Synthesis and Multispectroscopic Characterization of Organically Modified Polyoxometalates

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Organically modified 'Keggin-type' oxopolymetalates of general chemical formula $[R]_4[SiW_{11}O_{40}(SiR'')_2]$, ($R = H^+$, K^+ or $NR'_4{}^+$; R' = Me or Bu; R'' = Et, $CH{=}CH_2$, $C_{10}H_{21}$ or Ph) have been synthesised by three different procedures. Large quantities were obtained in high purity and good yield. Their structure has been established by a multispectroscopic study, elemental mass analysis, and time of flight spectrometry (^{252}Cf). Selection rules governing the latter technique are also detailed. IR, ^{29}Si and ^{183}W NMR spectroscopy confirm that two organic silicon groups are bonded to the surface of the lacunar $SiW_{11}O_{39}{}^{8-}$ heteropolyoxometalate.

Tungsten, molybdenum, niobium and vanadium polyoxometalates[1] have a quite small size (around 10 Å in diameter) and a very high electronic density. Consequently, they are interesting materials for modelling transition-metal oxides. Their structure is based on stacking of MO_6 octahedra[2] (M being a transition metal). These octahedra 'MO_6' can share edges or corners, leading to many clusters with different shapes.[3] Heteropolyoxometalates have been widely studied. They are obtained *via* the substitution of one (or more) metallic centres of the Periodic Table. An important recent interest deals with the anchoring of organic groups at the surface of these compounds.

The presence of many highly oxidized metallic centres make polyoxometalates good candidates for many applications. These compounds have been widely studied as catalysts,[4] electron microscope tracers,[5] analytical reagents,[6] and materials for photochemistry[7] and electrochromism.[8] Recently, some work in this laboratory has been focused on the electrochemical behaviour of these species and their properties in redox catalysis or electrocatalysis.[9] Many studies are in progress in order to correlate their structures with their properties. Some polyoxometalates have been characterised by X-ray diffraction.[1] However, for most, a structural model has been proposed on the basis of spectroscopic studies and chemical correlations. Heteropolyoxometalates with an organic group anchored to the backbone through a SiOM bond are interesting precursors for the synthesis of mixed organic–inorganic compounds. The synthesis of such precursors had been reported[10] but their structural characterisation appears to be incomplete, probably because single crystals suitable for X-ray studies were not obtained.

This paper presents a new synthesis of $[R]_4[SiW_{11}O_{40}(SiR'')_2]$, (where R is K^+ or $NR'_4{}^+$; R' = Me or Bu; R'' = Et, $CH_2{=}CH$, $C_{10}H_{21}$ or Ph). A more detailed characterisation is also performed on the basis of spectroscopic studies.

The nature of these compounds and their accurate chemical composition have been determined by time of flight (TOF) spectrometry (^{252}Cf). This new technique is able to measure molecular masses up to 20 000 of many chemical and biochemical systems.[11] This paper presents the first results obtained with TOF spectrometry on polyoxometalate compounds. The nature of the bonding has been determined by infrared spectroscopy, and the local environment of nuclei and symmetries in the molecules have been studied by liquid multinuclear magnetic resonance (^{1}H, ^{13}C, ^{29}Si and ^{183}W).

For the sake of clarity, we will focus on the experimental results obtained with the vinyl derivative.

Experimental

All chemical reagents were used as purchased [Dynamit-Nobel for the silicon derivatives, Aldrich for the tetraalkyl salts and deuteriated solvents, Carlo-Erba for dimethylformamide (dmf) and Prolabo for all other reagents]. Pure water was obtained by deionization and subsequent passage through a Millipore Q water-purification set. Hydrolysis of trichlorosilicon compounds with moist air occurs at a moderate rate, and all reactions were carried out under atmospheric conditions. Time of flight reference samples of $H_4SiW_{12}O_{40}\cdot nH_2O$ have been used as purchased (Prolabo); $NMe_4{}^+$ and $NBu_4{}^+$ salts were synthesised by precipitation with tetraalkylammonium bromide salts in water solution. These reference polyoxometalates have been checked by infrared, ^{29}Si and ^{183}W NMR spectroscopies, and electrochemical measurements.

A ^{252}Cf time of flight mass spectrometer at the Institut de Physique Nucléaire d'Orsay[12] was used. This instrument built at the Institut can measure routinely masses of molecular ions over a large mass range. Before TOF measurements, compounds were processed as very thin films deposited by the electrospray technique on a metallic surface. In the present experiment, the oxometalates were dissolved in acetonitrile-DMF mixtures. This solution was sprayed on a 1.5 μm thick aluminium-mylar foil. Fission fragments from the ^{252}Cf source pass through the solid film and desorb ions from the surface. A 15 kV accelerating voltage was established between the solid film and a grid located at 5 mm. The accelerated ions were detected after a time of flight distance of 50 cm, by a set of microchannel plates. Their time of flight was very precisely measured by using a time digital converter.[13] The TOF spectra of positive or negative ions (according to the polarity of the high voltage) were recorded in a few minutes and stored in the computer memory. Contaminant ions, H^+ and Na^+ or H^- and C_2H^-, which are always present in the TOF spectrum provide an internal mass calibration. An intense peak of mass $M = 242$, corresponding to the $NBu_4{}^+$ ions, can also be used with tetrabutylammonium salts.

Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer between 4000 and 250 cm^{-1}, with a 5 cm^{-1} resolution. Samples were prepared as KBr pellets (ratio polyoxometalate: KBr 1:100).

