Polyoxometalates with supporting phosphate ligand: synthesis and characterization of α-[SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$ †

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A novel series of Keggin species with a covalently bonding support-ligand, formulated α-[SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$ (M = Co^{II}, Mn^{II}, Ni^{II} or Cr^{III}), have been synthesized and characterized by elemental analyses, IR, CV, NMR and X-ray powder diffraction measurements. The structure is reminiscent of an ancient Chinese three-legged wine vessel, and is a possible model for POM–nucleotide interaction. An interesting property is the different thermal behaviors for this series in comparison with those for corresponding 3d metal monosubstituted Keggin polyoxometalates. This can be attributed largely to the pendant surface ligand and H bonding interaction. Compared with α-PW$_{11}$M, the orders of line broadening of ^{31}P NMR signals are the same for the two series of complexes α-PW$_{11}$M and α-SiW$_{11}$M–PO$_4$, but both contact and dipolar interactions might make a significant contribution to the chemical shift for phosphorus for the latter.

Introduction

The studies on hybrid materials of polyoxometalates (POMs) with organic or biochemical substances have led to great achievements in recent years, as they combine both inorganic and organic merits, possess new synergy properties and have diverse applications, ranging from photo- and electrochromism, magnetism to catalysis and medicine.[1–7] Several strategies to design materials based on POMs have recently been reported, including hybrid networks based on organic polymers covalently cross-linked by heteropolyanions,[8] supramolecular compounds based on POMs,[9] n-dimensional hybrid materials based on organic polyoxometalates,[10–19] functional films and gels doped with POMs,[20–23] mesoporous materials utilizing polyoxometalate cluster/surfactant salts as precursors, and so forth.[24–26] However, immobilization of POMs has been a key problem.[27] Covalent surface modification of POMs is of great interest in view of its importance in functionalization and in immobilization.[28–33]

Since Baker's pioneering work on the fundamental class of heteropolyanions [(Y^{y-})M^{m+}O$_5$X^{x+}O$_4$(W or Mo)$_{11}$-O$_{30}$]$^{(12-m-x+y)-}$, substituted heteropolyanions have been greatly expanded either in structures or in components.[34–37] This kind of complexes has also been expanded to organic systems,[38–41] especially to the search for multifunctional materials, as for example, hybrid molecular materials combining a magnetic component with an organic conducting component.[42]

From the functionalization and immobilization point of view, we have explored an approach for the synthesis of POMs with covalently bonding pendant surface ligands, including our prior study on the interactions of ATP with 3d metal ions in the presence of the monovacant heteropoly anion α-[SiW$_{11}$O$_{39}$]$^{8-}$, which generated pyrophosphate-linked metal-substituted tungstosilicates.[43] The strategy is to cross-link the inorganic clusters and to anchor the clusters via terminal ligand-support linkages, and perhaps through H-bonding interaction, to avoid structural collapse. We report here the synthesis and characterization of a novel series of heteropoly complexes containing the support-ligand PO$_4$ from AMP, which is reminiscent of an

A= metal-phosphate complex;
B= lacunary polyoxometalate;
C= polyoxometalate with support-ligand PO$_4$.
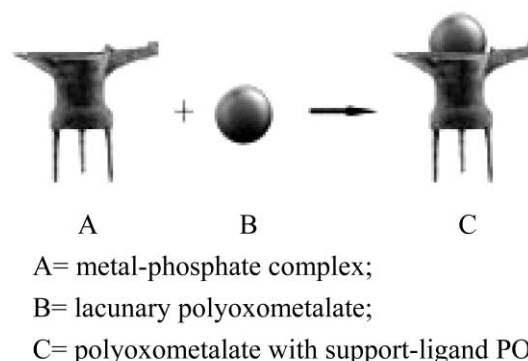
Scheme 1

ancient Chinese three-legged wine vessel, see Scheme 1, as well as being a possible model for POM–nucleotide interactions.

