> (iii) inorganic rigid templates that can be derivatized with organic or organometallic residues.<sup>[8–10]</sup>

The study of such reactive intermediates in terms of their intricate assembly equilibria, solution speciation and stability both in aqueous and in organic media is relevant to the success of the synthetic strategies mentioned above and therefore is receiving considerable attention.<sup>[11,12]</sup> In this respect, heteronuclear NMR spectroscopy has been the technique of choice to investigate the solution speciation and to identify the products. The main drawbacks inherent to such a technique are, however, the low sensitivity and the difficulties in structural assignments.<sup>[13,14]</sup>

Recently, electrospray mass spectrometry (ESI-MS) has been successfully employed for the inspection of different polynuclear metal complexes equilibrating in solution.<sup>[15,16]</sup> In these studies, ESI-MS has emerged as an effective tool for the investigation of rapidly exchanging systems, and has proved to be a powerful diagnostic alternative to NMR spectroscopy.<sup>[15–17]</sup>

ESI-MS has been underused in the analysis of polyoxoanion solutions, even though the soft ESI-mode allows the transfer of even large inorganic polyanions from solution to the gas phase.<sup>[18–20]</sup> In contrast, the Fast Atom Bombardment (FAB) ionization mode has been used very often for the characterization of POMs, providing information on their molecular mass and elemental composition. Such a technique, however, leads to extensive cationization and fragmentation of the POMs, and the necessary use of a matrix support often interferes with their solution chemistry.<sup>[21–24]</sup>

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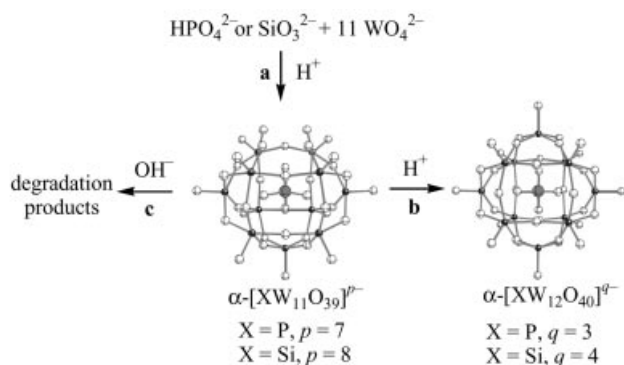
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We describe here the straightforward ESI-MS analysis of aqueous solutions containing lacunary Keggin-type polyoxotungstates with general formula  $\alpha$ -[XW<sub>11</sub>O<sub>39</sub>]<sup>p-</sup>. The present paper indicates a rapid and efficient protocol for the solution characterization of these polyanions based on: (i) the simultaneous examination of the multiply charged ions generated from the polyelectrolyte; (ii) the theoretical simulation of the isotopic cluster distributions determined experimentally for such ions; (iii) the use of the tandem mass spectrometric technique<sup>[25]</sup> to evaluate the fragmentation modes of the complex. Our results also include the new observation that the electrospray behavior of the inorganic polyanion depends on the nature of the alkali metal counterion and on the polyelectrolyte concentration. Thus, lithium salts at millimolar concentrations were found to be the best choice for the analytical protocol, allowing a fast and unambiguous solution characterization of the polyanion in agreement with the NMR results.

## Results and Discussion

Monovacant Keggin-type polyoxotungstates with formula  $\alpha$ -[XW<sub>11</sub>O<sub>39</sub>]<sup>p-</sup> (X = P, Si) were readily prepared by stoichiometric acidification of [WO<sub>4</sub>]<sup>2-</sup> in the presence of [HPO<sub>4</sub>]<sup>-</sup> or [SiO<sub>3</sub>]<sup>2-</sup> (Scheme 1, path a).<sup>[26]</sup> The defect nature and the purity of the polyoxotungstate formed in solution, obtained as lithium or sodium salt by ion-exchange chromatography, was checked by <sup>29</sup>Si, <sup>31</sup>P and <sup>183</sup>W NMR spectroscopy, this latter analysis giving a clean six-signal spectrum (C<sub>s</sub> symmetry) in agreement with literature data.<sup>[26]</sup>



Scheme 1. Synthesis and hydrolytic stability of mono-lacunary  $\alpha$ -Keggin polyoxotungstates with formula  $\alpha$ -[XW<sub>11</sub>O<sub>39</sub>]<sup>p-</sup> (X = P, Si)

The solution integrity of the lacunary complex is pH-dependent: reconstitution of the *T<sub>d</sub>*-symmetric, complete Keggin structure,  $\alpha$ -[XW<sub>12</sub>O<sub>40</sub>]<sup>q-</sup>, occurs readily upon further acidification (Scheme 1, path b), while addition of base leads to a progressive degradation of the structure producing lower order aggregates and eventually re-forming the original monomeric reagents (Scheme 1, path c).<sup>[1]</sup> The pH stability of the analyte is an important parameter to evaluate before the ESI-MS experiments. In fact, the electrospray process of aqueous solutions is known to produce a marked

acidity increase in the nebulized droplets formed under ESI positive-ion mode, while, under ESI negative-ion mode, a considerable pH increase is obtained.<sup>[27]</sup>