Table 1 Main infrared bands (cm^{-1}) (cation frequencies are omitted)

$SiW_{11}(SiCH{=}CH_2)$		SiW_{12}					
NBu_4	K	NBu_4	K	SiW_{11}	$Si(CH{=}CH)(OEt)_3$	$Si(CH{=}CH_2)O_n$	Assignment
3080	3080				3080	3060	
	2980				3020	3020	ν(CH)
	2920				3000	2960	
	2880				2970		
1600	1600				1600	1600	ν(C=C)
						1410	
						1280	
						1130	ν(SiO) vbr
						1040	ν(SiO) vbr
1050	1050						ν(SiO)
1020		1010	1020	1000			
			1000				$\nu(SiO)_{central}$
					1010		
					990		
					980		
980							
965	970	970	980	960			$\nu_{asym}(W{=}O)$
950							
925	930	920	930				
900	905			890			
	885	885	880	870			$\nu_{asym}(WOW)$
860	850						
810	780	800	780	800			
760	730			740			
710	700			720			
					730	770	
615	620				593	550	ν(SiC)
540	535	535	545	515			$\nu_{sym}(WOW)$
					460		ν(SiCl)
390	380	390	380	370			
350	340	340	340				$\nu_{sym}(WOW)$

Proton and ^{13}C-{^1H} NMR broad-band-decoupled measurements were made on a Bruker AM200 spectrometer using standard procedures. Potassium and hydrogen-ion salts were dissolved in D_2O (98%), NBu_4^+ salts in $(CD_3)_2SO$ or dmf-$(CD_3)_2CO$ (90:10) mixtures (0.2 mol dm^{-3}). Silicon-29 NMR spectra were recorded on a Bruker AM250 spectrometer working at 49.696 MHz. A pulse width of 4 μs (t_{90} = 15 μs) and a relaxation delay of 40 s were chosen in order to obtain a complete relaxation of both Si nuclei. Tungsten-183 NMR spectra were recorded on a Bruker AM500 spectrometer (12 T) at a frequency of 20.81 MHz [pulse length: 20μs (t_{90} = 40 μs), recycle time = 2.0 s, 10 mm outside diameter NMR tubes]. Chemical shifts were measured with respect to external references. The replacement method was used and usual corrections were applied in order to minimize the effects of the dielectric variations of the solvents.

The following nomenclature will be used: SiW_{12}, SiW_{11} for α-$[SiW_{12}O_{40}]^{4-}$ and α-$[SiW_{11}O_{39}]^{8-}$ polyoxometalates respectively; $SiW_{11}(SiR'')$ for the SiW_{11}-based substituted polyoxometalate, irrespective of the number of bonded SiR″ groups (R″ = $CH{=}CH_2$, $C_{10}H_{21}$ or Ph); the cation is fixed before the oxometalate, irrespective of the stoichiometry, *e.g.* K_4[α-$SiW_{12}O_{40}$] is symbolised as $KSiW_{12}$, and the tetrabutylammonium salt as NBu_4SiW_{12}.

Synthesis.—The compound $KSiW_{11}$ was synthesised using the procedure described by Hervé and Tezé.[14] This product was characterised by IR (Table 1), ^{29}Si NMR (δ −85.4 in D_2O) spectroscopy and polarography (half-wave potentials $E_{\frac{1}{2}}$ = −780 and −940 mV in buffered aqueous acetate solution at pH 4.7).

The desired organometallic polyoxometalates were synthesised by allowing $KSiW_{11}O_{39}$ to react with $SiR''X_3$ (X = Cl or OEt; R″ = $CH{=}CH_2$, $C_{10}H_{21}$ or Ph). These reactions have been studied in two solvents: water and acetonitrile. The synthetic procedures are described for $SiW_{11}(SiCH{=}CH_2)$ but they can be adopted for any organic group. However, the synthesis of $SiW_{11}(SiC_{10}H_{21})$ in water has some experimental limitations owing to the immiscibility of trichlorosilano compounds with long alkyl chains.

Reactions in water. The compound $KSiW_{11}$ (10 g, 3.1 × 10^{-4} mol) was dissolved in water (150 cm^3) at room temperature. Trichloro(vinyl)silane (1 cm^3, 7 × 10^{-2} mol) was added dropwise in 2 min with vigorous stirring. Upon addition of the first drops the solution was pale yellow. After a few minutes small white particles appeared. This reaction is exothermic. The mixture was stirred for 20 h, then filtered on a small-porosity filter funnel. The filtrate was then purified by different procedures depending on the nature of the cation.

Potassium salts were obtained by drying this solution with a Rotovapor, then purified by dissolution in water, filtering and drying. Tetraalkylammonium salts (methyl and butyl) were obtained by addition of the corresponding bromide salts (*ca.* 10 g). A rapid precipitation of the corresponding salt occurs. Tetramethylammonium salts are soluble both in organic solvents (dmf, acetonitrile, acetone), and mixtures with high amounts of water, and therefore were dried by evaporation of the solvents on a Rotovapor. The tetrabutylammonium salts were purified (essentially removing organically modified silica clusters $R''SiO_n$) by successive dissolution in dmf, precipitation of the polyoxometalate salt by addition of a large amount of water, and filtering.

