New Organosilyl Derivatives of the Dawson Polyoxometalate $[\alpha_2\text{-}P_2W_{17}O_{61}(RSi)_2O]^{6-}$: Synthesis and Mass Spectrometric Investigation

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Abstract: In the field of functionalized polyoxometalates, organosilyl derivatives of polyoxotungstate constitute a special class of hybrid organic–inorganic system. The first organosilyl derivative of the monovacant Dawson heteropolyoxotungstate $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ was obtained by three different methods. The use of two organosilanes as reagents enabled the preparation of the functionalized polyoxometalate $[\alpha_2\text{-}P_2W_{17}O_{61}(RSi)_2O]^{6-}$ in good yield. Electrospray (ESI-MS) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry, and ^{183}W, ^{31}P, and ^{29}Si NMR spectroscopy were used to characterize the composite systems. In several cases, ESI-MS analyses generated reduction processes which were compared to those related to $[PMo_{11}VO_{40}]^{4-}$, the highly reducible Keggin polyoxometalate.

Keywords: mass spectrometry • organic–inorganic hybrid composites • organosilanes • polyoxometalates

Introduction

Control of the functionalization of inorganic nanobuilding blocks (NBBs) is crucial for the elaboration of new hybrid organic–inorganic systems.[1] These inorganic NBBs have been chosen because they cover a large domain of properties, sizes, and structures. Indeed, the interactions between the organic and inorganic moieties define the nature of the hybrid systems. In the field of hybrid organic–inorganic materials, the systems based on polyoxometalates (POMs) constitute a major class of compounds. In fact, these metallic oxo clusters play a great role in important domains such as catalysis, electro- and photochromism, magnetism, and medicine.[2]

Several recent studies describe the covalent functionalization of POMs, for which the covalent grafting of organic functions is dependent on the nature of the starting POM. Recently Peng and co-workers described the functionalization of isopolyoxomolybdate with organoimido groups, the goal being to bridge together two polyoxomolybdates.[3] As for lacunary heteropolyoxotungstates, the most current functionalization of POMs consists of the grafting of electrophilic groups on the lacunary surface. Three main groups of electrophilic reagents have been described. Namely, organostannyl derivatives, which have been largely studied by Pope and co-workers,[4] organophosphoryl derivatives, for which we very recently described dimeric systems based on a divacant polyoxotungstate,[5] and organosilyl compounds, the studies of which have mostly been concerned with the functionalization of lacunary Keggin type anions, namely mono-, di-, and trivacant POMs.[6,7,8] To the best of our knowledge, nothing has been reported on the synthesis of organosilyl derivatives of lacunary Dawson polyoxotungstates. Herein, we describe the synthesis and characterization of new functionalized POMs by reaction of the monovacant polyoxotungstate $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with organosilane groups. These derivatives have been characterized by a combination of multinuclear NMR spectroscopy (^{183}W, ^{29}Si and ^{31}P) and

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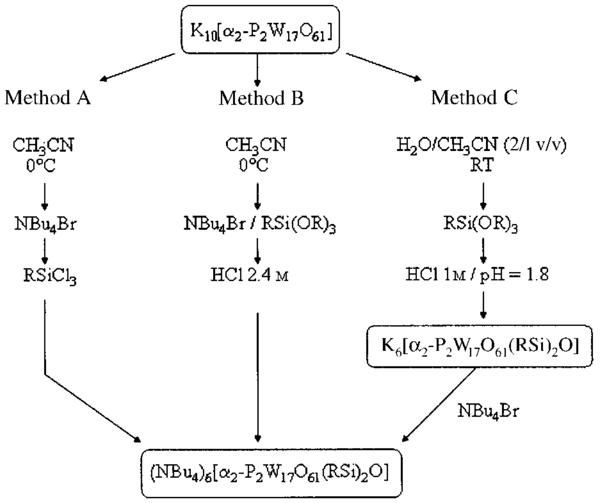
mass spectrometry (MALDI-TOF). This is followed by a detailed electrospray ionization mass spectrometry (ESI-MS) study in which, depending on the experimental conditions (solvent, counterions, spectrometer and concentrations), the presence of reduced hybrid POM cluster anions was observed. These features are discussed and compared to the mass data obtained from a highly reducible Keggin polyoxomolybdovanadate $[PMo_{11}VO_{40}]^{4-}$.