Table 1 presents the negative-ion ESI-MS data collected for the lacunary polyoxotungstates  $\alpha$ -[PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> (Entries 1–5) and  $\alpha$ -[SiW<sub>11</sub>O<sub>39</sub>]<sup>8-</sup> (Entries 6, 7), using water/methanol (1:1) as the mobile phase. In the case of  $\alpha$ -[PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup>, the electrospray behavior of both the lithium and sodium derivatives has been analyzed under analogous conditions (see Exp. Sect.). Table 1 also includes the results obtained for the reference monomer Li<sub>2</sub>WO<sub>4</sub> (Entries 8, 9).

As a general feature, at millimolar concentrations the mass spectrum of the heteropolyanion is dominated by two peaks corresponding to the doubly and triply charged molecular ions (vide infra). Other ionic species, ascribable to an ES-induced decomposition, can be identified as the monocharged ions [HWO<sub>4</sub>]<sup>-</sup>, [LiW<sub>6</sub>O<sub>19</sub>]<sup>-</sup> and the analogous [NaW<sub>6</sub>O<sub>19</sub>]<sup>-</sup>, observed at *m/z* = 249, 1415, 1431, respectively.

Both the charge state and the molecular composition of all the ions detected in the mass spectra have been assigned through examination of the experimental isotopic cluster distributions. This approach is exemplified in Figure 1 for the doubly and triply charged molecular species derived from Li<sub>7</sub>PW<sub>11</sub>O<sub>39</sub>. In the mass spectrum of the latter (Table 1, Entry 1), the base peak is found at *m/z* = 1353 and features a double-charge signature with an isotopic separation of ca. 0.50 *m/z* units (Figure 1, part a), while the other diagnostic ion peak is found at *m/z* = 900 and displays the isotopic envelope spaced by ca. 0.33 *m/z* units, i.e. a triple charge (Figure 1, part b). Theoretical simulation of both the observed isotopic patterns allows the assignment the pertinent molecular formula, [Li<sub>4</sub>PW<sub>11</sub>O<sub>39</sub>]<sup>3-</sup> + H<sup>+</sup><sup>2-</sup> and [Li<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>]<sup>4-</sup> + H<sup>+</sup><sup>3-</sup>, with the highest peak of the calculated isotopic distributions located at *m/z* = 1353.00 and 899.67, respectively.

Such results indicate that the lithium salt Li<sub>7</sub>PW<sub>11</sub>O<sub>39</sub> is a suitable precursor for the ESI-MS analysis of the lacunary polyanion since both Li<sup>+</sup>-for-H<sup>+</sup> exchange (cationization) and fragmentation are observed only to a small extent (see Table 1, Entry 1).

A more complicated spectrum is obtained in the case of the sodium salt (Table 1, Entry 4), whose ESI behavior shows a high degree of cationization and the formation of the non-lacunary derivative, indicated by peaks for [NaPW<sub>12</sub>O<sub>40</sub>]<sup>2-</sup> at *m/z* = 1450 and [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> at *m/z* = 959 with an overall relative intensity of 14%.

The first point at issue is very well represented in Figure 2, which shows the expanded spectrum of the sodium salt in the *m/z* range from 1340 to 1410. The simulated isotopic distributions agree with the presence of at least four doubly charged molecular ions whose compositions differ by the number of sodium and/or proton counterions as indicated by the general formula [Na<sub>x</sub>H<sub>y</sub>PW<sub>11</sub>O<sub>39</sub>]<sup>2-</sup>.

The second aspect of the problem is the ESI-induced production of the W<sub>12</sub>-containing species by inclusion of a formal WO<sub>4</sub><sup>4+</sup> unit into the W<sub>11</sub> precursor. Such a phenomenon may be ascribed to an intrinsic weakness of the vacant

Table 1. Counterion ( $\text{Li}^+$ ,  $\text{Na}^+$ ) and concentration effect on the ESI-MS data collected for lacunary polyoxotungstates  $\alpha$ - $[\text{XW}_{11}\text{O}_{39}]^{p-}$  ( $\text{X} = \text{P}, \text{Si}$ ) and for the monomeric precursor  $\text{Li}_2\text{WO}_4$