Results and discussion

Synthesis of α-[SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$ (M = Co^{II}, Mn^{II}, Ni^{II} or Cr^{III})

The key conditions for preparing terminally ligated phosphato complexes are the pH of aqueous solution, molecular ratio and temperature. Adenosine 5′-monophosphate sodium salt (AMP) was used as a source of support ligands. 3d transition metal ions were candidates as central atoms due to appropriate complex stability constants of M–AMP (log$K_{(M-AMP)}$ = 2–3 for M^{2+}–phosphate coordination).[44] Three kinds of metal ion binding modes in M–AMP complexes are proposed, see Fig. 1. The B and C binding modes are important in aqueous solution, and are favored modes for preparing the title compounds. A schematic representation of the primary coordination spheres of M in a monosubstituted Keggin type polyoxometalate with support-ligand (L) is shown in Fig. 1(D). The preparation route was in two steps. In the first step, the intermediate transition metal complex M–AMP was formed with a ratio M : P = 1 : 1. This requires an acidic aqueous condition (pH = 2–3) to avoid the hydrolysis of M^{n+} and the precipitation of metal phosphates. The formation of the M–AMP complex is observable
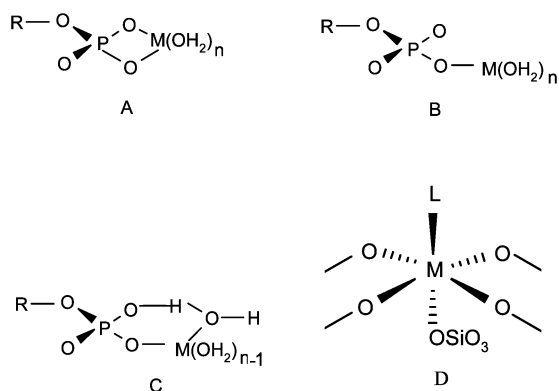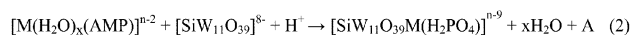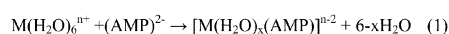
Fig. 1 (A), (B) and (C): metal ion binding modes in M–AMP complexes (reproduced from ref. 44); (D): schematic representation of the primary coordination spheres of M in monosubstituted Keggin type polyoxometalates with support-ligand (L).

via change in colors of the solutions. The complex stability will differ from one metal ion to the next. In the second step, reactive monovacant 11-tungstosilic anion coordinated to the transition metal complex M–AMP, resulting in a new complex in which an M–PO$_4$ group is bound to the monovacant 11-tungstosilic anion. This suggested that the dephosphorylation of AMP occurred during the coordinating reaction in the second step, see Scheme 2. The dephosphorylation of AMP should be more difficult than that of ATP for some transition metal ions.[44] In fact, this has been observed in some synthetic experiments: no substantial amounts of SiW$_{11}$Zn–PO$_4$ were obtained, unlike in the case of SiW$_{11}$Zn–P$_2$O$_7$ where a polyoxometalate containing Zn–AMP fragment was characterized instead.[45] The ability of dephosphorylation of AMP is in the order Co ~ Mn > Ni ~ Cr > Zn according to the yields of [SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$ obtained.

$$M(H_2O)_6^{n+} + (AMP)^{2-} \rightarrow [M(H_2O)_x(AMP)]^{n-2} + 6-xH_2O \quad (1)$$

$$[M(H_2O)_x(AMP)]^{n-2} + [SiW_{11}O_{39}]^{8-} + H^+ \rightarrow [SiW_{11}O_{39}M(H_2PO_4)]^{n-9} + xH_2O + A \quad (2)$$

A=adenosine

Scheme 2

Formulation

The results of elemental analyses suggest that the polyanions are protonated, either in the tungstate part or in the phosphate part. Empirical bond-strength–bond-length parameters are used in calculation of bond-strength sums and in prediction of hydrogen atom positions.[46–49] Possible protonation sites in the tungstate part are corner- and edge-sharing oxygen atoms (O$_{b/c}$), and possible protonation sites in the phosphate part are unshared oxygen atoms (O$_t$). The bond-strength sums calculated indicate that the basicity of oxygen is in the series O$_t$ > O$_{b/c}$. We therefore deduce that the phosphates are protonated and the complexes can be formulated as [SiW$_{11}$O$_{39}$M(L)]$^{n-}$, where L = H$_2$PO$_4^-$.

