Investigation of the thermal decomposition of some metal-substituted Keggin tungstophosphates

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Abstract

The thermal decomposition of the tetrabutylammonium (TBA) salts $(TBA)_4H_3[PW_{11}O_{39}]$ and $(TBA)_4H_x$-$[PW_{11}M(H_2O)O_{39}]\cdot nH_2O$, $x = 3$-(oxidation number of M), M = Mn(II), Co(II), Ni(II), Cu(II) or Fe(III), $n = 0$–3, has been studied by thermal analyses and the decomposition products identified by powder X-ray diffraction, FTIR and NMR spectroscopy. The organic cation started to decompose in the 150–200°C range. The release of the metal M from the substituted polyoxoanions accompanied the initial degradation of the organic cations and $[PW_{12}O_{40}]^{3-}$ was formed as an intermediate at ca. 300°C. For a comparison, the thermal decomposition of $(TBA)_3[PW_{12}O_{40}]$ was also investigated. The thermal decomposition of the potassium salts of the lacunary and metal-substituted anions was also studied, but the formation of $[PW_{12}O_{40}]^{3-}$ was not observed. The temperature of decomposition of the $[PW_{11}M(H_2O)O_{39}]^{(4+x)-}$ anions was at least 150°C higher for the potassium than for the tetrabutylammonium salts. This study exemplified that the thermal stability of some Keggin anions was dependent on the counter-cation present. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heteropolytungstates of the Keggin type constitute an interesting group of compounds which have found applications in a variety of fields, such as catalysis, medicine, etc. [1–3]. This large class of anions includes the parent Keggin anions, $[XW_{12}O_{40}]^{n-}$, (X = P, As, B, Si, Ge and several metals), their lacunary derivatives and their metal complexes [1]. It is generally recognised that these heteropolyanions resemble fragments of close-packed metal oxide lattices [2]. Understanding their properties and reactivity

in different types of compounds seems to be highly desirable.

Transition-metal-substituted polyoxometalates of the general formula $[XW_{11}M(H_2O)O_{39}]^{n-}$, where (X = P or Si, and M = first row transition metal), have recently attracted considerable attention due to their potential use as homogeneous catalysts for oxidation with a variety of oxidants and substrates [4–8]. These anions, first described in the late sixties [9–11] are readily accessible. To ensure the solubility in the organic solvents convenient to some catalytic studies, several tetralkylammonium salts have been prepared either by precipitation or by phase-transfer processes [8]. A systematic study of these salts, however, has not been made.

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Despite the fact that the thermal robustness of Keggin-type anions is frequently mentioned, the thermal stability of their compounds seems to vary considerably, being dependent upon the type of transition metal in the structure and the nature of the counter-cation, among other factors [12]. However, except for studies of the parent Keggin compounds, reports on the thermal stability of different salts of Keggin polyoxotungstates are scarce.

In this work, we present our studies on the thermal decomposition of the tetrabutylammonium (TBA) salts of the $[PW_{11}M(H_2O)O_{39}]^{(7-m)-}$ anions ($m =$ oxidation number of M, M(II) = Mn, Co, Ni, Cu or M(III) = Fe) and $(TBA)_4H_3[PW_{11}O_{39}]$. The thermal decomposition of these salts occurs via the formation of the parent Keggin anion, $[PW_{12}O_{40}]^{3-}$, which is contrary to what is observed for the corresponding potassium salts. The thermal stability of these anions is strongly dependent on the counter-cations present, and the temperature of decomposition of the $[PW_{11}-M(H_2O)O_{39}]^{(7-m)-}$ anions is at least 150°C higher for the potassium than for the tetrabutylammonium salts. The decomposition follows different pathways.

For comparison, the thermal decomposition of $(TBA)_3[PW_{12}O_{40}]$ has also been investigated, the thermogravimetric behaviour of this compound was briefly described for identification purposes [13]. Studies on the thermal stability of the $[PW_{12}O_{40}]^{3-}$ anion, on a variety of metal [14–16] or alkylammonium [17] salts have also been reported. At least one report can be found for the transition-metal-substituted tungstophosphates [18], but none, to our knowledge, concerning the tetraalkylammonium salts. The abbreviations $PW_{11}M$, PW_{11} and PW_{12} will be used for the anions α-$[PW_{11}M(H_2O)O_{39}]^{(7-m)-}$, α-$[PW_{11}O_{39}]^{7-}$, and α-$[PW_{12}O_{40}]^{3-}$, respectively.