(*b*) *Reaction in acetonitrile*. The compound $KSiW_{11}$ (4 g, 1.25 × 10^{-4} mol) was dispersed in acetonitrile (150 cm^3) with vigorous stirring, at room temperature for 2 h. Then, $Si(CH{=}CH_2)Cl_3$ (0.2 cm^3, 1.5 × 10^{-2} mol) was added dropwise. The mixture was stirred for 20 h, then filtered. Tetrabutylammonium bromide (5 g) was added to the filtrate. A precipitate

Table 2 Main *m/z* values of organically modified polyoxometalates

	Positive ionization		Negative ionization	
Compound	*m/z*	Fragments	*m/z*	Fragments
NBu_4SiW_{12}	3845	$[M' + 4NBu_4 - 3H]^+$		
	4084	$[M' + 5NBu_4]^+$	2855	$[M' - O]^-$
$(M' = SiW_{12}O_{40})$	4324	$[M' + 6NBu_4]^+$		
NMe_4SiW_{12} $(M' = SiW_{12}O_{40})$	3243	$[M' + 5NMe_4]^+$	2855	$[M' - O]^-$
$HSiW_{12}$ $(M' = SiW_{12}O_{40})$	No peaks could be attributed		2857	$[M' - O]^-$
$NBu_4SiW_{11}(SiCH{=}CH_2)$	3765	$[M' + 4NBu_4]^+$		
	4008	$[M' + 5NBu_4 - 3H]^+$	2784	$[M' - O]^-$
$[M' = SiW_{11}O_{40}(SiC_2H_3)_2]$	4251	$[M' + 6NBu_4 - 4H]^+$	3026	$[M' - O + NBu_4]^-$
$NMe_4SiW_{11}(SiCH{=}CH_2)$ $[M' = SiW_{11}O_{40}(SiC_2H_3)_2]$	3167	$[M' + 5NMe_4 - 3H]^+$	2786	$[M' - O]^-$
$NBu_4SiW_{11}(SiC_{10}H_{21})$	3998	$[M' + 4NBu_4]^+$		
	4090	$[SiW_{12} + 5NBu_4]^+$	3010	$[M' - O]^-$
	4239	$[M' + 5NBu_4]^+$		
$[M' = SiW_{11}O_{40}(SiC_{10}H_{21})_2]$	4479	$[M' + 6NBu_4]^+$		
$NBu_4SiW_{11}(SiPh)$	3850	$[M' + 4NBu_4]^+$		
	4112	$[M' + 5NBu_4]^+$	2884	$[M' - O]^-$
$[M' = SiW_{11}O_{40}(SiC_6H_5)_2]$	4355	$[M' + 6NBu_4]^+$		

was obtained and removed by filtration. Then, water (*ca.* 100 cm^3) was added to the filtrate in order to precipitate a fine powder of $NBu_4SiW_{11}(SiCH{=}CH_2)$. Further purification by dissolution and precipitation was performed. Note that, following this procedure, only tetrabutylammonium salts can be obtained with reasonable purity.

(*c*) *Synthesis from trialkoxysilane compounds.* The compound $KSiW_{11}$ (4 g, 1.25 × 10^{-4} mol) was dissolved in water (100 cm^3). Triethoxy(vinyl)silane (1 cm^3, *ca.* 10^{-1} mol) was added with vigorous stirring. When the emulsion was dispersed, the pH was adjusted to pH 1 by addition of 1 mol dm^{-3} HCl solution. The reaction was vigorously stirred during 20 h. A white precipitate was removed by filtration and NBu_4Br (5 g) added to the filtrate. The precipitate thus formed was washed with Pr^iOH (200 cm^3) in order to remove the $RSiO_n$ fine particles and oligomers. The same product $NBu_4SiW_{11}(SiCH{=}CH_2)$ was obtained. However, this synthesis is more convenient than those described in (*a*) and (*b*) because of the lower reactivity of the trialkoxysilicon reagents.

All the products are white powders. The H^+ and K^+ salts are soluble in water up to 0.04 mol dm^{-3}, and appear to be quite stable around pH 1–6, $NMe_4{}^+$ salts are slightly soluble in acetonitrile and dmf (0.02 mol dm^{-3}), water, and in acetonitrile–water mixtures (0.05 mol dm^{-3}) and $NBu_4{}^+$ salts are readily soluble in organic solvents such as dmf, Me_2SO and propylene carbonate (0.3 mol dm^{-3}) and in acetonitrile (0.05 mol dm^{-3}). Solutions of the tetrabutylammonium salts appear to be quite stable in these solvents and remain unaltered after 2 weeks at 80 °C.

Elemental analysis performed on the tetrabutylammonium salt was in agreement with the formula proposed by Knoth,[10] $[NBu_4]_4[SiW_{11}O_{40}(SiCH{=}CH_2)_2]$ (Found: C, 21.9; H, 3.9; N, 1.7; O, 17.5; W, 52.7; Si, 2.3; Calc. for $C_{68}H_{150}N_4O_{40}Si_3W_{11}$: C, 21.7; H, 4.0; N, 1.5; O, 17.0; W, 53.6; Si, 2.2%).

Results

Spectroscopic Studies. Time of flight spectrometry. Thin films of oxometalates were deposited following procedures described in the Experimental section. The higher-intensity peaks and interpretations are reported in Table 2.

(*a*) *Reference compounds: salts of* SiW_{12}. A wide variety of SiW_{12} salts are available and they have been chosen as reference for TOF measurements.

Fig. 1(*a*) shows the negative-ion low-resolution (1:800) TOF spectrum of $(NBu_4)SiW_{12}$. The spectra of $(NMe_4)SiW_{12}$ and $HSiW_{12}$ are quite similar. All peaks have been unambiguously assigned to clusters of formula $Si_xW_yO_z$. A set of peaks the intensities of which decrease regularly up to a turn-back point of higher intensity (corresponding to *m/z* 2857) is observed. This peak corresponds to the mass of $[SiW_{12}O_{39}]^-$ anion obtained from $SiW_{12}O_{40}$ *via* the loss of one oxygen atom. Higher-mass peaks are observed corresponding to $NBu_4 + SiW_{11}O_{39}$ and $SiW_{12}O_{40} + WO_3$ collision fragments. Lighter-mass peaks correspond to the loss of one WO_4 fragment and thereafter to sequential loss of WO_3 entities up to the SiW_6O_{20} cluster. Then parallel clusters are observed without silicon, and W_nO_{3n} fragments (n = 1–6); W_nO_{3n+1} fragments and sub-oxides W_nO_{3n-x} (x = 1–3) are also observed.