Results and Discussion

Synthesis and spectroscopic characterization: Several studies have been devoted to the synthesis of hybrid materials based on organosilyl–POM derivatives. The first work, by Judeinstein and co-workers,[9] concerned the synthesis of hybrid polymers, another described the synthesis of a hybrid gel,[10] and very recently the synthesis of Langmuir–Blodget monolayer was reported by Chambers and co-workers.[11] In all these studies, organosilyl derivatives are commonly used because of the great variety of their organic functions. In fact, the reactivity of the organosilyl reagent differs depending on the nature of X in $RSiX_3$ (X = Cl or OR). The hydrolysis of Si–Cl bonds is rapid, whereas for Si–OR bonds the hydrolysis is usually accelerated by addition of hydrochloric acid. The addition, however, can generate the formation of a Keggin anion as impurity depending on the nature of the starting lacunary POM. In the case of $[PW_9O_{34}]^{9-}$ ions, to prevent the formation of this impurity, only organotrichlorosilanes were used.[8] However, the diversity of organotrialkoxysilanes is larger than that of organotrichlorosilanes for the elaboration of hybrid materials, but only a few POMs are stable enough towards the addition of HCl. Very recently Neumann and co-workers described the formation of organosilyl derivatives of $[SiW_{11}O_{39}]^{8-}$ in acidic aqueous solution.[12]



Scheme 1. Synthetic routes for preparation of $[\alpha_2\text{-}P_2W_{17}O_{61}(PhSi)_2O]^{6-}$ as tetrabutylammonium or potassium salts by Methods A–C.

In this study, our aim was to investigate different methods of synthesis using $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20\,H_2O$ and different organosilanes to obtain derivatives of POMs soluble in organic solvents and in aqueous media. Three methods were used depending on the nature of the organosilane (Scheme 1). In Method A, which was applied only to organotrichlorosilanes, the reaction was performed under phase-transfer conditions in pure actonitrile. Methods B and C were used for trialkoxysilanes. Method B was carried out similarly to Method A in acetonitrile. The addition of a hydrochloric acid solution allowed the grafting of organosilanes on the lacunary surface of the POM, and the tetrabutylammonium salt acted as phase-transfer agent. For both Methods A and B, the pure product was obtained after precipitation of the mother solution with ethanol followed by recrystallization in dimethyl formamide. Method C was performed in a mixed H_2O/CH_3CN solution in the absence of tetrabutylammonium, and the reaction occurred when the pH of the solution was adjusted to 1.8. Moreover, in method C the reaction mixture was stirred overnight at room temperature, contrary to Methods A and B in which the solution was left to stand at 0 °C for 6 h. The resulting product was a potassium salt. After evaporation of the acetonitrile, the crude product was recovered by precipitation with an aqueous solution of tetrabutylammonium bromide.

For all the methods, two equivalents of organosilane reacted with one equivalent of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$. The derivatives were characterized by several techniques such as IR and multinuclear NMR spectroscopy (^{183}W, ^{29}Si, and ^{31}P) and mass spectrometry. Although different organic groups were tested, we focused our attention exclusively on phenylsilane and a modified phenysilane bearing a phosphonate group (see inset in Figure 4).

For methods A, B, and C, spectra obtained by MALDI-TOF mass spectrometry in the positive ion mode displayed the same peaks in the region of m/z 5500–6500, regularly spaced with 242.5 u, corresponding to the mass of the NBu_4^+ counterion. These peaks were therefore assigned to the cationic entities $[M + x\mathrm{NBu_4} + (7-x)\mathrm{H}]^+$ (Figure 1), where M is the mass of one $\{P_2W_{17}O_{61}\}$ unit and one $\{C_6H_5\text{-}Si\text{-}O\text{-}Si\text{-}C_6H_5\}$ unit. The observed experimental values are consistent with the calculated mass for the different cations, within the estimated experimental accuracy of ±2 u in the m/z 5500–6500 range (see Experimental Section). Thus, the MALDI-TOF results unambiguously confirm that the poly-

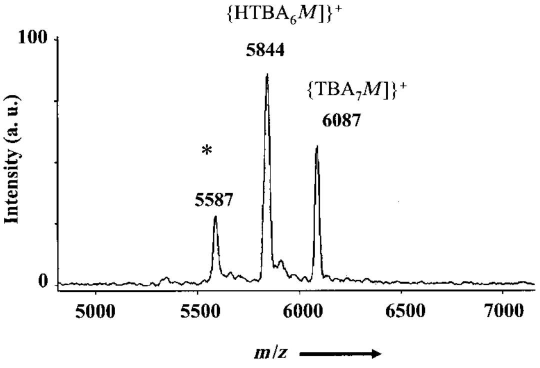


Figure 1. Positive-ion MALDI-TOF mass spectrum of $[\alpha_2\text{-}P_2W_{17}O_{61}(PhSi)_2O]^{6-}$. The peak * corresponds nominally to $[H_2TBA_5M{-}O]^+$. This loss of an oxygen atom could however not be interpreted.

anionic structure was maintained and that two phenylsilanes were grafted on the POM, and in addition they indicated the presence of one Si-O-Si bond between the two silyl groups.