Electrophoresis is an important method to verify that M^{n+} is incorporated into the parent polyanion, and was carried out for SiW$_{11}$M–PO$_4$ (M = Co^{II} or Cr^{III}). A colored band moved toward the anode, which was purple for the Co^{II} complex and light green for the Cr^{III} complex, with nothing observed in the opposite direction for the both samples. Co(NO$_3$)$_2$ and Co$_3$(PO$_4$)$_2$ were referenced in the test, and color bands moved toward the cathode for the both samples. This suggests that M^{n+} ions were incorporated into lacunary tungstosilic anions rather than being simple counter-ions and that no observable decomposed fragments of metal phosphates were present (Fig. S1, ESI†) which also was supported by thin layer chromatography (TLC) (Fig. S2, ESI†).

IR spectra

The IR spectra of SiW$_{11}$M–PO$_4$ species are similar to those of [SiW$_{11}$O$_{39}$M(P$_2$O$_7$)]$^{7-}$, but markedly different from that of the precursor SiW$_{11}$ (Figs. S3 and S4, ESI†). The bands at ~960, ~900 and 800–700 cm^{-1} are respectively assigned to the asymmetric stretching vibrations of W–O$_d$ bonds, Si–O$_a$ bonds and W–O$_{b/c}$–W bonds,[50] and at 650–700 cm^{-1} to the stretching vibration of M–O.[51] The (W–O–W) vibrations at ~800 cm^{-1} for SiW$_{11}$M–PO$_4$ species are quite similar to those for the Keggin species SiW$_{11}$M.[52] This indicates that oxygen atoms located in the vacant positions of the anion [SiW$_{11}$O$_{39}$]$^{8-}$ have coordinated to the M^{n+} ion linking with –PO$_4$ group.

^{183}W NMR spectra

The ^{183}W NMR spectrum for SiW$_{11}$Co–PO$_4$ was measured to verify the formulation. Although six lines would be expected in ^{183}W NMR spectra for the anticipated C_s symmetry structure of α-[SiW$_{11}$O$_{39}$M(L)]$^{n-}$, only four bands are observed for SiW$_{11}$Co–PO$_4$, see Table 1 and Fig. 2. The tungsten atoms adjacent to the paramagnetic Co^{II} center presumably undergo rapid relaxation and are undetectable.[53,54]
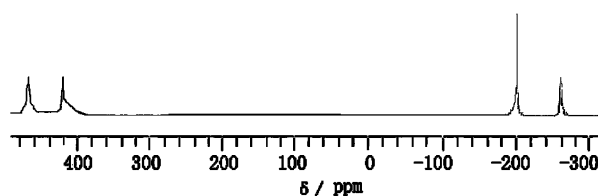

Fig. 2 ^{183}W NMR spectrum of α-[SiW$_{11}$O$_{39}$Co(H$_2$PO$_4$)]$^{7-}$.

^{31}P NMR spectra

^{31}P NMR spectroscopy is a critical method to verify phosphato complexes.[55] An expected single chemical shift is observed in each ^{31}P NMR spectrum for SiW$_{11}$M–PO$_4$ (M = Co^{II}, Mn^{II}, Ni^{II} or Cr^{III}), see Fig. 3. The data are presented in Table 2. The influence of d electrons on the terminally ligated phosphorus atoms is much less than that on the P atoms located inside the polyoxometalate cluster. Sequentially, only small downfield shifts of ^{31}P signals were observed, as in the case of α-SiW$_{11}$M–P$_2$O$_7$. It is deduced from this fact that the spread of the unpaired d electron density to the pendant surface ligand is much less than to the atoms inside the Keggin cluster. The order of line broadening is Cr^{III} (40.47 Hz) < Co^{II} (120.75 Hz) < Ni^{II} (133.24 Hz) < Mn^{II} (1828.3 Hz). Compared with α-PW$_{11}$M, the orders of line broadening are the same for the two series of complexes (α-PW$_{11}$M and α-SiW$_{11}$M–PO$_4$). Many reasons can result in line broadening. Jorris *et al.*[53] found that complexes
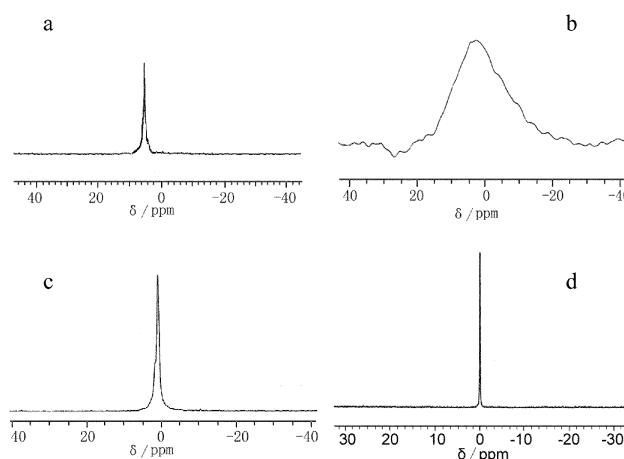
Fig. 3 ^{31}P NMR spectra of [SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$, M = Co (a), Mn (b), Ni (c) and Cr (d).