2. Experimental section

2.1. Sample synthesis

All chemicals were used as received from suppliers. The following compounds were prepared by the methods reported in the literature, namely $(TBA)_3$-$[PW_{12}O_{40}]$ [13], $K_7[PW_{11}O_{39}]\cdot 7H_2O$ [19], $K_5[PW_{11}$-$M(H_2O)O_{39}]\cdot nH_2O$ (M = Mn, $n = 13$, M = Co, $n = 12$, M = Ni, $n = 11$, M = Cu, $n = 13$) [20–22], and $K_4[PW_{11}Fe(H_2O)O_{39}]\cdot 6H_2O$ [23].

$(TBA)_4H_x[PW_{11}M(H_2O)O_{39}]\cdot nH_2O$, where M = Mn, Co, Ni, Cu and $x = 1$ and also M = Fe and $x = 0$ were prepared by cation metathesis in aqueous solutions. To a solution of $K_{4+x}[PW_{11}M(H_2O)O_{39}]$ (10^{-3} mol in 50 cm^3) at 70°C, an excess of (TBA)Br (5×10^{-3} mol in 25 cm^3) was gradually added. After filtration, the precipitate was washed with water and absolute ethanol (M = Cu) or re-crystallised from acetonitrile by the addition of water. These compounds provided analytical results consistent with their formulations, as indicated below. The values of the total weight loss (substracted the corresponding hydration water) observed during the thermogravimetric analysis (as a mass percentage, %TG) as well as infrared spectroscopy data and solid–liquid phase transition temperature are presented:

α-$[(C_4H_9)_4N]_4H[PW_{11}Mn(H_2O)O_{39}]\cdot 3H_2O$. %TG, 28.1 (27.8). IR (cm^{-1}): 1073 (sh), 1057 (s), 955 (vs), 887 (s), 811 (vs), 724 (s), 592(w). Solid–liquid phase transition (with decomposition) at 295°C.

α-$[(C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]\cdot 2H_2O$. %TG, 27.2 (27.4). IR (cm^{-1}): 1063 (s), 956 (vs), 888 (s), 818 (vs), 720 (s), 593(w). Solid–liquid phase transition (with decomposition) at 300°C.

α-$[(C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]\cdot H_2O$. %TG, 27.8 (27.5). IR (cm^{-1}): 1065 (s), 956 (vs), 888 (s), 812 (vs), 722 (s), 593(w). Solid-liquid phase transition (with decomposition) at 305°C.

α-$[(C_4H_9)_4N]_4H[PW_{11}CuO_{39}]$. %TG, 27.6 (27.2). IR (cm^{-1}): 1101 (s), 1067(s), 960 (vs), 884 (s), 813 (vs), 739 (s), 700(s), 596(w). Evidence for the absence of water co-ordinated to the copper ion in this compound is presented elsewhere [24].

α-$[(C_4H_9)_4N]_4[PW_{11}Fe(H_2O)O_{39}]\cdot 2H_2O$. %TG, 27.0 (27.1). IR (cm^{-1}): 1069 (s), 961 (vs), 884 (s), 809 (vs), 698 (m), 594(w).

A similar method was used to prepare α-$[(C_4H_9)_4N]_4H_3[PW_{11}O_{39}]$. Its IR spectrum was in agreement with that found in the literature [25]. No solid–liquid phase transition was observed.

2.2. Physical measurements

Thermogravimetric analyses (TG) were carried out in air between 30° and 700°C at a heating rate of

$10^{\circ}C\ min^{-1}$, on a Mettler M3 thermobalance equipped with a TC 10 A microprocessor. DSC determinations were made in the 30–550°C range, on a Shimadzu DSC-50 differential scanning calorimeter at $10^{\circ}C\ min^{-1}$, using α-Al_2O_3 as reference. Air access was ensured by pinholes on the container lid.

The water content (water of hydration) was determined from the weight loss up to 100–110°C. The total weight loss was determined by TG on heating to 700°C, assuming a residue with the formula $11WO_3 \cdot 1/2P_2O_5 \cdot MO_{x/2}$. Samples calcined in an oven at 700°C for 3 h were used for the identification of the main components of the final decomposition products.