The ^{183}W NMR spectrum exhibits nine lines with 1:2:2:2:2:2:2:2:2 relative intensities (Figure 2). These features confirmed that the $\{\alpha_2\text{-}P_2W_{17}O_{61}\}$ framework retained its original symmetry, with two organosilyl units grafted on the surface. Moreover, the shifting of the lines with respect to those of the lacunary anion is consistent with a modification of the lacunary surface. Heteronuclear $^2J_{W,P}$ couplings are not resolved but some homonuclear tungsten–tungsten couplings were partially observed and are presented in the Experimental Section. However, no definitive assignment was possible due to the complexity of the lines. ^{31}P and ^{183}W NMR data suggested the presence of a sole species with a symmetric grafting of the two organosilane groups, the original symmetry of the starting POM being conserved.

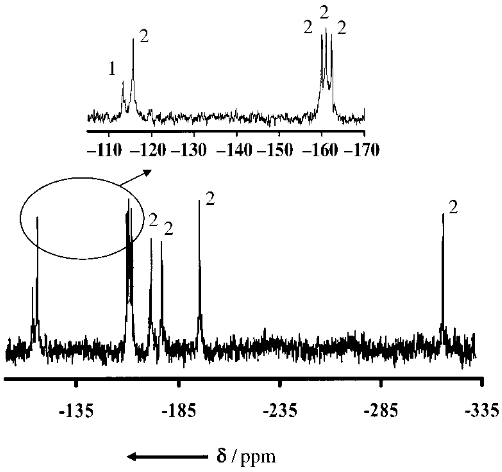


Figure 2. ^{183}W NMR (12.5 MHz) spectrum of $[\alpha_2\text{-}P_2W_{17}O_{61}(PhSi)_2O]^{6-}$.

These different data allowed us to establish the formula $[P_2W_{17}O_{61}(PhSi)_2O]^{6-}$, for which two isomers (**I** and **II**) can be considered; the two phenylsilane groups can be grafted in two different positions on the lacunary surface through four different oxygen atoms (Figure 3).

In **I**, *each* phenylsilane group is linked to the same diad, while in **II** *each* phenylsilane is bonded to two different diads. Accordingly, **I** would generate two lines in the ^{29}Si NMR spectrum, whereas for **II** only one line is expected. As in the ^{29}Si NMR spectrum, which was recorded under ^{1}H broad-band decoupling, only one line is observed at $\delta = -65.1$ ppm, with two different couplings $^2J(^{183}W,^{29}Si) = 10$ and 20 Hz,[20] it can be concluded that each silyl group is linked to two tungsten atoms located in two different diads (**II**). Moreover, these $^2J(^{183}W,^{29}Si)$ coupling values are consistent with those observed by Judeinstein and co-workers[6] for the derivatives $[SiW_{11}O_{39}(RSi)_2O]^{4-}$, and by Hill and co-workers for $[PW_{11}O_{39}(PhPO)_2]^{3-}$.[13]

The ^{31}P NMR spectrum exhibits two lines at $\delta = -8.8$ and -11.9 ppm, which are attributed to $\{PW_6\}$ and $\{PW_9\}$ moieties, respectively. This result confirmed that the POM structure was maintained and that only one species was present in solution. To observe the organosilyl groups, a modified phenylsilane incorporating a *para*-phosphonate group was used (Figure 4). This modification allowed us to observe one additional line without coupling $^2J(^{183}W,^{31}P)$, with a relative intensity of 2 compared with the corresponding lines of the POM framework (Figure 4). This is consistent with the presence of two organosilyl groups on the POM and the grafting of each silyl group on two different diads, as confirmed by ^{29}Si NMR experiments (see above).

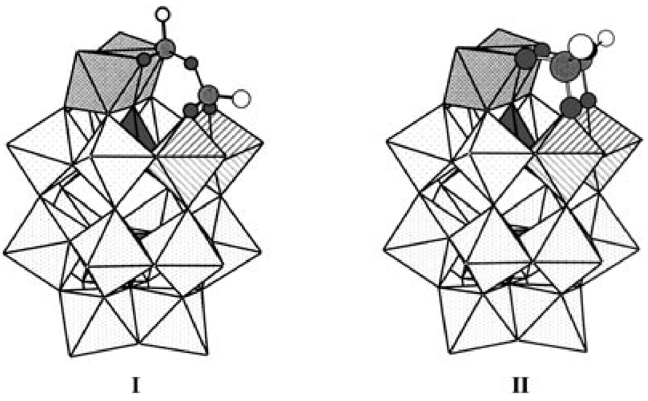


Figure 3. Schematic representation of the grafting of two organosilanes on the lacunary surface of the polyoxotungstate framework.