Entry	Precursor (mM)	Ions $m/z^{[a]}$ (%)	Identification
1	$\text{Li}_7\text{PW}_{11}\text{O}_{39}$ (2)	1353 (100)	$[\text{Li}_4\text{HPW}_{11}\text{O}_{39}]^{2-}$
		900 (55)	$[\text{Li}_3\text{HPW}_{11}\text{O}_{39}]^{3-}$
		1415 (30)	$[\text{LiW}_6\text{O}_{19}]^-$
		249 (62)	$[\text{HWO}_4]^-$
2	$\text{Li}_7\text{PW}_{11}\text{O}_{39}$ (0.2)	1353 (25)	$[\text{Li}_4\text{HPW}_{11}\text{O}_{39}]^{2-}$
		900 (55)	$[\text{Li}_3\text{HPW}_{11}\text{O}_{39}]^{3-}$
		1415 (15)	$[\text{LiW}_6\text{O}_{19}]^-$
		959 (2)	$[\text{PW}_{12}\text{O}_{40}]^{3-}$
		249 (100)	$[\text{HWO}_4]^-$
3	$\text{Li}_7\text{PW}_{11}\text{O}_{39}$ (0.02)	1353 (5)	$[\text{Li}_4\text{HPW}_{11}\text{O}_{39}]^{2-}$
		900 (15)	$[\text{Li}_3\text{HPW}_{11}\text{O}_{39}]^{3-}$
		1442 (8)	$[\text{LiPW}_{12}\text{O}_{40}]^{2-}$
		959 (100)	$[\text{PW}_{12}\text{O}_{40}]^{3-}$
		249 (30)	$[\text{HWO}_4]^-$
4	$\text{Na}_7\text{PW}_{11}\text{O}_{39}$ (2)	1352–1396 (53)	$[\text{Na}_x\text{H}_y\text{PW}_{11}\text{O}_{39}]^{2-}$ [b]
		923–908 (100)	$[\text{Na}_x\text{H}_y\text{PW}_{11}\text{O}_{39}]^{3-}$ [c]
		1431 (42)	$[\text{NaW}_6\text{O}_{19}]^-$
		1450 (3)	$[\text{NaPW}_{12}\text{O}_{40}]^{2-}$
		959 (11)	$[\text{PW}_{12}\text{O}_{40}]^{3-}$
		249 (30)	$[\text{HWO}_4]^-$
5	$\text{Na}_7\text{PW}_{11}\text{O}_{39}$ (0.02)	1352–1396 (80)	$[\text{Na}_x\text{H}_y\text{PW}_{11}\text{O}_{39}]^{2-}$ [b]
		923–908 (10)	$[\text{Na}_x\text{H}_y\text{PW}_{11}\text{O}_{39}]^{3-}$ [c]
		1450 (45)	$[\text{NaPW}_{12}\text{O}_{40}]^{2-}$
		959 (100)	$[\text{PW}_{12}\text{O}_{40}]^{3-}$
		249 (32)	$[\text{HWO}_4]^-$
6	$\text{Li}_8\text{SiW}_{11}\text{O}_{39}$ (2)	1358 (100)	$[\text{Li}_6\text{SiW}_{11}\text{O}_{39}]^{2-}$
		903 (5)	$[\text{Li}_5\text{SiW}_{11}\text{O}_{39}]^{3-}$
		1444 (5)	$[\text{Li}_2\text{SiW}_{12}\text{O}_{40}]^{2-}$
		960 (25)	$[\text{LiSiW}_{12}\text{O}_{40}]^{3-}$
		1415 (25)	$[\text{LiW}_6\text{O}_{19}]^-$
		1396 (40)	$[\text{Na}_5\text{HSiW}_{11}\text{O}_{39}]^{2-}$
7	$\text{Na}_8\text{SiW}_{11}\text{O}_{39}$ (2) <sup>[d]</sup>	1407 (40)	$[\text{Na}_6\text{SiW}_{11}\text{O}_{39}]^{2-}$
		930 (100)	$[\text{Na}_5\text{SiW}_{11}\text{O}_{39}]^{3-}$
		1460 (30)	$[\text{Na}_2\text{SiW}_{12}\text{O}_{40}]^{2-}$
		958 (50)	$[\text{HSiW}_{12}\text{O}_{40}]^{3-}$
		966 (20)	$[\text{NaSiW}_{12}\text{O}_{40}]^{3-}$
		1431 (n.d) <sup>[d]</sup>	$[\text{NaW}_6\text{O}_{19}]^-$
8	$\text{Li}_2\text{WO}_4$ (2)	249 (100)	$[\text{HWO}_4]^-$
9	$\text{Li}_2\text{WO}_4$ (0.02)	249 (50)	$[\text{HWO}_4]^-$
		704 (100)	$[\text{W}_6\text{O}_{19}]^{2-}$
		1409(40)	$[\text{HW}_6\text{O}_{19}]^-$