Infrared spectra were recorded on a Mattson 7000 FTIR spectrometer. The spectra of all compounds were obtained in KBr pellets after heating in the TG ended at different preset temperatures up to 700°C. Some compounds were studied with a Specac variable high-temperature cell (25–450°C) with AgCl windows, equipped with a Eurotherm temperature controller. The results of both these techniques were similar.

^{31}P and ^{1}H NMR spectra were carried out in 5-mm tubes on a Bruker AMX 300 spectrometer. ^{31}P spectra were recorded using 85% aqueous H_3PO_4 as external reference.

X-ray powder diffraction patterns were measured on a Rigaku D/Max III instrument, using CuK_α radiation, in the 3<2θ<50° range.

Solid–liquid phase-transition temperatures were determined on a Richart Thermovar microscope (up to 320°C).

3. Results and discussion

3.1. Characterisation of the compounds by infrared spectroscopy

The TBA salts $(TBA)_4H_x[PW_{11}M(H_2O)O_{39}]$, M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, x = 1, Fe^{III}, x = 0, have been prepared by several authors, mainly for catalytic studies of the anions in organic media [8], but structural studies have not generally been reported or are incomplete.

The infrared spectra of the TBA salts of the metal-substituted anions show absorption bands typical of the metal-substituted Keggin tungstophosphate anions

in the 700–1100 cm^{-1} range [26] (see Section 2). (the position of the $\nu(W–O_t)$ bands (O_t = terminal oxygen) between 955–961 cm^{-1} is slightly shifted to lower wave numbers compared to the corresponding potassium salts, the difference being 4–7 cm^{-1} and much smaller than that observed with the parent Keggin compound [13].

The P–O stretching vibrations of the central phosphate group are known to give rise, usually, to one or two bands in the Keggin-type anions (observed at 1050–1100 cm^{-1}). The only band observed in the spectrum of $[PW_{12}O_{40}]^{3-}$ is split into two for the lacunary or for metal-substituted anions, due to the decrease in symmetry. The splitting ($\Delta\nu$) of the ν_3 asymmetric stretch vibration frequencies of the phosphate moiety of the $PW_{11}M$ anions is less pronounced for these TBA than for the corresponding potassium compounds [26,27], being only observed for the compounds with M = Cu or Mn. The value of the splitting, $\Delta\nu$, reflects the alteration of symmetry around the central PO_4 moiety. Comparison of the values of $\Delta\nu$ observed for a series of related anions with different M may provide an indirect measure of the strength of the interaction of the metal M with the oxygen of the central PO_4 group [26]. This is the case of the potassium salts of the $PW_{11}M$ anions [26,27]. For other series, like the potassium salts of similar $[PMo_{11}M(H_2O)O_{39}]^{(7-m)-}$ anions [26] or the related Dawson anions $[P_2W_{17}M(H_2O)O_{61}]^{n-}$ [27], the values of $\Delta\nu$ are much smaller. This fact has been attributed to a larger degree of flexibility of these anions [26]. In the case of the potassium salts of $[PMo_{11}-M(H_2O)O_{39}]^{(7-m)-}$, it has been reported that no splitting is observed for M = Ni(II), Fe(III) and Co(II); only a small one for Mn(II) and a larger one for Cu^{II} [26], exactly as we have found for the referred TBA tungstophosphates we have studied.

The mean value of the two $\nu(PO_4)$ frequencies, on the other hand, has been found to be related to the strength of the PO bonds [28]. In our study, no noticeable difference could be observed between the TBA and K^+ salts. In view of these facts, we consider that we may not infer, from the smaller splitting observed, that a stronger metal–oxygen (PO_4) bond exists for the studied TBA than for the corresponding K salts. We can, however, conclude that the counter-cation seems to have influence in the restoration of symmetry of the polyanion. For the PW_{12} anion, the P–O stretching

vibration is insensitive to the size of the counter-cation [13,15]; therefore, size effects cannot, possibly, be held responsible for the observed difference. Hydrogen bonding in the crystals has, certainly, a different influence in the heavily hydrated potassium salts and in the TBA compounds, and the so-called greater rigidity of the tungsten anions may, then, be dependent on the H-bonding interactions. The lack of crystal structures of this type of compounds prevents, in our opinion, a clear assessment of the influence of the, possibly involved, several electronic and steric effects.

All the prepared $(TBA)_4H_x[PW_{11}M(H_2O)O_{39}]$ compounds are isostructural, crystallising with a cubic lattice with a values in the range referred by Coronado et al. [29] for M=Ni(II), Co(II), and Mn(II). This structure is different from that of the corresponding potassium salts [27,30].