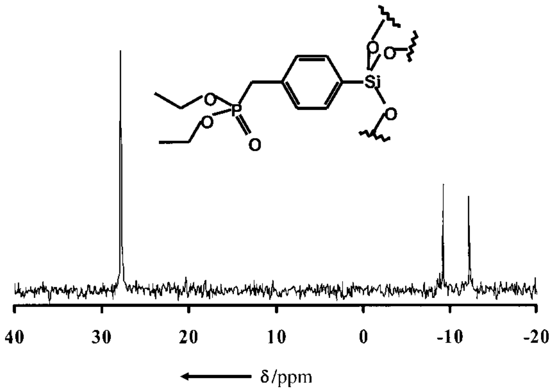


Figure 4. ^{31}P NMR (121.5 MHz) spectrum of $[\alpha_2\text{-}P_2W_{17}O_{61}\{4\text{-}[(C_2H_5O)_2P(=O)CH_2]\text{-}C_6H_4\text{-}Si\}_2O]^{6-}$ with a schematic drawing of the ligand.

Study by ESI-MS: In recent work, we showed that ESI-MS can be reliably used to characterize the structure of composite systems.[5] Herein, ESI-MS was used again as the dominant technique to analyze the mixtures obtained by methods A–C. Indeed, this technique requires only a small quantity of product and permits direct analyses of the mother solution.

For each method, but in particular for methods A and B, the final product gave the same negative-ion mass spectrum with two main intense signals that were attributed to $[(NBu_4)_3M]^{3-}$ and $[(NBu_4)_2M]^{4-}$, respectively.[20] For method C, mass spectra were recorded at two different stages of the synthesis: from the primary H_2O/CH_3CN solution in the absence of tetrabutylammonium, and after precipitation with an aqueous solution of tetrabutylammonium bromide. The first stage corresponds to the formation of a potassium salt of $[P_2W_{17}O_{61}(C_6H_5SiOSiC_6H_5)]^{6-}$. The negative-ion mass spectrum was obtained by using a 10^{-3} M solution in CH_3CN/H_2O (v/v 1/2) at 200 °C.[20] Identical results were obtained at 400 °C. Three sets of multiply charged ions were detected corresponding to three different charge states 5−, 4−, and 3−. For charge state 5−, in addition to the expected signal at *m*/*z* 878, six other peaks were observed regularly spaced at intervals of about 8 on the *m*/*z* scale. Three possible explanations were first envisaged to account for these peaks: 1) the addition of acetonitrile as solvate molecules (*m*/*z* 8.2), 2) the substitution of protons from the organic moiety for potassium cations (*m*/*z* 7.6), or 3) the addition of potassium cations with reduction of the resulting aggregate with the POM anion (*m*/*z* 7.8). In this latter hypothesis, reduction of the POM is required to maintain the 5− charge state. The occurrence of electrochemical oxidation or reduction reactions has been observed before[14] and is thought to depend on the redox properties of the analyte, the concentration, and the flow dynamics in the electrospray emitter.[15] For the set of peaks corresponding to charge states 4− and 3−, the same additional peaks were observed with increments of 10 and 13 on the *m*/*z* scale, respectively, for which the same attributions could be proposed.

The solvate molecules hypothesis was tested first by modifying the value of the declustering potential. The increase of this potential enhanced the loss of residual solvent molecules and led to a modification of the relative intensities of the different charge states. However, we did not observe these two phenomena, which was not in favor of the addition of acetonitrile as solvate molecules. To further test the solvate molecule hypothesis, a change of solvent was investigated. After subsequent evaporation of the acetonitrile/water solvent, the product was dissolved in a solution of $MeOH/H_2O$ (v/v: 50/50) to give a concentration of 10^{-3} M, and mass spectra were recorded under the same experimental conditions. The resulting data (Figure 5a) displayed the same multiplicity of peaks as before with similar *m*/*z* values.[20] This important result eliminated the solvate molecules hypothesis, as the increment for methanol should have changed to 6.4, 8, or 10.7 for charge states 5−, 4−, and 3−, respectively.

Mass spectra were also recorded for a concentration of 10^{-5} M, in the same medium ($MeOH/H_2O$) and with same experimental protocol. In this case, only the signals normally expected were observed, indicating a dependence on dilution for the appearance of incremental signals with potassium (Figure 4b).[20]

Finally, we proceeded to test the influence of organic groups which could, though it seemed unlikely, provide protons for substitution with potassium cations. For this, we chose a saturated Keggin POM known for its high capacity to be reduced, namely $[PMo_{11}VO_{40}]^{4-}$.[16] We analyzed this POM under similar conditions of sampling, concentration (10^{-3} M), solvent ($MeOH/H_2O$), temperature, and ion spray voltage. Three sets of multiply charged ions corresponding to three different charge states 4−, 3−, and 2− (Figure 6) were detected.[20] As for the organosilyl derivatives, the set of peaks corresponding to the charge state 4− presented five signals regularly spaced at intervals of 10, which were assigned to an increment of potassium ions. Here, as no protons are available for substitution, the only possible attribution is the addition of potassium cations with reduction of the resulting aggregate with the $[PMo_{11}VO_{40}]^{4-}$ polyoxome-