[a]  $m/z$  values refer to the highest peak of the ion clusters. [b] % includes contribution of  $[\text{Na}_5\text{PW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1396$ ),  $[\text{Na}_4\text{HPW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1385$ ),  $[\text{Na}_2\text{H}_3\text{PW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1363$ ),  $[\text{NaH}_4\text{PW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1352$ ), see Figure 2. [c] % includes contribution of  $[\text{Na}_4\text{PW}_{11}\text{O}_{39}]^{3-}$  ( $m/z = 923$ ),  $[\text{Na}_3\text{HPW}_{11}\text{O}_{39}]^{3-}$  ( $m/z = 916$ ) and  $[\text{Na}_2\text{H}_2\text{PW}_{11}\text{O}_{39}]^{3-}$  ( $m/z = 908$ ). [d] Ions ascribable to potassium-containing species were also observed:  $[\text{Na}_x\text{K}_y\text{SiW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1415$ – $1447$ ) and  $[\text{NaK}_4\text{SiW}_{11}\text{O}_{39}]^{3-}$  ( $m/z = 952$ ).

polyoxometalate structure as its sodium salt. The importance of the nature of the counteranion in determining the solution behavior of polyoxometalates in terms of their stability, spectroscopic response, selectivity of reactions and reaction rates has been documented in several literature reports.<sup>[26,28–31]</sup> In particular, the lithium form of the lacunary tungstophosphate anion has been indicated as the precursor of choice for high temperature hydrothermal synthesis due to its peculiar stability.<sup>[32,33]</sup> The ESI-MS results support this latter observation.

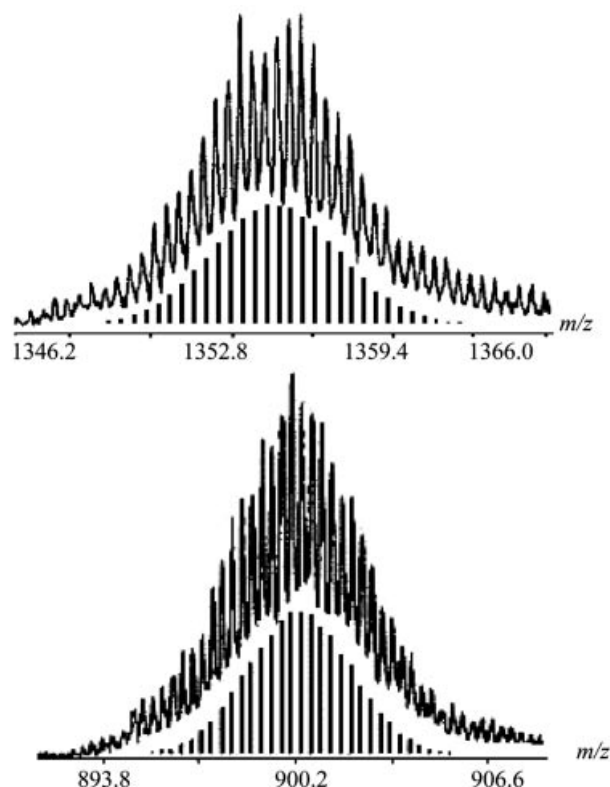


Figure 1. Experimental and calculated isotopic distribution for ion  $[\text{Li}_4\text{HPW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1353$ ) and ion  $[\text{Li}_3\text{HPW}_{11}\text{O}_{39}]^{3-}$  ( $m/z = 900$ )

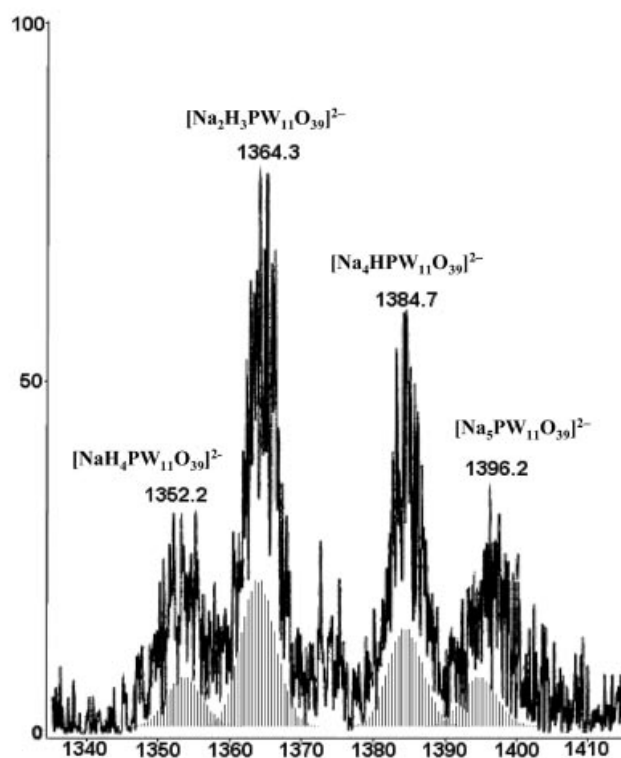


Figure 2. Experimental and calculated isotopic distributions of ions with general formula  $[\text{Na}_x\text{H}_y\text{PW}_{11}\text{O}_{39}]^{2-}$  ( $m/z = 1352$ – $1396$ )