3.2. Thermal decomposition studies

The thermal stabilities of all TBA compounds were studied by TG and DSC and the decomposition products analysed by infrared, ^{31}P and ^{1}H NMR spectroscopy as well as X-ray diffraction.

The thermograms of the PW_{11} and $PW_{11}M$ compounds show a weight loss corresponding to the loss of water of hydration at temperatures below 100–110°C, and several other steps (3–4) between 150° and 650°C, due to the TBA and polyoxotungstate decomposition. The onset of the TBA decomposition varies with the compound under consideration (Table 1) but at least 70% of the total weight loss takes place below 450°C (over 90% for the $PW_{11}Cu$) and 80% up to 500°C.

The thermal decomposition of the cation of $(TBA)_3[PW_{12}O_{40}]$ starts at a higher temperature ($\cong310°C$) than the lacunary and metal-substituted compounds. The infrared spectra of $(TBA)_3$-$[PW_{12}O_{40}]$, after thermogravimetric analysis, showed that the anion started to decompose at $\approx450°C$ and was totally destroyed at 600°C. The infrared spectrum suggests the presence of WO_3 in the residue [31]. The total weight loss was consistent with decomposition to a mixture of oxides. Investigation of the X-ray diffraction pattern of the residue of calcination at 700°C using JCPDS-ICDD files showed the presence of the tetragonal phase of tungsten trioxide doped with P_2O_5. This was identified in the decomposition of $H_3[PW_{12}O_{40}]\cdot6H_2O$ [32].

Table 1
Temperatures (°C) of decomposition of PW_{11} and $PW_{11}M$ anions in different salts

Anion	TBA salts, decomposition interval [a]	TBA salts, formation of PW_{12} [b]	K salts [c]
PW_{11}	200–584	300	450
$PW_{11}Mn$	150–592	310	480
$PW_{11}Co$	163–603	310	500
$PW_{11}Ni$	190–644	320	450
$PW_{11}Cu$	186–508	280	460
$PW_{11}Fe$	193–562	290	550

[a] Minimum value corresponds to the onset of decomposition of the organic part.
[b] Minimum temperature to end TG and detect only PW_{12} in the residue by infrared spectroscopy.
[c] Maximum limit of stability.

In the case of PW_{11} and $PW_{11}M$ compounds, the infrared spectra were obtained after completion of the TG analysis at different preset temperatures (up to 700°C) or the spectra were obtained at different temperatures up to 450°C with a variable temperature cell. In all the cases, no significant changes were observed in the infrared spectra of the compounds heated to 250°C, except for the loss of water.

The spectra of the TBA salts of PW_{11} and of some $PW_{11}M$ showed the splitting of the $\nu_{as}(P–O)$ vibration [26,27], but others did not show this. Therefore, two different situations were found to occur. When the spectra have two bands due to the asymmetric stretching of the P–O bonds, the splitting disappears on heating to a minimum temperature in the 280–310°C range, the specific temperature varying with the salt considered (see Table 1) and where one band at ca. 1080 cm^{-1} was observed (see Figs. 1 and 2). When the infrared spectra of the $PW_{11}M$ compounds have only one $\nu(P–O)$ band, this band shifted from the original position at 1063–1070 cm^{-1} to 1080 cm^{-1} on heat treatment. In all the cases, the frequencies observed for other infrared bands coincided with those of $(TBA)_3[PW_{12}O_{40}]$ [13]. These facts suggest the presence of PW_{12} in the residue. The 1080–1081 cm^{-1} band is characteristic of the PW_{12} anion and it appeared in the spectra of several compounds (acid, Na, K, NH$_4$, and other salts) [13–15].

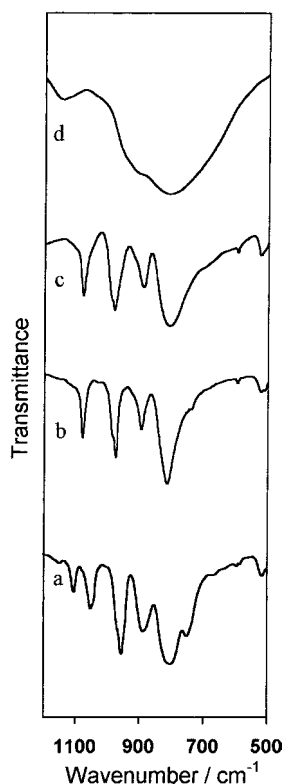The formation of the PW_{12} anion as an intermediary in the decomposition of PW_{11} and $PW_{11}M$ was con-

Fig. 1. IR spectra of $(TBA)_4H_3[PW_{11}O_{39}]$ (A), and after heating to $T = 300°C$ (B), $T = 400°C$ (C) and $T = 600°C$ (D).