Table 1 ^{183}W NMR chemical shifts (from 1 M Na$_2$WO$_4$) for SiW$_{11}$Co–L, L = PO$_4$ or P$_2$O$_7$ (297 K, saturated solution of K salts in D$_2$O, ppm)

Complex	δ/ppm				Ref.
α-SiW$_{11}$Co–PO$_4$	461.00	413.89	−205.63	−266.74	This work
α-SiW$_{11}$Co–P$_2$O$_7$	457.47	412.15	−220.02	−283.32	This work
α-SiW$_{11}$Co–D$_2$O	437.6	390.2	−222.2	−280.2	53

Table 2 ^{31}P NMR chemical shifts (from 85% H$_3$PO$_4$) and line widths ($\Delta v_{1/2}$) for [SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$ (at 298 K, in DMSO)

Complex	δ/ppm	$\Delta v_{1/2}$/Hz	Ref.
α-[SiW$_{11}$O$_{39}$Co(H$_2$PO$_4$)]$^{7-}$	+3.732	120.75	This work
α-[SiW$_{11}$O$_{39}$Mn(H$_2$PO$_4$)]$^{7-}$	+2.521	1828.3	This work
α-[SiW$_{11}$O$_{39}$Ni(H$_2$PO$_4$)]$^{7-}$	+0.973	133.24	This work
α-[SiW$_{11}$O$_{39}$Cr(H$_2$PO$_4$)]$^{6-}$	+0.96078	40.47	This work
α-[PW$_{11}$O$_{39}$Co(D$_2$O)]$^{5-}$	+458	28	53
α-[PW$_{11}$O$_{39}$Ni(D$_2$O)]$^{5-}$	+472	1650	53

Table 3 Cyclic voltammetry data (in V^a) for [SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$

Complex	E_{pc}	E_{pa}	E_{pc}	E_{pa}	ΔE_{pc}
α-SiW$_{11}$Co–PO$_4$	−0.828	−0.792	−0.976	−0.934	0.148
α-SiW$_{11}$Mn–PO$_4$	−0.854	−0.816	−0.970	−0.926	0.116
α-SiW$_{11}$Ni–PO$_4$	−0.830	−0.760	−0.960	−0.900	0.130
α-SiW$_{11}$Cr–PO$_4$	−0.780	−0.708	−0.956	−0.908	0.176

^{a} HAc–NaAc buffer solution, pH = 4.7; scan rate, 100 mV s^{-1}.

containing paramagnetic ions with orbitally non-degenerate ground states gave very broad ^{31}P signals. The electronic ground states of the paramagnetic ions in octahedral geometry are as follows: Cr^{III} (^{4}A$_{2g}$), Co^{II} (^{4}T$_{1g}$), Ni^{II} (^{3}A$_{2g}$) and Mn^{II} (^{6}A$_{1g}$). Although Cr^{III} and Ni^{II} have orbitally non-degenerate ground states, the narrow line widths might be attributed to sizable configurational interaction of the singlet ground state and a triply degenerate excited state.[56] The chemical shift mechanism for the P atoms in the pendant phosphato species might quite different from that in the monosubstituted Keggin species that is primarily of a contact shift character, according to the criterion that a pure contact shift mechanism would result in the ratios of the changes in line widths being proportional to the square of the ratios of the corresponding changes of chemical shifts.[53,57] Therefore it is deduced that both contact and dipolar interactions might make significant contributions to the chemical shift mechanism for P.