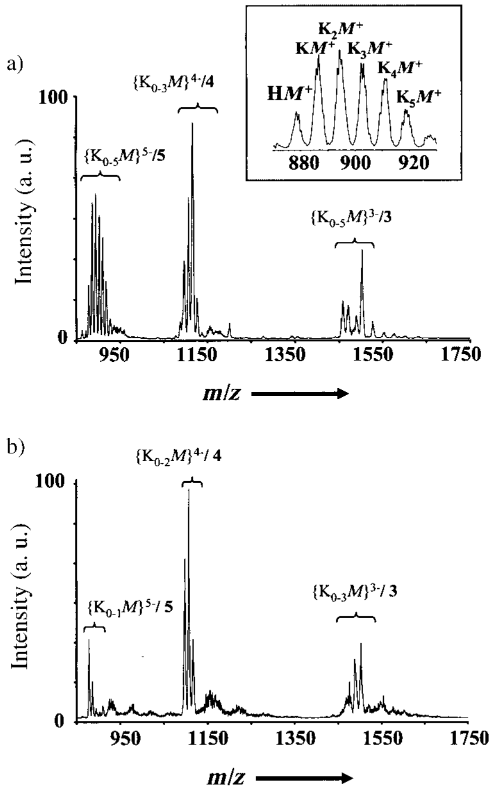


Figure 5. Negative-ion ESI mass spectra of potassium salts of $[P_2W_{17}O_{61}(C_6H_5SiOSiC_6H_5)]^{6-}$ obtained by Method C in $MeOH/H_2O$ (v/v: 50/50): a) at a concentration of 10^{-3} M and b) at a concentration of 10^{-5} M. The inset is an expansion of the $\{K_{0-5}M\}^{5-}/5$ signals.

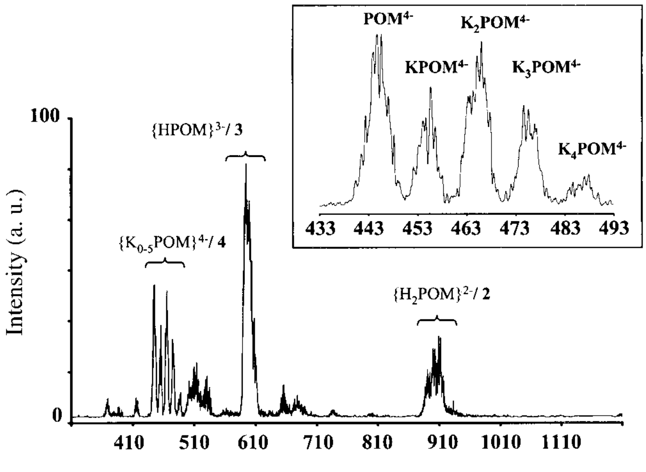


Figure 6. Negative-ion ESI mass spectrum of $[PMo_{11}VO_{40}]^{4-}$ (denoted POM) at a concentration of 10^{-3} M. The inset is an expansion of the $\{K_{0-4}POM\}^{4-}/4$ signals.

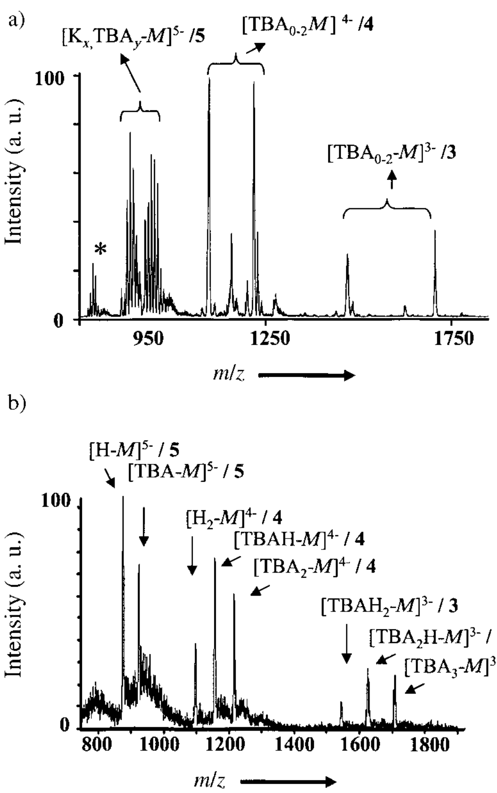


Figure 7. Negative-ion ESI mass spectra of $[P_2W_{17}O_{61}(C_6H_5Si)_2O]^{6-}$ obtained by Method C and precipitated by using tetrabutylammonium bromide in acetonitrile at a concentration of 10^{-3} M a) on an API 3000 (ESI/MS/MS) PE-SCIEX triple quadrupole and b) on a HP 5989B single quadrupole.

talate. We therefore concluded that hypothesis 3 was the one to be retained for the attribution of the incremental peaks in the hybrid system.