All the observed peaks have a large linewidth. This is inherent with the transition-metal complexes and clusters, the natural isotopic abundances of which cover a wide range. As a consequence, the isotopic distribution of the high molecular masses is quite broad due to the large number of different isotopes. The influence of these isotopes is observed on the low *m/z* part of the spectrum [Fig. 1(*b*)]. Series of peaks spaced by one unit mass are observed, with a pattern of intensities for peaks of $m/z = M$, $M + 1$, *etc.*, which corresponds to the natural abundances of the tungsten isotopes.

The positive-ion low-resolution TOF spectrum of $(NBu_4)SiW_{12}$ is shown in Fig. 1(*c*). At higher *m/z* three major peaks are observed. They correspond to masses of 3845, 4084 and 4324. The mass difference between these fragments ($\Delta m \approx 242$) corresponds to one NBu_4 fragment. The lightest of these peaks corresponds to the parent ion $(NBu_4)_4SiW_{12}O_{40}{}^+$, the most intense to $(NBu_4)_5SiW_{12}O_{40}{}^+$, and the next one to $(NBu_4)_6SiW_{12}O_{40}{}^+$ fragments. Between *m/z* 1000 and 3500 wide oscillations are observed. Their period is complex (*m/z* changes between 170 and 210) and could correspond to the loss of WO_p (p = 0–4) fragments. When very long acquisition times are used, low-intensity peaks of very high mass are observed. They correspond to $(SiW_{12}O_{40})_n$ (n = 2–4) fragments arising from ion association inside the plasma medium. Small peaks assigned to $[SiW_{12}O_{40} + (WO)_n]$ (n = up to 10–20) are also observed. The structure of the positive-ion TOF spectrum of $(NMe_4)SiW_{12}$ is similar.