In the negative-ion mode ESI-MS spectrum of the undecatungstosilicate species  $\alpha$ -[Li<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub>] (Table 1, Entry 6), the quasi-molecular ion peaks ([Li<sub>6</sub>SiW<sub>11</sub>O<sub>39</sub>]<sup>2-</sup> at  $m/z$  = 1358 and [Li<sub>5</sub>SiW<sub>11</sub>O<sub>39</sub>]<sup>3-</sup> at  $m/z$  = 903) are observed together with a 30% total intensity of the W<sub>12</sub> anion ([Li<sub>2</sub>SiW<sub>12</sub>O<sub>40</sub>]<sup>2-</sup> at  $m/z$  = 1444 and [LiSiW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> at  $m/z$  = 960). This evidence is consistent with the limited pH stability range registered in aqueous solution for this lacunary species.<sup>[1]</sup> The sodium salt (Table 1, Entry 7) again shows a more complicated spectrum.

The Collision Induced Dissociation (CID) of both saturated and lacunary derivatives has been analyzed for tungstophosphate anions as their lithium salts. MS/MS experiments performed on the doubly and triply charged precursors show the multiple loss of WO<sub>3</sub> fragments and oxygen atoms to yield di- or trivacant structures (W<sub>10</sub>- or W<sub>9</sub>-containing anions, respectively; Table 2). This behavior is known to dominate the gas-phase fragmentation of polyoxotungstates as generally observed under FAB-MS conditions.<sup>[21–24]</sup> As expected, due to the stability of the saturated complex, MS/MS experiments on the W<sub>12</sub> species require high CID energy conditions of up to 3 V.

In order to optimize the ESI-MS protocol for these highly charged inorganic complexes, the spectra were recorded at different analyte concentrations (Table 1). Surprisingly, the spray of dilute solutions (initial polyanion concentration  $\leq 10^{-5}$  M) yields different mass spectra. In particular, starting with the vacant W<sub>11</sub> polyanion as its lithium or sodium salt (Table 1, Entries 3, 5), the peak corresponding to the saturated W<sub>12</sub> anion becomes the dominant one. These results are in contrast to the NMR characterization of the species and with the ESI results achieved at higher concentrations. This ESI-MS behavior can be conveniently monitored by progressive dilution of the initially sprayed POM solution ([Li<sub>7</sub>PW<sub>11</sub>O<sub>39</sub>]<sub>0</sub> =  $2 \times 10^{-3}$  M) with the mobile phase. The spectra recorded at different time intervals (Figure 3) show the evolution of the original W<sub>11</sub> anion (ion peaks at  $m/z$  = 900 and 1353) to the W<sub>12</sub> species (ion peaks at  $m/z$  = 959 and 1442).

The origin of the phenomenon can be discussed on the basis of the following control experiments: (i) the spray of an equimolar solution ( $2 \times 10^{-3}$  M) of Li<sub>2</sub>WO<sub>4</sub> and Li<sub>7</sub>PW<sub>11</sub>O<sub>39</sub> yields peaks ascribable only to the two reagents, with no trace of the W<sub>12</sub> anion, thus indicating that no solution reaction is taking place under the conditions adopted; (ii) when these two ions are isolated within the instrument ion-trap, no gas-phase reaction is again ob-

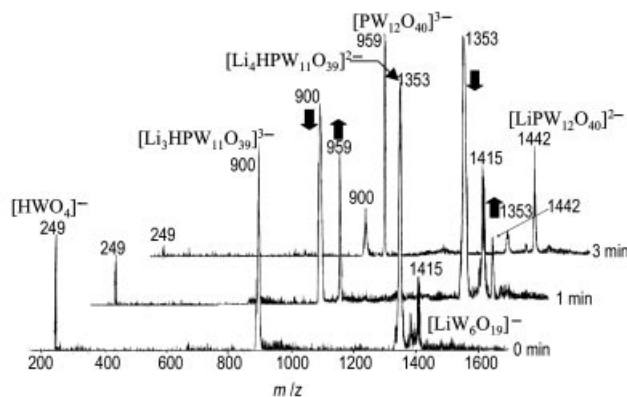


Figure 3. Evolution of the ESI-MS spectrum with time collected for  $\alpha$ -[Li<sub>7</sub>PW<sub>11</sub>O<sub>39</sub>] (initial concentration of  $2 \times 10^{-3}$  M) upon progressive dilution

served; (iii) an aggregation process is also detected when sub-millimolar Li<sub>2</sub>WO<sub>4</sub> solutions are sprayed (Table 1, Entries 8, 9), producing the hexatungstate complex, revealed as its dianion [W<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> at  $m/z$  = 704 or in its monoprotonated form at  $m/z$  = 1409. This latter result is of particular interest in the study of the nucleation of polyoxometalate structures.