Cyclic voltammetry

Cyclic voltammetric and polarographic behaviors of the phosphoric derivatives show no remarkable differences compared with the precursor α-SiW$_{11}$, showing two clearly resolved two-electron reductions of the polytungstate "ligand". CV data for SiW$_{11}$M–PO$_4$ are listed in Table 3 and curves are shown in Fig. 4. Generally, the differences between the first and the second reduction waves for SiW$_{11}$M–L (L = PO$_4$ or P$_2$O$_7$), where transition metal ions are in +2 oxidation state, are 15–40 mV less than that for α-SiW$_{11}$(ΔE_{pc} = 160 mV) due to lower repulsion energy in the −7 charged SiW$_{11}$M–L polyanions than in the −8 charged SiW$_{11}$ polyanion. They therefore are expected to generate a new series of heteropoly blues, giving rise to mixed-valence species in which delocalized electrons may coexist and interact with localized magnetic moments.[58] In consideration that transition metal monosubstituted Keggin anions have been used in many catalytic reactions, polyoxometalates with support-ligands without sizable change in oxidation properties should be promising species in catalytic applications.
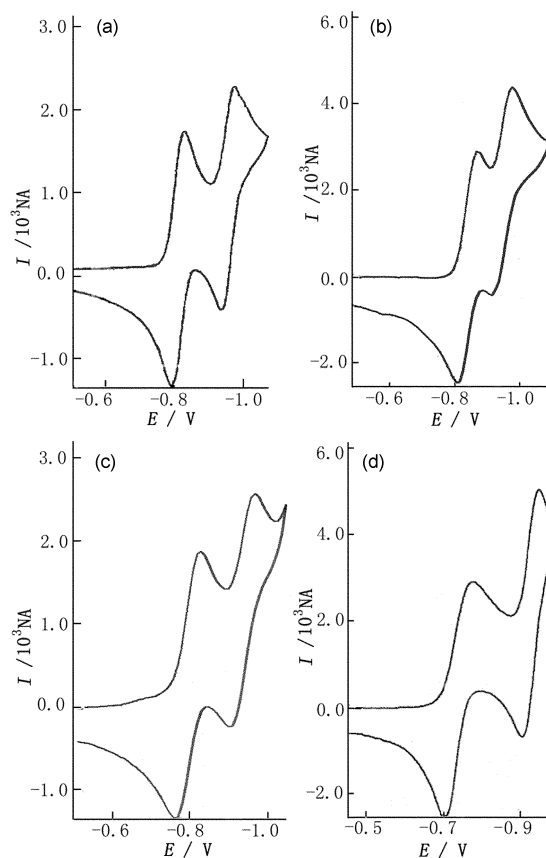
Fig. 4 Cyclic voltammetry of [SiW$_{11}$O$_{39}$M(H$_2$PO$_4$)]$^{n-}$, M = Co (a), Mn (b), Ni (c) and Cr (d).

Thermal stability

Thermal gravimetric analysis for SiW$_{11}$Co–PO$_4$ was performed and the TG-DTA graph is shown in Fig. S5 (ESI†). There are two strong endothermal peaks below 300 °C in the DTA curve corresponding to the loss of water of hydration and a strong endothermal peak at 750 °C corresponding to a phase transformation of the decomposed sample. Polyoxometalates with or without the support-ligand PO$_4$ exhibit different thermal behavior. The former series seems to be more stable under calcination. This was most obvious for the SiW$_{11}$Co/SiW$_{11}$-Co–PO$_4$ complexes than for the others due to significant changes in their color in calcination. When SiW$_{11}$Co and SiW$_{11}$Co–PO$_4$ powders were put separately in a ceramic plate and calcined in an oven at *ca.* 520 °C for 30 min, the former changed in color from red to green and became insoluble in water, whereas the latter showed little change either in color (Fig. 5) or in solubility (Fig. S6, ESI†) as well as IR spectrum (Fig. S7, ESI†). It is evident that SiW$_{11}$Co–PO$_4$ is more stable than SiW$_{11}$Co under calcination. Experiments showed that observable decomposition did not occur until above 600 °C for SiW$_{11}$Co–PO$_4$. This phenomenon is also observed for SiW$_{11}$Co–P$_2$O$_7$. This suggests that the increased thermal stability is attributed largely to the pendant surface ligand –H$_2$PO$_4$ or –H$_3$P$_2$O$_7$ in this species, and possibly also to H-bonding interaction. This is of interest from the viewpoint of immobilization of POMs, as well of distinction between the
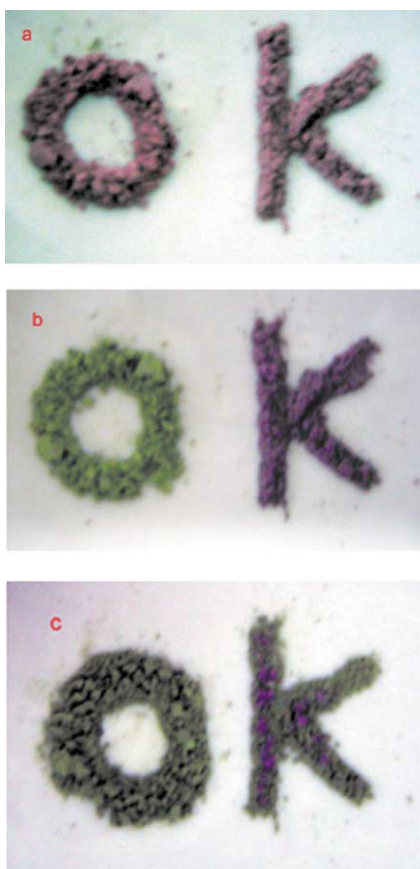
Fig. 5 Photographs for $SiW_{11}Co$ (letter "O") and $SiW_{11}Co-PO_4$ (letter "K"): (a) both O and K were red before heating, (b) the letter O became green and the letter K red after calcination at 520 °C for 30 min, (c) both O and K become green after calcination at 600 °C.