The positive-ion TOF spectrum of the H^+ salt is shown in

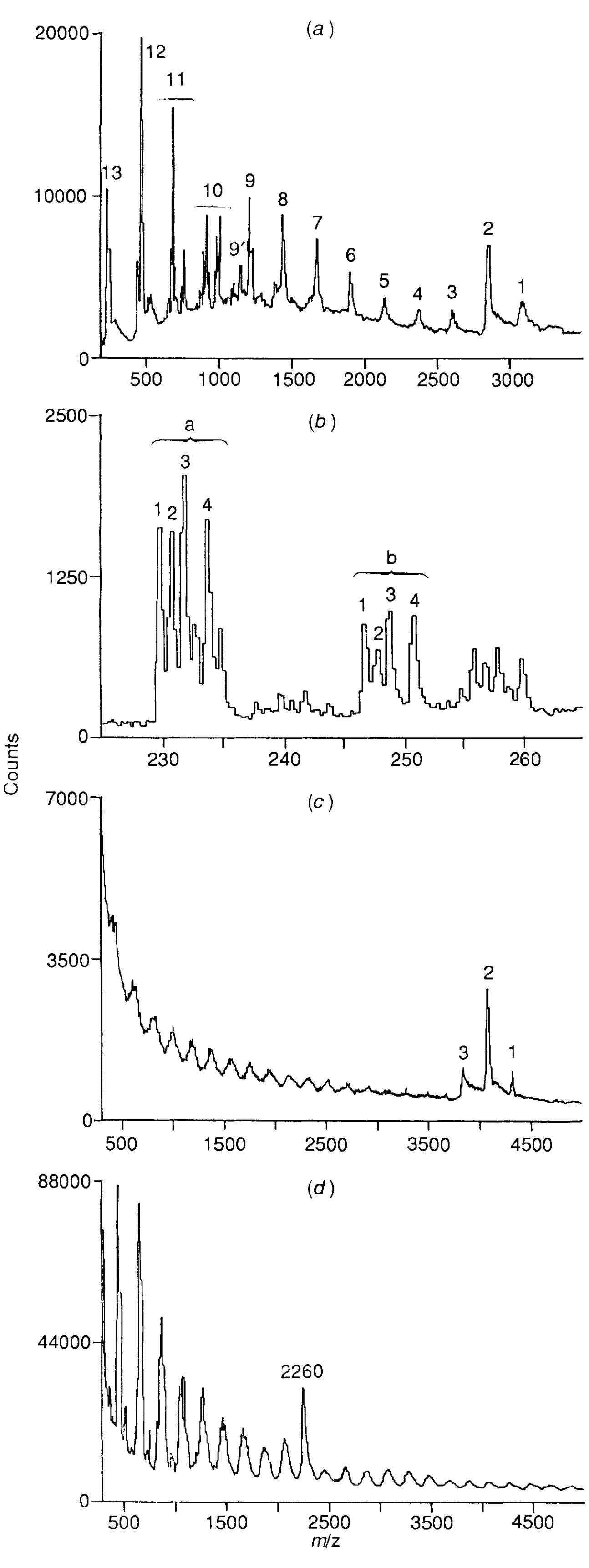


Fig. 1 Time of flight mass spectra. (*a*) Negative ions of the compound $[NBu_4]_4[SiW_{12}O_{40}]$, full spectrum, low resolution. Main peaks [index, *m*/*z*, fragment ($M' = SiW_{12}O_{40}$)]: 1, 3074, $[M' - O + NBu_4]^-$; 2, 2855, $[M - O]^-$; 3, 2607, $[M' - O - WO_4]^-$; 4, 2372, $[M' - O - WO_4 - 2WO_3]^- = [SiW_{10}O_{32}]^-$; 5, 2137, $[SiW_9O_{29}]^-$; 6, 1908, $[SiW_8O_{26}]^-$; 7, 1680, $[SiW_7O_{23}]^-$; 8, 1450, $[SiW_6O_{20}]^-$; 1391, $[W_6O_{18}]^-$; 9, 1219, $[SiW_5O_{17}]^-$; 1188, $[W_5O_{15}]^-$; 10, 1003, $[SiW_4O_{15}]^-$; 987, $[SiW_4O_{14}]^-$; 944, $[W_4O_{13}]^-$; 927, $[W_4O_{12}]^-$; 910, $[W_4O_{11}]^-$; 895, $[W_4O_{10}]^-$; 11, 772, $[SiW_3O_{12}]^-$; 754, $[SiW_3O_{11}]^-$; 711, $[W_3O_{10}]^-$; 694, $[W_3O_9]^-$; 679, $[W_3O_8]^-$; 662, $[W_3O_7]^-$; 645, $[W_3O_6]^-$; 12, 540, $[SiW_2O_9]^-$; 522, $[SiW_2O_8]^-$; 481, $[W_2O_7]^-$; 463, $[W_2O_6]^-$; 13, 248, $[WO_4]^-$; 232, $[WO_3]^-$. (*b*) Negative ions of $[NBu_4]_4[SiW_{12}O_{40}]$, low *m*/*z*, high resolution. Main peaks [index, *m*/*z*, fragment ($M' = {}^iWO_3$, where *i* refers to the natural abundance of the isotope)]: a_1, 229.8 $[M']^-$ (^{182}W, 26.3%); a_2, 230.8, $[M']^-$ (^{183}W, 14.3%); a_3, 231.8, $[M']^-$ (^{184}W, 30.7%); a_4, 233.8, $[M']^-$, (^{186}W, 28.6%); b_1, 246.8, $[M' + O]^-$, (^{182}W, 26.3%); b_2, 247.8, $[M' + O]^-$, (^{183}W, 14.3%); b_3, 248.8, $[M' + O]^-$, (^{184}W, 30.7%); b_4, 250.8, $[M' + O]^-$, (^{186}W, 28.6%). (*c*) Positive ions of $[NBu_4]_4[SiW_{12}O_{40}]$, full spectrum, low resolution. Main peaks [index, *m*/*z*, fragment ($M' = SiW_{12}O_{40}$)]: 1, 4327, $[M' + 6NBu_4]^+$; 2, 4083, $[M' + 5NBu_4]^+$; 3, 3843, $[M' + 4NBu_4]^+$. (*d*) Positive ions of $H_4[SiW_{12}O_{40}]$, full spectrum, low resolution

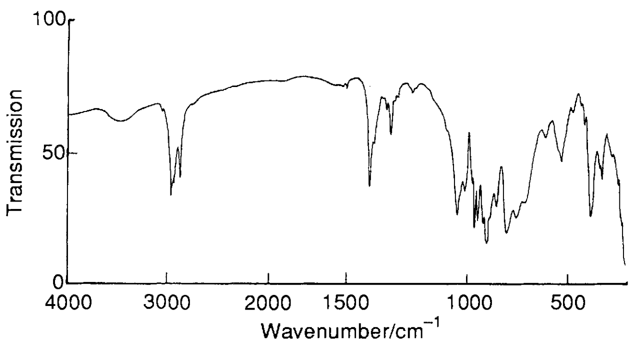


Fig. 2 Infrared spectrum of $NBu_4SiW_{11}(SiCH{=}CH_2)$

Fig. 1(*d*). A straightforward assignment appears to be quite difficult. The observed masses do not correspond to any evident fragmentation processes. Variations of the bond strength between alkaline-metal cation-oxometalates or alkylammonium oxometalates observed by IR and Raman[15] spectroscopies could account for such a phenomenon.

Some selection rules can be deduced from TOF measurements performed on these reference compounds. (*i*) Both positive- and negative-ion TOF spectra could be obtained on polyoxometalates. (*ii*) Negative-ion TOF mass spectra present many high-mass peaks. A regularly decreasing shape at higher masses and a turn-back point of higher intensity are characteristic of the anion. A regular loss of oxygen is observed accompanied by redistribution reactions and hydrogen capture as already observed by fast atom bombardment (FAB) mass spectrometry.[16] (*iii*) Positive-ion TOF mass spectra of the salts with heavier cations (NBu_4, NMe_4) present few peaks of higher mass, corresponding to the total mass of the anion (*N* negative charges) and *N* cations, anion and $N + 1$ cations, anion and $N + 2$ cations. They are obtained *via* plasma reactions, which have also been observed by FAB mass spectrometry. (*iv*) The difference between the highest positive- and negative-ion TOF mass peaks corresponds to ($N + 1$) times the number of cations. Consequently, the charge of the polyoxometalate can be evaluated by using such measurements.

(*b*) *Organically modified polyoxometalates.* The TOF spectra of many organically modified polyoxometalate NMe_4- and NBu_4-$SiW_{11}(SiR'')$ salts have been recorded. They present the same shape as those of the reference compounds. Values of the main peaks and their attributions are summarised in Table 2.