Considering the ESI process and the generation of POM-based gas-phase ions, the observed changes of ion charge and structure can be ascribed to the relief of coulombic stress as solvent is removed upon the transfer of the ions from the charged droplets to the gas phase.<sup>[27]</sup>

This might well be the driving force for the ESI-induced polyoxometalate aggregation in the incipient gas phase, producing species with lower charge or with a reduced charge density. However, the opportunity to detect structural rearrangement of the charged analytes should be related both to the composition and to the time of residency of the species within the charged droplets generated by the ESI process. It is then conceivable that at particularly high polyelectrolyte concentration the rapid droplet fission allows the minimization and eventual suppression of any side reactions.<sup>[34]</sup>

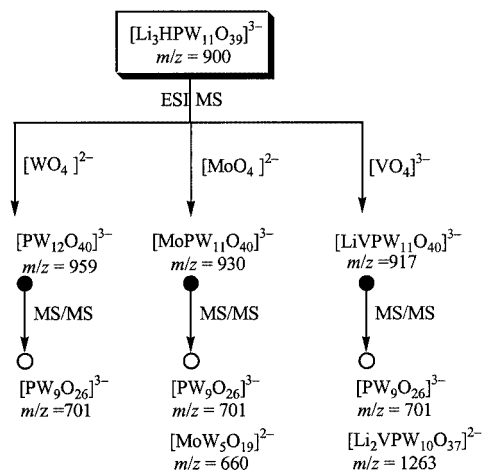
As the reconstitution of the W<sub>12</sub> structure occurs very efficiently for the undecatungstate complex sprayed at sub-millimolar concentration, a set of experiments was designed to detect the inclusion of a hetero-transition metal based MO<sup>n+</sup> unit within the lacunary site, under analogous ESI-

Table 2. MS/MS fragment ions of precursor ions **I** originating from lithium salts of mono-lacunary (W<sub>11</sub>) and saturated (W<sub>12</sub>) polyoxotungstophosphate anions under ESI-MS conditions

<b>I</b> ( $m/z$ ) <sup>[a]</sup>	Fragment ions ( $m/z$ ) <sup>[a]</sup>	Lost fragments
[Li <sub>4</sub> HPW <sub>11</sub> O <sub>39</sub> ] <sup>2-</sup> (1353)	[Li <sub>3</sub> PW <sub>10</sub> O <sub>35</sub> ] <sup>2-</sup> (1225)	<b>I</b> – WO <sub>3</sub> – LiOH
[Li <sub>3</sub> HPW <sub>11</sub> O <sub>39</sub> ] <sup>3-</sup> (900)	[Li <sub>3</sub> PW <sub>10</sub> O <sub>35</sub> ] <sup>2-</sup> (1225), [Li <sub>2</sub> HPW <sub>9</sub> O <sub>32</sub> ] <sup>2-</sup> (1106)	<b>I</b> – WO <sub>3</sub> – OH, <b>I</b> – 2 WO <sub>3</sub> – OLi
[LiPW <sub>12</sub> O <sub>40</sub> ] <sup>2-</sup> (1442)	[W <sub>11</sub> O <sub>34</sub> ] <sup>2-</sup> (1283), [PW <sub>12</sub> O <sub>40</sub> ] <sup>3-</sup> (959)	<b>I</b> – PWO <sub>6</sub> – Li, <b>I</b> – Li
[PW <sub>12</sub> O <sub>40</sub> ] <sup>3-</sup> (959)	[PW <sub>9</sub> O <sub>26</sub> ] <sup>3-</sup> (701) <sup>[b]</sup>	<b>I</b> – 3 WO <sub>3</sub> – 5 O

<sup>[a]</sup>  $m/z$  values refer to the highest peak of the ion clusters. <sup>[b]</sup> Assigned according to the literature.<sup>[19]</sup>





Scheme 2. Formation of the triply charged ions ( $m/z$ ) in the ESI-MS spectrum of  $\alpha$ -[Li<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>] collected at sub-millimolar concentration ( $10^{-5}$  M) in the presence of stoichiometric [MoO<sub>4</sub>]<sup>2-</sup> or [VO<sub>4</sub>]<sup>3-</sup>, showing the evolution to a dodecametallate structure as confirmed also by tandem MS/MS experiments