Electrospray mass spectra were also recorded for the final product obtained by method C after precipitation from an aqueous solution by tetrabutylammonium bromide. The mass spectrum (Figure 7a) displayed several sets of peaks corresponding to ions of three different charge states 5−, 4−, and 3−, with either protons, tetrabutylammonium (TBA), or potassium cations as counterions.[20] For the charge state 5−, in addition to the expected signal of $\{H[M]\}^{5-}$, several regularly spaced peaks were attributed, as discussed before, to the reduced aggregate $\{K_{1\text{-}5}[M]\}^{5-}$ ions. In addition to the signal corresponding to the ion with one TBA counterion $\{TBA[M]\}^{5-}$, four other peaks were observed regularly spaced at intervals of about 8 on the *m*/*z* scale. Again these features were attributed to a reduced aggregate of the POM with potassium ions. The charge state 4− was detected with several combinations of counterions. Similarly, the charge state 3− was detected with one proton and two TBA ions, or three TBA ions as counterions. In both charge states, neither potassium was found, nor any sign of reduced aggregates. The reduction reaction therefore seems related to the presence of potassium counterions.

In this particular case, a second instrument was used to record additional mass spectra: an HP5989B quadrupole mass spectrometer, fitted with an electrospray source incorporating a glass transfer capillary[17] at the interface between the atmospheric pressure region and the primary stage pumping zone of the instrument. Surprisingly, the mass spectra displayed neither signals of potassium nor any significant presence of reduced aggregates of the POM (Figure 7b).[20] The reasons for this result are still being investigated. It seems, however, that the electrospray source geometry may also play an important role in the redox behavior of these weakly bonded aggregates.

The reduction processes on the studied POM were therefore found to depend on three factors: 1) the concentration of the solution, 2) the geometry of the electrospray source, and 3) the nature of the counterions, as reduced aggregates were observed only in the presence of potassium cations and not TBA. Factors 1) and 2) might be expected as they should indeed play an important role in the flow dynamics and electrospray current that determine the flux of analyte molecules on the metallic surface of the emitter capillary that served here as cathode.[14b] The exact element of the source geometry responsible for the onset of the redox process in this paticular case, however, remains to be found. The electrospray emitter is suspected but the presence of the heated transfer capillary should also be taken into account, as such devices have been known to disrupt weak interactions in noncovalently bound complexes.[18] Here, as potassium ions were easily displaced by TBA in solution, the aggregates were thought to be very weakly bound. Furthermore, the shape of the peaks and noise in the mass spectra recorded on the instrument equipped with the Analytica of Branford ion source indicated the presence of low quantities of reduced potassium aggregates could not be excluded.

The reduced aggregates with up to five potassium ions implied the existence of a hybrid POM bearing up to 10 charges. This, in turn, implied that four W atoms might be in the oxidation state +v. This seemed quite surprising as, to our knowledge, such entities have never been observed in solution by classic electrochemistry. The fact that reduced aggregates were only observed with potassium ions was also rather unexpected and remains to be explained. A detailed study on these phenomena with other POMs is currently underway in our laboratory and will be reported shortly.

Conclusion

The synthesis of the new functionalized POM $[\alpha_2\text{-}P_2W_{17}O_{61}(RSi)_2O]^{6-}$ (see **I** in Figure 3) constitutes an alternative way for the elaboration of new hybrid materials. Moreover, even if no X-ray structure is available, the perfect combination of NMR spectroscopy and mass spectrometry serves as a valuable alternative tool in the characterization of these new NBBs. These new derivatives corresponded to the grafting of two organosilanes linked together by an Si-O-Si bridge. Each organosilane forms two Si-O-W bonds with two different diads of the POM framework. This work was followed by a thorough study by ESI-MS which showed unusual redox phenomena in the form of reduced clusters of POMs with potassium ions. The observation of this reduction was found to depend on the geometry of the electrospray source, on the concentration of the solution analyzed, and on the nature of the counterion (potassium or TBA). Although much remains to be done to achieve a complete understanding of these processes, one can imagine ESI-MS could be used as a means to check the redox properties of these systems under catalytic conditions, particularly in homogeneous catalysis, where the operating conditions are comparable to that used in electrospray mass spectrometry. Furthermore, the elaboration of sophisticated hybrid systems based on these hybrid NBBs is now in progress and will be reported in due course.