two series of complexes $SiW_{11}M$ and $SiW_{11}M-L$ (L = $-H_2PO_4$ or $-H_3P_2O_7$).

X-Ray powder diffraction

Our endeavor to obtain structural resolution by single-crystal X-ray diffraction for any of the species was unsuccessful. X-Ray powder diffraction patterns were then measured for $SiW_{11}M-PO_4$ (M = Co^{II}, Mn^{II} or Ni^{II}). 2θ Data and indexation are presented in Tables S1–3 (ESI†). Their X-ray patterns are almost identical and show a characteristic pattern of the Keggin crystal structure (Fig. S8, ESI†).

Experimental

Synthesis

$K_8[SiW_{11}O_{39}]\cdot13H_2O$ (SiW_{11}). This was prepared according to the literature method[59] and identified by its IR spectrum and cyclic voltammetry. All common laboratory chemicals were of reagent grade. AMP was a Sigma product.

$K_4H_3[SiW_{11}O_{39}Co(H_2PO_4)]$ ($SiW_{11}Co-PO_4$). In a typical process, AMP (0.5 g, 1.4 mmol) was dissolved in 30 mL of water, then 0.5 g of $Co(NO_3)_2\cdot6H_2O$ (1.7 mmol) was added under stirring and heating for 10 min in a bath of 85 °C, pH = 2.6. When the color of the solution changed from pink to purple, 3.2 g of SiW_{11} (1.0 mmol) were added. After heating for another 10 min the solution was filtered. A red precipitate (4 g, 1.2 mmol) was isolated from the filtrate upon addition of 1 g of KCl and a solution of water–acetone (1 : 1, v/v). The red powder was recrystallized from aqueous KCl–acetonitrile (3 : 1), and purple needle crystals were harvested after several days. Elemental analysis: calc. (found) for $K_4H_3[SiW_{11}O_{39}Co(H_2PO_4)]\cdot15H_2O$ (%): K, 4.78 (4.54); Co, 1.81 (1.75); P, 0.95

(0.92); W, 62.05 (60.26); weight loss of water on heating, 8.28 (8.56). IR (cm^{-1}): 1000w, 958s, 901s, 808s, 755sh, 696s and 525s.

The preparation procedure for the following complexes was similar to that for $SiW_{11}Co-PO_4$. For details see ESI.†

$K_4H_3[SiW_{11}O_{39}Mn(H_2PO_4)]$ ($SiW_{11}Mn-PO_4$). Elemental analysis: calc. (found) for $K_4H_3[SiW_{11}O_{39}Mn(H_2PO_4)]\cdot11H_2O$ (%): K, 4.90 (5.02); Mn, 1.73 (1.80); P, 0.97 (0.94); W, 63.58 (62.34); weight loss of water on heating, 6.22 (6.30). IR (cm^{-1}): 998w, 955s, 904s, 815s, 705s and 538s.