For the $(NBu_4)SiW_{11}(SiCH{=}CH_2)$ compound, the main positive-ion peaks are found at $m/z = 3765$, 4008 (main peak) and 4251, while negative-ion peaks are found at $m/z = 2784$ and 3026. The difference between the positive- and negative-ion masses corresponds to five tetrabutylammonium cations. Following the selection rules previously described, the formula $[NBu_4]_4[SiW_{11}O_{40}(SiCH{=}CH_2)_2]$ can be deduced for the so-called vinyl-derived SiW_{11} compound. A similar formula can be

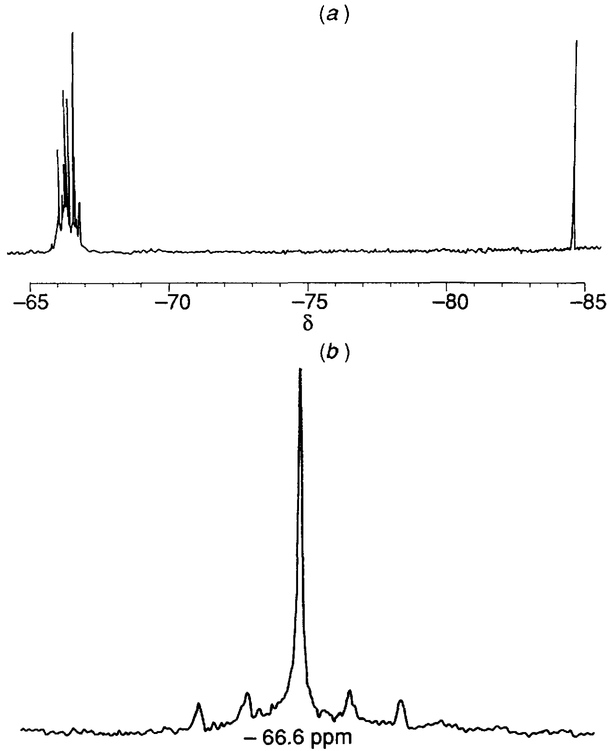


Fig. 3 Silicon-29 NMR spectra $NBu_4SiW_{11}(SiCH{=}CH_2)$ (*a*) undecoupled, (*b*) $\{^1H\}$ broad-band decoupled, signal arising from organically modified Si shown

proposed from TOF measurements performed on the tetramethylammonium salt.

These experiments show that all these compounds have the same general formula: $[R]_4[SiW_{11}O_{40}(SiR'')_2]$ ($R = K^+$, NBu_4^+ or NMe_4^+; $R'' = CH{=}CH_2$, $C_{10}H_{21}$ or Ph). This formula is consistent with the chemical analysis.

Infrared. The IR spectrum of $SiW_{11}(SiCH{=}CH_2)$ is presented in Fig. 2, and the main bands and their assignments together with those of reference compounds [SiW_{12}, SiW_{11}, $Si(CH{=}CH_2)Cl_3$ and $Si(CH{=}CH_2)O_n$] are presented in Table 1.

Infrared spectroscopy appears to be a very sensitive method to probe the purity of polyoxometalates. The presence of organically modified silica clusters ($R''SiO_n$ impurities) is evidenced by a very strong wide band centred around 1140 cm^{-1}, and a decrease in the intensity of the band of 950 cm^{-1}. Such impurities can be removed by further dissolution–filtration–precipitation. After each purification step the $SiW_{11}(SiCH{=}CH_2)$ compounds were checked by infrared spectroscopy. The K^+, NMe_4^+ and NBu_4^+ salts present the same spectral shape, but it appears that those of the tetraalkylammonium salts are better resolved.

The infrared spectra of polyoxometalates and organically modified derivatives present similarities and differences. The $SiW_{11}(SiR'')$ compounds show the characteristic features of Keggin structures: SiW_{11} or SiW_{12} anions are characterised by a bond located respectively at 1000 and 1010 cm^{-1} and assigned to the ν(Si–O) mode of the central SiO_4 tetrahedron. Those vibrations are observed at 1020 and 980 cm^{-1} for the organically modified polyoxometalates $SiW_{11}(SiR'')$. The IR spectra of $SiW_{11}(SiR'')$ (Fig. 2) also exhibits the vibrations characteristic of the Keggin W–O backbone [$\nu_{asym}(W{=}O)$, $\nu_{asym}(W{-}O{-}W)$ and $\nu_{sym}(WOW)$].

IR bonds between 3500 and 1200 cm^{-1} appear for organically modified polyoxometalates, corresponding to vibrational modes of organic groups (Table 1). They are close to those observed for $R''SiO_n$ and $Si(CH{=}CH_2)Cl_3$.

The IR spectra of $SiW_{11}(SiR'')$ compounds presents also major changes in the low-frequency range. An intense band is observed at 1050 cm^{-1} which could be assigned to ν(Si–O) modes in Si–O–Si configurations, as proposed by Knoth.[10] Hydrolysed trichloro- or trialkoxy-silanes, $R''SiO_n$, lead to such ν(Si–O) vibrations characterised by two wide and intense bands located at 1130 and 1040 cm^{-1}. An intense band at 860 cm^{-1} is also observed. The latter vibration is not observed for other polyoxometalates or $R''SiO_n$ aggregates. The nature of the organic group R and the synthesis procedure (water or organic solvent) do not modify the frequencies of these absorption bands.

Infrared spectroscopy is a very sensitive method to observe even small modifications in polyoxometalate structure. The strong similarities between the low-frequency IR spectrum ($\nu < 1200$ cm^{-1}) of each $SiW_{11}(SiR'')$ derivative and those of the Keggin anion strongly suggest that all the $SiW_{11}(SiR'')$ compounds are isostructural with the Keggin structure.

NMR Chemical shifts and coupling constants in the ^1H and ^{13}C NMR spectra of $SiW_{11}(SiR'')$ compounds are not very different from those of the trialkoxy(vinyl)silanes $Si(CH{=}CH_2)(OR)_3$ (R = Me or Et). Thus the electronic environment of the ^1H and ^{13}C nuclei are not greatly affected by the presence of surrounding tungsten atoms. This observation is general for all the $SiW_{11}(SiR'')$ compounds.