Experimental Section

General procedures and chemicals: $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 10H_2O$ and $K_4[PMo_{11}VO_{40}]$ were prepared according to the literature.[16], [19] Other reagents and solvents were purchased from Aldrich and used as received. IR spectra (4000–250 cm^{-1}) were recorded on a Nicolet Magna 550 spectrometer sampled with KBr pellet samples. ESI-MS measurements were carried out with an API 3000 (ESI/MS/MS) PE-SCIEX triple quadrupole mass spectrometer and HP 5989B single quadrupole mass spectrometer equipped with an electrospray source from Analytica of Branford. Both instruments were operated in the negative-ion mode. For the API 3000 (ESI/MS/MS) PE SCIEX triple quadrupole mass spectrometer, the experiments were performed either by direct infusion with a syringe pump with a flow rate of 10 $\mu L\,min^{-1}$ or by flow injection acquisition with a flow rate of 200 $\mu L\,min^{-1}$. Standard experimental conditions were as follows: sample concentration: 10^{-3} to 10^{-5} M, nebulizing gas: N_2, ion spray voltage: −5.00 kV, temperature: 200–400 °C, declustering potential: −20 V, focusing potential: −200 V, entrance potential: 10 V. For the HP 5989B single quadrupole mass spectrometer the source parameters were: $V_{needle} = 0$ V, $V_{cyl} = 3500$ V, $V_{end} = 3000$ V, and $V_{cap} = 3500$ V. Purified air was used as nebulizing and drying gas, the presence of oxygen helped to prevent corona discharge which is often a problem in negative-ion operation. The pressures of nebulizing and drying gas were 0.34 and 1.7 bar, respectively, and the nebulizing gas was heated to approximately 150 °C. Mass spectra were obtained by direct infusion with a Harvard Apparatus syringe pump of 10^{-4}, 5.10^{-5}, or 10^{-5} M sample solutions in pure distilled acetonitrile at a flow rate of 5 $\mu L\,min^{-1}$. The cone voltage V_c was varied, but most often used at low values of 10 to 40 V relative to the capillary exit voltage. The mass spectra depicted are the result of approximately 20 scans summed from m/z 500 to 1950. The mass axis was calibrated by using the cluster ions observed from a 50 $ng\,\mu L^{-1}$ solution of SDS (sodium dodecylsulfate) in acetonitrile.

The MALDI-TOF mass spectra were recorded by using a Voyager Elite Time-of-Flight Mass Spectrometer (PerSeptive Biosystems, Boston, MA, USA). In this apparatus, the pulsed N_2 laser beam (337 nm, 3 ns pulse duration, repetition rate 2 Hz) was focused onto the target with an incidence angle of 45°. In all these experiments the mass spectrometer was tuned in the linear mode by using delayed extraction and a beam wire guide. The target voltage was set to +20 kV. The extraction delay and pulse voltage were adjusted to obtain the best mass resolution, and the wire guide voltage was adjusted to obtain the best transmission. All mass spectra were recorded and averaged over 256 laser shots by a Tektronix TDS 520 oscilloscope (Beaverton, OR, USA). The samples were prepared as follows: the compound (2 mg) was dissolved in acetonitrile (500 µL; solution A), and dithranol (12 mg) was dissolved in CH_2Cl_2 (500 µL; matrix solution). Then 1 µL of solution A was added to 50 µL of the matrix solution. An external calibration of the instrument with a POE 5000 standard was used.

The ^{31}P NMR spectra (121.5 MHz) were obtained at room temperature in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probe head. The chemical shifts are given according to the IUPAC convention with respect to 85% H_3PO_4. The ^{29}Si NMR (59.6 MHz) and ^{183}W NMR (12.5 MHz) spectra were recorded at 300 K on nearly saturated DMF/CD_3CN (90/10, v/v) solutions in 10 mm o.d. tubes on the same spectrometer equipped with a low-frequency special VSP probe head. For the ^{183}W NMR spectra (12.5 MHz), the chemical shifts are given with respect to a 2 M Na_2WO_4 aqueous solution and were determined by the substitution method using a saturated D_2O solution of tungstosilicic acid $H_4SiW_{12}O_{40}$ as a secondary standard ($\delta = -103.8$ ppm).