Fig. 2. IR spectra of $(TBA)_4H[PW_{11}CuO_{39}]$ (A), and after heating to $T = 300°C$ (B), $T = 400°C$ (C) and $T = 500°C$ (D).

firmed by the ^{31}P NMR spectra of the acetonitrile soluble fraction of the residue obtained after calcination in the 300–350°C range. The amounts which dissolved in acetonitrile depended on the original compound and on the heating temperatures. These residues, being amorphous, could not be studied by powder X-ray diffraction. ^{31}P NMR spectra of the acetonitrite solutions of $(TBA)_3[PW_{12}O_{40}]$ and $(TBA)_4H_3[PW_{11}O_{39}]$ showed one peak at -14.2 and -12.1 ppm, respectively [33,34]. The ^{31}P NMR spectra of the soluble portion of the decomposition products showed only one narrow peak at -14.1 to -14.2 ppm (Fig. 3) when the transformation was complete. The corresponding ^{1}H NMR spectra showed four multiplets (centred at ca. 3.11, 1.62, 1.38 and 0.99 ppm), assigned to the protons of TBA on comparison with the spectra of the PW_{12} or PW_{11} salts of this cation.

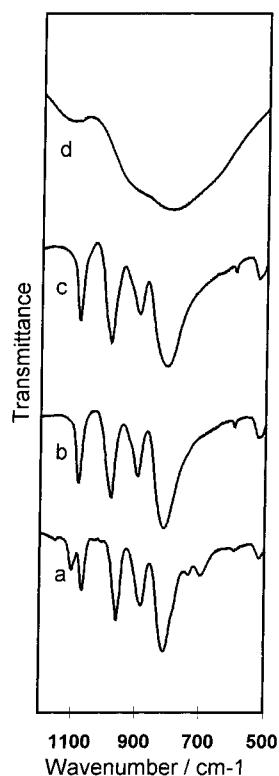^{1}H NMR spectra of the acetonitrile solutions obtained from samples (M = Cu, Mn) heated to

425°C showed that no organic cations remain; however, NH_4^+ could be detected in low concentrations, corresponding to a triplet at $\delta = 6.0$ ppm ($J_{N-H} = 53.2$ Hz).