$K_5H_2[SiW_{11}O_{39}Ni(H_2PO_4)]$ ($SiW_{11}Ni-PO_4$). Elemental analysis: calc. (found) for $K_5H_2[SiW_{11}O_{39}Ni(H_2PO_4)]\cdot8H_2O$ (%): K, 6.15 (6.27); Ni, 1.86 (1.78); P, 0.98 (0.93); W, 63.78 (62.86); weight loss of water on heating, 4.54 (4.64). IR (cm^{-1}): 999w, 957s, 904s, 788s, 700s and 522s.

$K_3H_3[SiW_{11}O_{39}Cr(H_2PO_4)]$ ($SiW_{11}Cr-PO_4$). Elemental analysis: calc. (found) for $K_3H_3[SiW_{11}O_{39}Cr(H_2PO_4)]\cdot10H_2O$ (%): K, 3.75 (4.00); Cr, 1.67 (1.54); P, 0.99 (0.94); W, 64.76 (63.39); weight loss of water on heating, 5.76 (5.64). IR (cm^{-1}): 1006w, 965s, 916vs, 786vs, 673w and 524s.

Physical measurements

Elemental analyses were carried on a Plasma-Spec(I) ICP emission spectrometer for W, P, Si and transition metal elements and on a PE-3030 atomic absorption spectrophotometer for K. Water weight losses were determined by calcination in an oven for 15 min at *ca.* 300 °C for each sample and as well as by thermal analyses on a NETZSCH STA 449c thermal analyzer for $SiW_{11}Co-PO_4$. IR spectra were recorded on a FTS-7 spectrophotometer with KBr pellets and cyclic voltammograms on a 384B polarographic analyzer with 303A electrodes. NMR spectra were taken on a Bruker AMX 400 MHz NMR spectrometer. NMR chemical shifts for ^{31}P and ^{183}W were referenced to 85% H_3PO_4 and $Na_2WO_4\cdot2H_2O$, respectively. X-Ray powder diffraction measurements were carried on a D/max-IIIC X-ray diffractometer.

Electrophoresis

Solutions of $SiW_{11}Co-PO_4$, $SiW_{11}Co$, $Co(NO_3)_2$ and $Co_3(PO_4)_2$ (a small amount of dilute H_3PO_4 was added to fully dissolve the sample) were loaded onto the holes located in the middle of an agarose gel (1%) plate and the gel was just submerged in a solution of NaAc (pH 5.0). Electrophoresis was carried out under 80 V for about 5–10 min when colored bands for the four samples were observed separately running in opposite directions. The same experiment was performed for $SiW_{11}Cr-PO_4$.

Thin layer chromatography (TLC)

TLC was performed in a mixed solvent of methanol–ammonia–brombutanoic acid–water (50 : 15 : 5 : 30) for $Co_3(PO_4)_2$, $SiW_{11}Co$ and $SiW_{11}Co-PO_4$. Photographs were taken after 40 min immersion with a thin-layer plate of Al_2O_3.

Conclusion

A novel series formulated as $\alpha-[SiW_{11}O_{39}M(H_2PO_4)]^{n-}$ (M = Co^{II}, Mn^{II}, Ni^{II} or Cr^{III}) has been synthesized in two steps from precursor $\alpha-SiW_{11}$ and M-AMP complexes. The dephosphorylation of AMP occurred during coordinating reaction in the second step, leaving the PO_4 group as a pendant support-ligand. When NaH_2PO_4 was used as a support-ligand, substantial amounts of $[SiW_{11}O_{39}M(H_2PO_4)]^{n-}$ were obtained only for M = Co^{II} or Mn^{II} complexes, suggesting that $H_2PO_4^-$ is a poor ligand in comparison with AMP. This procedure provides a way to functionalize POMs and to prepare hybrid materials. A significant property is the increased thermal stability† in these

species compared with the corresponding transition metal monosubstituted Keggin polyanions. This is an interesting from the viewpoint of immobilization of POMs, as well as of distinction between the two series of $SiW_{11}M$ and $SiW_{11}M–L$ (L = $–H_2PO_4$ or $–H_3P_2O_7$). In addition, POMs containing pendant surface ligands, such as phosphato or pyrophosphato group, have great potential in the syntheses of hybrid materials and in functionallization for POMs. This novel series of complexes is expected to have the ability to anchor clusters on matrices *via* terminal phosphato group-support linkages and H-bonding. Further research on these aspects is underway. As a possible model reaction for POM–nucleotide interaction, this study will be also of significance in biochemistry.[60]

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