Synthesis by Method A

$(NBu_4)_6[\alpha_2\text{-}P_2W_{17}O_{61}(C_6H_5Si)_2O]$ from $C_6H_5SiCl_3$: $C_6H_5SiCl_3$ (65 µL, 4 mmol) was added dropwise to a suspension of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ (1 g, 0.2 mmol) and NBu_4Br (0.42 g, 1.3 mmol) in acetonitrile (60 mL) at 0 °C. The resulting mixture was stirred for six hours. Then the acetonitrile solution was concentrated to half its volume and the crude product was filtered after precipitation of the mother solution with ethanol. The analysis was performed after purification by crystallization in DMF. Yield: 1.1 g (0.19 mmol, 94 %). ^1H NMR (300 MHz, CD_3CN) : $\delta = 7.8$ (m, 3H), 7.4 ppm (m, 2H); ^{29}Si NMR (59.6 MHz, DMF/CD_3CN, TMS): $\delta = -65.1$ ppm (s, $^2J(^{29}Si,^{183}W) = 10$, 20 Hz, 2Si); ^{31}P NMR (121.5 MHz, DMF/CD_3CN, H_3PO_4): $\delta = -8.8$ (s, PW_8), −11.9 ppm (s, PW_9); ^{183}W NMR (12.5 MHz, DMF/CD_3CN, Na_2WO_4): $\delta = -113.4$ (s, 1W), −115.8 (s, 2W), −160.1 (s, 2W), −161.0 (s, 2W), −162.3 (s, 2W), −171.7 (s, 2W), −177.0 (s, 2W), −195.7 (s, 2W), −315.9 ppm (s, 2W); IR (KBr): $\tilde{\nu} = 3068$ (vw), 3040 (vw), 1129 (w), 1090 (vs), 1042 (s), 1031 (w), 949.5 (vs), 918 (vs), 806 (vs), 759 cm^{-1} (vs); MALDI-TOF MS: positive-ion mode: 5844 ($\{HTBA_6[M]\}^+$, calcd: 5845.6) and 6086.6 ($\{TBA_7[M]\}^+$, calcd: 6087).

Synthesis by Method B

$(NBu_4)_6[\alpha_2\text{-}P_2W_{17}O_{61}(C_6H_5Si)_2O]$ from $C_6H_5Si(OCH_3)_3$: $C_6H_5Si(OCH_3)_3$ (82 µL, 0.44 mmol) was added to a suspension of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ (1 g, 0.2 mmol) and NBu_4Br (0.42 g, 1.3 mmol) in acetonitrile (60 mL) at 0 °C, followed by addition of a hydrochloric aqueous solution (2.5 mL, 2.4 M). The synthesis and analysis was analogous to that previously described.

$(NBu_4)_6[\alpha_2\text{-}P_2W_{17}O_{61}(4\text{-}((C_2H_5O)_2P(=O)CH_2)\text{-}C_6H_4\text{-}Si)_2O]$: The procedure was similar except the starting $4\text{-}((C_2H_5O)_2P(O)CH_2)\text{-}C_6H_4\text{-}Si(OC_2H_5)_3$ (82×10^{-3} g, 0.21 mmol). Yield: 1.0 g (0.16 mmol, 82 %). ^1H NMR (300 MHz, CD_3CN): $\delta = 7.8$ (d, 2H), 7.3 (d, 2H), 4.0 (q, 4H), 1.2 (t, 6H), n.d. ppm (d, 2H of Ar-CH_2-P); ^{31}P NMR (121.5 MHz, DMF/CD_3CN, H_3PO_4): $\delta = 27.8$ (s, 2, -$-P(=O)(OC_2H_5)_2$), −9.2 (s, 1, PW_8), −12.2 ppm (s, 1, PW_9); IR (KBr): $\tilde{\nu} = 3070$ (vw), 3044 (vw), 1128 (w), 1087 (vs), 1043 (s), 1032 (w), 950 (vs), 918 (vs), 805 (vs), 760 cm^{-1} (vs); ESI-MS: most intense peaks, m/z (%): 947 (90) ($[K(POM)]^{5-}$, calcd: 945.8 u), 1173.9 (90) ($[H_2(POM)]^{4-}$, calcd: 1174.2 u), 1294.1 (100) ($[TBA_2POM]^{4-}$, calcd: 1293.7 u), 1806.7 (30) ($[TBA_3\text{-}POM]^{3-}$, calcd: 1805.8 u).

Synthesis by Method C

$(NBu_4)_6[\alpha_2\text{-}P_2W_{17}O_{61}(C_6H_5Si)_2O]$ from $C_6H_5Si(OCH_3)_3$: A solution of H_2O/CH_3CN (20/10 mL v/v) became turbid when $C_6H_5Si(OCH_3)_3$ (82 µL, 0.44 mmol) was added dropwise at room temperature. Then solid $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ (1 g, 0.2 mmol) was added to the solution which had been acidified to pH ≈ 1.8 with 1 M HCl. The clear solution was stirred overnight. The analysis by ESI-MS and ^{31}P NMR spectroscopy showed that this potassium derivative was in a pure form (see Discussion). Then CH_3CN was evaporated and NBu_4Br (0.84 g, 2.6 mmol) was added to the aqueous solution to precipitate the expected product as a tetrabutylammonium salt. Then, the product was crystallized as above in Method A in DMF. The analysis was similar.

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