The beginning of the decomposition of the intermediate PW_{12} anion, to what is possibly a final mixture of oxides, occurs at temperatures near 450°C and its complete degradation is observed at temperatures >500°C. The presence of WO_3 in the final residue is deduced from the infrared spectra [31] (Figs. 1 and 2) and confirmed by the powder X-ray diffraction pattern of the products obtained after calcination at 700°C. Orthorhombic WO_3 was the only compound identified, using the JCPDS-ICDD data [32], in the decomposition products of the $PW_{11}M$ compounds (due to the small amounts present, the fate of the metal M and of P could not be determined). The final product of decomposition of the lacunary TBA compound is the same tetragonal phase of tungsten trioxide doped with P_2O_5 [32] as obtained in the
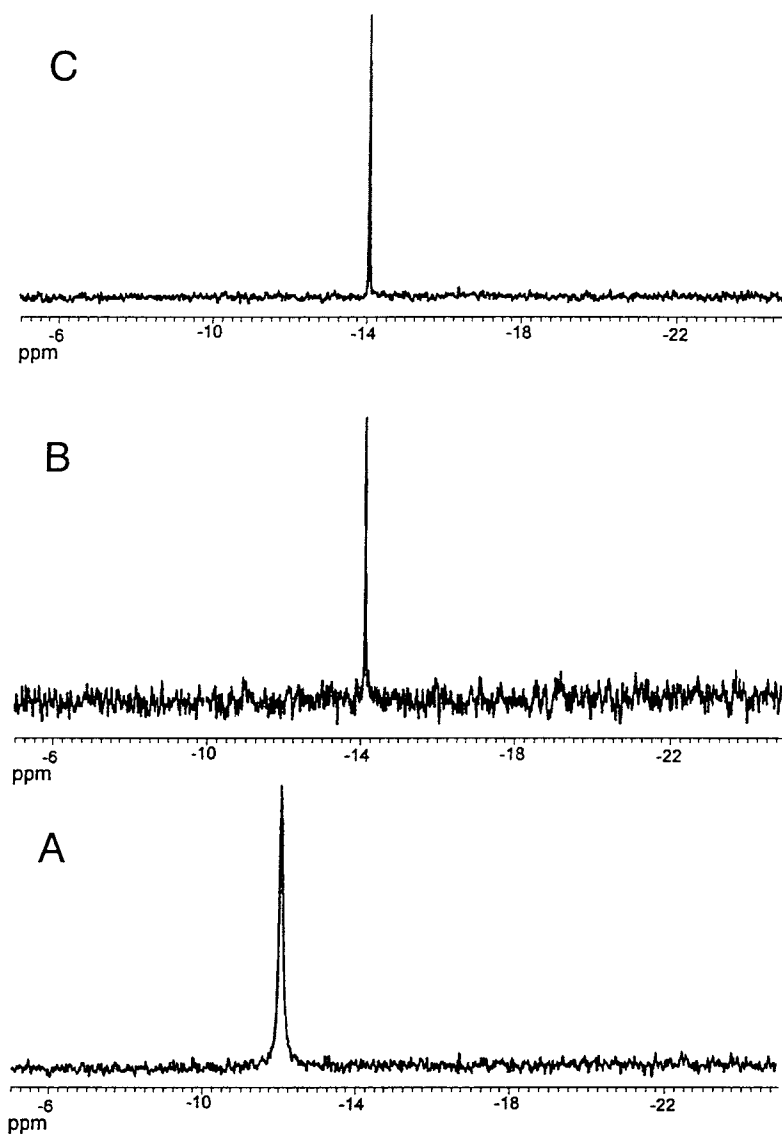
Fig. 3. ^{31}P NMR spectra of the acetonitrile solution of $(TBA)_4H_3[PW_{11}O_{39}]$ (A), and the soluble part of the residue after heat treatment to $T = 340°C$ of $(TBA)_4H_3[PW_{11}O_{39}]$ (B) and $(TBA)_4H[PW_{11}Co(H_2O)O_{39}]$ (C).

decomposition of the $(TBA)_3[PW_{12}O_{40}]$, referred to above.

DSC experiments up to 550°C were performed on all the compounds. The decomposition of $(TBA)_3[PW_{12}O_{40}]$ produced two strong exotherms, centred at 417° and 486°C. These are attributed to the decomposition, in air, of the organic cation and the final degradation of the anion (Fig. 4). A similar behaviour was observed for all other compounds

(except $PW_{11}Ni$), with only small changes in the position of the exotherms (see Table 2). The solid–liquid phase transition observed by microscopy in some of the compounds at temperatures <320°C, namely for M = Mn, Co, Ni, was possibly responsible for a weak endotherm in the 300–320°C range. What we believe to be the transformation $PW_{11}M{\rightarrow}PW_{12}$, together with the initial decomposition of the cation, was held responsible for a broad exotherm of medium

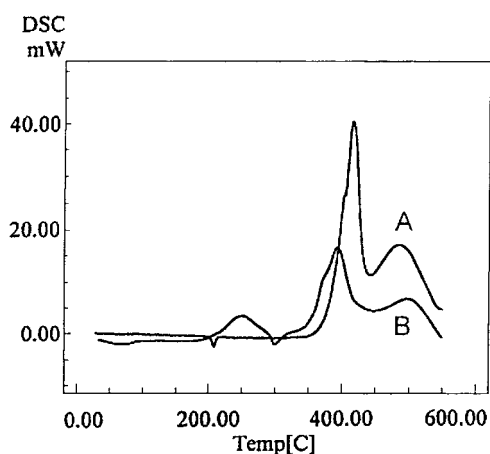Fig. 4. DSC plots of $(TBA)_3[PW_{12}O_{40}]$ (A), and $(TBA)_4H$-$[PW_{11}Mn(H_2O)O_{39}]$ (B).

intensity, observed below 290°C in the DSC plots of the transition-metal substituted compounds (Fig. 4). For $PW_{11}Cu$, this peak was close to the other exotherms at higher temperatures and the corresponding intensity was not well defined.