MS conditions (Scheme 2). To this aim, a solution of Li<sub>3</sub>PW<sub>11</sub>O<sub>39</sub> ( $10^{-5}$  M) was sprayed in the presence of equimolar amounts of molybdate and vanadate anions. Inspection of the triply charged  $m/z$  region (Scheme 2) gives a clear indication that the monosubstituted Keggin species forms by incorporation of either an Mo<sup>VI</sup> or a V<sup>V</sup> atom within the polyoxotungstate structure, yielding ion peaks at  $m/z = 930$  ([MoPW<sub>11</sub>O<sub>40</sub>]<sup>3-</sup>) and 917 ([LiVPW<sub>11</sub>O<sub>40</sub>]<sup>3-</sup>).<sup>[35]</sup> This process competes, however, with the production of the dodecatungstate anion, by far the main process emerging in all the recorded spectra, where the ion peak at  $m/z = 959$  appears always as the most intense one.<sup>[35]</sup> MS/MS experiments performed on the resulting [Li<sub>*n*</sub>MPW<sub>11</sub>O<sub>40</sub>]<sup>3-</sup> ( $M = V^V, Mo^{VI}; n = 0, 1$ ) anions yield fragments that are consistent with the expected Keggin structure (the peak at  $m/z = 701$ , identified as [PW<sub>9</sub>O<sub>26</sub>]<sup>3-</sup>, is common to all the three dodecatungstate structures)<sup>[19]</sup> and monosubstitution with the hetero-transition metal (see the lacunary fragments incorporating vanadium or molybdenum in Scheme 2).

The ESI-induced metalation of the lacunary undecatungstate establishes a new route to the gas-phase detection of the Mo and V monosubstituted species whose hydrolytic instability hampers the synthetic protocol.<sup>[36,37]</sup> As a matter of fact, the direct hydrothermal metalation (H<sub>2</sub>O, 150 °C) of the lacunary precursor ( $2 \times 10^{-3}$  M) in the presence of stoichiometric amounts of tungstate, molybdate or vanadate anions, in the first two cases does not lead to products, while in the latter case the disubstituted complex is formed. This conclusion has been reached by ESI-MS analysis of the reaction mixtures, showing, for the vanadium-containing system, the replacement of the reagent signals with two new ion peaks at  $m/z = 873$  and 1313, attributed to [LiHPV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>3-</sup> and [Li<sub>2</sub>HPV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>2-</sup>, respectively.<sup>[38]</sup>

## Conclusion

This study highlights the use of ESI-MS to address the solution structure of polyoxometalates. The results collected delineate a precise protocol for the straightforward characterization of highly charged mono-vacant undecatungsto complexes, thus providing a convenient alternative to heteronuclear NMR spectroscopy. Although extreme care is required to correlate the ESI-MS data with the content of the original solution, it has been shown that the ESI technique allows the isolation of discrete ion-paired structures whose stoichiometry, composition and gas-phase reactivity can be readily defined. Both the role of the counterion on the gas-phase transfer of polyoxometalate-based ion-pairs and the effect of the polyelectrolyte concentration in promoting an ESI-induced aggregation process are fundamental aspects that need further clarification.

## Experimental Section

**Materials:** Monovacant Keggin-type polyoxotungstates with formula  $\alpha$ -[XW<sub>11</sub>O<sub>39</sub>]<sup>*p*-</sup> ( $X = P, Si$ ) were prepared by literature procedures<sup>[26]</sup> and characterized in solution by heteronuclear NMR spectroscopy as follows:  $\alpha$ -[Li<sub>3</sub>PW<sub>11</sub>O<sub>39</sub>]: <sup>31</sup>P NMR (162.00 MHz, D<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub> 85%):  $\delta = -11.2$  ppm. <sup>183</sup>W NMR (16.67 MHz, H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>):  $\delta = -98.0$  (2 W),  $-98.6$  (2 W),  $-103.3$  (2 W),  $-121.0$  (1 W),  $-132.0$  (2 W)  $-151.8$  (2 W) ppm.  $\alpha$ -[Na<sub>7</sub>PW<sub>11</sub>O<sub>39</sub>]: <sup>183</sup>W NMR (16.67 MHz, H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>):  $\delta = -99.0$  (2 W),  $-103.9$  (2 W),  $-110.7$  (2 W),  $-118.6$  (1 W),  $-134.0$  (2 W)  $-154.8$  (2 W) ppm.  $\alpha$ -[Na<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub>]: <sup>29</sup>Si NMR (79.50 MHz, D<sub>2</sub>O, TMS):  $\delta = -84.5$  ppm. <sup>183</sup>W NMR (16.67 MHz, H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>):  $\delta = -100.9$  (2 W),  $-116.4$  (2 W),  $-121.5$  (1 W),  $-128.4$  (2 W),  $-143.2$  (2 W)  $-176.5$  (2 W) ppm.  $\alpha$ -[Li<sub>3</sub>SiW<sub>11</sub>O<sub>39</sub>]: <sup>183</sup>W NMR (16.67 MHz, H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>):  $\delta = -106.7$  (2 W),  $-108.7$  (2 W),  $-122.0$  (2 W),  $-123.1$  (1 W)  $-144.9$  (2 W)  $-175.1$  (2 W) ppm. All other reagents were obtained from commercial sources and used as received. HPLC grade solvents were generally used. Cation-exchange chromatography was performed on Amberlite IR 120 resin.