The ^{29}Si NMR spectrum of the $(NBu_4)SiW_{11}(SiCH{=}CH_2)$ salt is presented on Fig. 3, recorded by simple irradiation (*a*) or with broad-band $\{^1H\}$ decoupling (*b*). The undecoupled spectrum presents two set of peaks. The most unshielded one is located at δ −84.5 and appears as a single peak. It corresponds to the silicon atom located inside the central tetrahedron of the polyanion. This resonance is weakly shifted with respect to those reported for Keggin polyoxometalates and their lacunary homologues (δ −85.3 for H- or NBu_4-SiW_{12} salts dissolved in water or dmf, −84.7 for $KSiW_{11}$ in water). The second ^{29}Si resonance is located around δ −66. It corresponds to a complex multiplet, with intensity about twice that of the central silicon atom. It can be assigned to the ^{29}Si resonance corresponding to the organically modified silicon. The ^{29}Si NMR spectrum is simplified by decoupling procedures. A single intense peak surrounded by two pairs of small-intensity signals (around 5–10% of the major peak), centred on the same frequency are observed. The chemical shift of the central peak is δ −66.6, and its linewidth is less than 0.5 Hz. The two small doublets correspond to coupling effects with tungsten atoms, $^2J(SiW)$ 5.5 and 16.7 Hz. This means that the silicon atoms are bonded to two structurally different tungsten atoms (bond length and angles).

The uniqueness of the ^{29}Si resonance observed for the organically modified silicon nucleus evidences the equivalence of the two anchored groups. The chemical shift should be compared with those reported for $Si(CH{=}CH_2)(OR)_3$ molecules in order to measure the partial shielding effect. The chemical shifts of different SiOX environments (X = Si or W) are reported in Table 3. The ^{29}Si resonance shifts to high field (shielding) when the second neighbour X of the silicon atom is substituted by tungsten. Such effect is observed for both the central SiO_4 [δ(Si*OSi) −105, δ(Si*OW) −85] and the anchored silicon atoms [δ(Si*OSi) −80,[17] δ(Si*OW) −66]. It could be related to the lower electronegativity of the tungsten atom. Small chemical shift variations (2 ppm) between SiW_{11} and $SiW_{11}(SiCH{=}CH_2)$ could be related to a second-order effect (small variations of interatomic distances or angles).

The ^{183}W NMR spectrum of $SiW_{11}(SiCH{=}CH_2)$ exhibits six peaks. Since the number and relative intensities of ^{183}W NMR resonances are characteristic of the symmetry of the polyoxometalate,[19] this spectrum is characteristic of C_s symmetry, as in SiW_{11}. This means that the symmetry of the polyoxometalate does not change upon addition of the two organosilicon groups. Moreover these two groups must be symmetrically anchored to the edges of the hole in the lacunar SiW_{11} polyoxometalate as proposed by Knoth.[10] Nonetheless,

Table 3 Results of multinuclear NMR experiments [δ refered to $SiMe_4$ for ^1H, ^{13}C and ^{29}Si, and Na_2WO_4 (2 mol dm^{-3}, pH 9) for ^{183}W], with relative intensities in square brackets

Nucleus	$SiW_{11}Si(CH{=}CH_2)$	$Si(CH{=}CH_2)(OEt)_3$	Comments
^1H		1.2 (t)	$Si(OCH_2C\mathit{H}_3)_3$
		3.8 (d)	$Si(OC\mathit{H}_2CH_3)_3$
	5.9 (m)	5.9 (m)	$C\mathit{H}_2{=}C\mathit{H}Si$
	6.1 (m)	6.1 (m)	
			ABC system
^{13}C		18.5	$Si(OCH_2\mathit{C}H_3)_3$
NBu_4		58.8	$Si(O\mathit{C}H_2CH_3)_3$
in $(CD_3)_2SO$	132.6	130.8	$\mathit{C}H_2{=}\mathit{C}HSi$
	135.3	136.5	
^{29}Si	−84.5[1]		Central SiO_4
			(−85.32 for SiW_{12})
	−66.6[2]	−60.3	$(W^1O)(W^2O)(SiO)\mathit{Si}(CH{=}CH_2)$
	$^2J(Si\text{-}W^1)$ = 5.5 Hz		−79.4 for $Si(CH{=}CH_2)(OSiMe_3)_3$[a]
	$^2J(Si\text{-}W^2)$ = 16.7 Hz		
^{183}W			SiW_{11} in D_2O[b]
	−106.1[2]		−100.8[2]
	−107.2[2]		−116.1[2]
	−112.5[1]		−121.3[1]
	−126.6[2]		−127.9[2]
	−170.8[2]		−143.2[2]
	−247.1[2]		−176.1[2]

[a] *cf.* Ref. 17. [b] *cf.* Ref. 18.

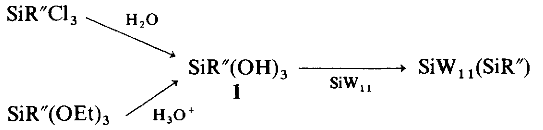
a large chemical shift up to 100 ppm compared with SiW_{11} was observed for some tungsten atoms. This could be explained by some changes in the electron distribution induced both by electronegativity changes of the silicon group or/and changes in bond angles and distances.

Discussion

Three syntheses of organically modified oxopolymetalates have been described. They have been successfully used to prepare up to 25 g of pure $SiW_{11}(SiR'')$ compounds in 80% yield (purity checked up to 99% by IR, ^{29}Si and ^{183}W NMR spectroscopy). This work shows that the trialkoxy precursors $SiR''(OEt)_3$ could be also be used for the synthesis of organically modified polyoxometalates. These precursors are less reactive towards water than chlorosilanes allowing less drastic synthesis conditions.