The behaviour of the TBA salts was completely different from those of the corresponding K^+ salts. These potassium compounds are heavily hydrated and de-hydration occurs at $T < 220°C$. Decomposition was observed at $T > 450°C$ (values obtained from infrared spectroscopy experiments Table 1). No PW_{12} was detected as an intermediate in the decomposition of these potassium salts and the infrared spectrum of $PW_{11}M$ anions was observed up to the onset of

decomposition. The infrared spectra of the final decomposition products indicated that WO_3 was the main component in the residue [31].

The metal-substituted anions studied are known to release the metal cation M in acid solutions, the rate of reaction depending on the charge on the M, the concentration and temperature [9,23]. Low pH favours the transformation of the lacunary anion, PW_{11} into the Keggin parent anion PW_{12} [1]. However, the observed transformation was not expected to occur during the thermal treatment of these compounds, particularly in view of the thermal stability of the PW_{11} and $PW_{11}M$ anions in the potassium salts.

The release of the metal from the host Keggin structure together with the $PM_{11} \rightarrow PM_{12}$ transformation was reported to occur during heat treatment of the vanadium mixed-polyanions in $H_4PM_{11}VO_{40}$, $M = Mo$, W [35]. To our knowledge, no other case has been reported.

If we assume that protons are possibly involved in the release of the metal M and in the transformation of the transition-metal substituted polyoxotungstates into the Keggin parent polyanion, as shown in Eq. (1) for the lacunary anion (the oxide form for the released P was used as a simplification), the number of protons in the formula of the compound is not sufficient for decomposition to take place. No balanced equations could be found for the decomposition without protons on the reagents side (this is not the case of the decomposition of the $H_4PM_{11}VO_{40}$ found in the literature [35] for which balanced equations can be assumed that do not require any external source of

Table 2
DSC peaks of tetrabutylammonium salts (°C) [a,b]

Anion	Exo	Endo	Exo	Exo
PW_{12} [c]			417[d]	486
PW_{11}		323	402	485
$PW_{11}Mn$	249	300	394[d]	498
$PW_{11}Co$	225, 242(sh)	316	345, 388[d]	507
$PW_{11}Ni$	(200–290) [f]	311, 327	several ill-defined peaks	
$PW_{11}Cu$			321, 347, 382	460(sh)
$PW_{11}Fe$	237(sh), 275(sh)		310[e], 398	460(sh)

[a] Peaks corresponding to de hydration are not shown.
[b] Values obtained in the conditions referred to in Section 2; 5–20°C variations could be observed, depending on experimental conditions.
[c] A narrow endothermic peak was observed at 208°C, possibly due to a phase transition.
[d] Peaks having a shoulder at a lower temperature.
[e] Peaks having a shoulder at a higher temperature.
[f] Broad and ill-defined peak.

protons). We believe that the necessary protons could
be provided by the decomposition of the TBA cations,
which accounts for the fact that no metal release has
been observed for the potassium salts. Tetralkylammo-
nium species appear to be able to act as proton
donors towards the negative framework sites of zeo-
lites, decomposing by Hofmann elimination [36]. A
similar process could take place in the case of the TBA
salts just described. The presence of NH_4^+ as counter
cation of the formed PW_{12} is in accordance with this
possibility.

$$12[H_3PW_{11}O_{39}]^{4-} + 15H^+ \rightarrow 11[PW_{12}O_{40}]^{3-}$$
$$+25.5H_2O + 0.5P_2O_5 \tag{1}$$
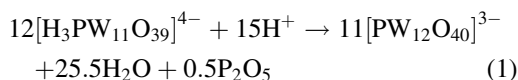
4. Conclusions

The thermal decomposition of the tetrabutylammo-
nium salts $(TBA)_4H_3[PW_{11}O_{39}]$ and $(TBA)_4H_{3-m}$
$[PW_{11}M^m(H_2O)O_{39}]$ (M = Mn(II), Co(II), Ni(II),
Cu(II) or Fe(III)) occurs in the 150–650°C range.
The release of the metal M from the substituted
polyoxoanions accompanies the initial degradation
of the organic cations, and the anion $[PW_{12}O_{40}]^{3-}$
is formed at ca. 300°C as an intermediate in the
decomposition of all the TBA salts studied. The
degradation of the $[PW_{12}O_{40}]^{3-}$ anion then occurs
at T>450°C. The parent Keggin anion is not formed
during the thermal decomposition of the correspond-
ing potassium salts, which are stable up to 450°C. In
this case, the substituted (or the lacunary) anions
decompose directly to oxides.

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