**Methods:** NMR spectra were obtained with a Bruker Avance DRX 400 instrument, equipped with a standard (<sup>31</sup>P-<sup>109</sup>Ag) 10-mm broadband probe which could be tuned below its specifications. Hydrothermal syntheses were performed in a closed reactor (HPR-1000/10S, Milestone) equipped with temperature and pressure control units and irradiated inside the cavity of an MW Ethos-1600 labstation (Milestone). ESI-MS full-scan mass spectra were performed with a Mariner Time-of-Flight Mass Spectrometer (Perspective Biosystem) and with a Finnigan LCQ instrument, obtaining comparable results. The  $m/z$  values refer to the highest peak of the ion clusters. All experiments were performed in negative mode by direct infusion with a syringe pump. Standard experimental conditions given for the LCQ instrument were as follows: sample concentration ( $10^{-3}$  to  $10^{-5}$  M), mobile phase (H<sub>2</sub>O/CH<sub>3</sub>OH, 1:1) flow rate 8  $\mu$ L min<sup>-1</sup>, nebulizing gas N<sub>2</sub>: 40 units flow rate, spray voltage  $-4.00$  kV, capillary voltage  $-25$  V, capillary temperature 150 °C, tube lenses offset, 30 V. The parameters related to octupoles and detector were those achieved by the automatic setup procedure. The tuning of the spray parameters i.e. flow rate ( $3-13$   $\mu$ L min<sup>-1</sup>), nebulizing gas (20–70 units flow rate), negative spray voltage (2–4.50 kV), negative capillary voltage (3–28 V) and capillary temperature (70–160 °C) was investigated and did not

affect the spectra. The collision-induced decomposition of selected ions was obtained by applying a supplementary radio frequency voltage (tickling voltage) to the end-cap electrodes of the ion-trap in Finnigan LCQ instrument (resonance activation).

**Hydrothermal Synthesis:**  $\alpha$ -[Li<sub>7</sub>PW<sub>11</sub>O<sub>39</sub>] (60  $\mu$ mol) was dissolved in water (30 mL). The solution was then divided into three portions (10 mL each), in the presence of a stoichiometric amount of Li<sub>2</sub>WO<sub>4</sub> (reaction 1), Na<sub>2</sub>MoO<sub>4</sub> (reaction 2) or Na<sub>3</sub>VO<sub>4</sub> (reaction 3). The reaction mixtures were then placed in three closed units of the multi-section microwave reactor system (HPR-1000/10S) inside the Microwave labstation and irradiated ( $\nu$  = 2.45 GHz) according to the following parameters: initial power 300 W; initial time 4 min;  $T_{\max}$  = 150 °C, final power 150 W, reaction time 5 min. ESI-MS analysis was used to monitor the reaction outcome. Reaction 1: MS (ESI-LCQ):  $m/z$  (%) = 249 (90) [HWO<sub>4</sub>]<sup>−</sup>, 900 (53) [Li<sub>3</sub>HPW<sub>11</sub>O<sub>39</sub>]<sup>3−</sup>, 1353 (100) [Li<sub>4</sub>HPW<sub>11</sub>O<sub>39</sub>]<sup>2−</sup>, 1415 (50) [LiW<sub>6</sub>O<sub>19</sub>]<sup>−</sup>. Reaction 2: MS (ESI-LCQ):  $m/z$  (%) = 163 (100) [HMoO<sub>4</sub>]<sup>−</sup>, 249 (75) [HWO<sub>4</sub>]<sup>−</sup>, 900 (48) [Li<sub>3</sub>HPW<sub>11</sub>O<sub>39</sub>]<sup>3−</sup>, 1353 (70) [Li<sub>4</sub>HPW<sub>11</sub>O<sub>39</sub>]<sup>2−</sup>, 1415 (40) [LiW<sub>6</sub>O<sub>19</sub>]<sup>−</sup>. Reaction 3: MS (ESI-LCQ):  $m/z$  (%) = 249 (100) [HWO<sub>4</sub>]<sup>−</sup>, 873 (45) [LiHPV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>3−</sup>, 959 (15) [PW<sub>12</sub>O<sub>40</sub>]<sup>3−</sup>, 1313 (50) [Li<sub>2</sub>HPV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>2−</sup>, 1324 (48) [NaLi<sub>2</sub>PV<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>2−</sup>, 1415 (10) [LiW<sub>6</sub>O<sub>19</sub>]<sup>−</sup>.

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