From the comparison of the experimental conditions, it can be assumed that the first intermediate is an hydroxylated silicon compound **1** (even in acetonitrile the amount of water is about 2%). At low pH, SiOH bonds are known to condense and form silica aggregates or $RSiO_n$ gels.[20]

Organically modified $SiW_{11}(SiR'')$ compounds are first obtained (yellow coloration) showing the greater reactivity of the SiW_{11} lacunar site. Such a reactivity is confirmed by the fact that quasi-stoichiometric conditions (molar ratio $SiR''Cl_3$:SiW_{11} = 3:1) lead mainly to $SiW_{11}(SiR'')$ (around 75% weight), and SiW_{12}, $RSiO_n$ impurities. The reaction steps are summarised in Scheme 1.



Scheme 1 Reaction steps

Accurate structural information has been obtained by using complementary spectroscopic techniques. This work shows that TOF spectrometry (^{252}Cf) is a particularly good technique to measure the molecular masses and charge of polyoxometalates. The results are in agreement with elemental analysis and results reported by Knoth[10] for $[R]^{4+}[Si_3W_{12}O_{40}R''_2]^{4-}$, where R = H^+, K^+, $NMe_4{}^+$ or $NBu_4{}^+$ and R″ = Et, $CH{=}CH_2$, $C_{10}H_{21}$ or Ph. Selection rules have been determined both in positive- and negative-ion ionization. The latter mode gives the anion mass, while the former leads to a measurement of the anion charge. Moreover, TOF spectrometry is sensitive to the relative intensity of the interactions between the polyanion and different counter cations. Highly charged small cations such as H^+ lead to strong anion–anion interactions, while tetraalkylammonium cations with low charge density lead to anion–cation interactions.[15] Fragmentation of the anions has been observed, and could provide an accurate measurement of the relative strength of the different bonds. TOF spectrometry could be a tool to measure interactions in small solid particles (clusters, colloids).

The IR spectra of the different $SiW_{11}(SiR'')$ salts show that the Keggin structure remains unaffected by the organic modification. A straightforward assignment of the different absorption bands is very difficult without any force-field calculation. However, infrared spectra appears to be an accurate analytical tool (fingerprint) to determine the purity of $SiW_{11}(SiR'')$ salts.

The ^{183}W NMR spectra show that the C_s symmetry of the lacunar Keggin polyoxometalate is conserved in the organically modified compound. An important shielding effect is observed for some W nuclei, and assigned to the presence of the electron-donor group SiR″ and to small structural changes (angles and distances). The most shielded tungsten nucleus could be certainly the closer to the organosilicon group. Experiments are in progress in order to give a better assignment of the different ^{183}W resonances.

The ^{29}Si NMR experiments give some information on the nature of the bonding of the organosilicon group. Two ^{29}Si resonances with a relative magnitude of 1:2 are observed, corresponding respectively to the silicon inside the central SiO_4 tetrahedron and to two equivalent Si atoms anchored at the surface of the oxide network. Moreover, two $^2J(SiW)$ couplings, not reported previously in the literature, have been observed. They show that second silicon neighbours (tungsten nuclei) are quite different.

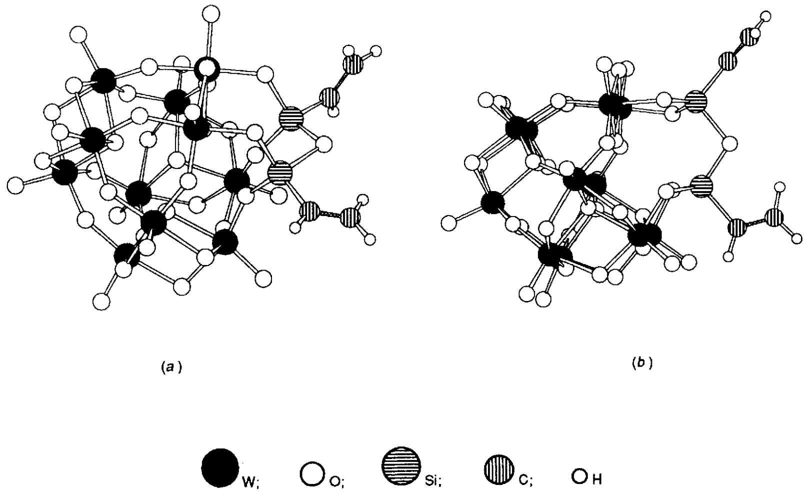


Fig. 4 Proposed structures for $SiW_{11}(SiCH=CH_2)$ (central SiO_4 tetrahedra omitted)

The packing of the lacunar SiW_{11} structure needs two SiO_4 tetrahedra, while one $TiO_5(C_5H_5)$ octahedron is sufficient to form α-$[(\eta^5-C_5H_5)TiPW_{11}O_{39}]^{4-}$.[21] Molecular models which satisfy the spectroscopic and analytical requirements are presented in Fig. 4. Both structures (*a*) and (*b*) are consistent with mass analyses, IR and ^{183}W NMR experiments, as the structural parameters (bond distances and angles) are in agreement with literature data. However, model (*a*) conserves two equivalent anchored silicon atoms, whereas (*b*) presents two silicon atoms with different shells. Therefore, in agreement with ^{29}Si NMR experiments, only model (*a*) is reliable.

Several $SiW_{11}(SiR'')$ (R'' = Et, Ph or $C_{10}H_{21}$) compounds have also been synthesised and characterised. They are isostructural with $SiW_{11}(SiCH=CH_2)$.

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