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Three sandglass-type molybdophosphates obtained via a new route: Synthesis and characterization of $X_7[PMo_8O_{30}]$ ($X = Na^+, K^+, NH_4^+$)

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ABSTRACT

Three new polyoxometalates $X_7[PMo_8O_{30}]$ ($X = Na^+$, 1; K^+, 2; NH_4^+, 3) have been synthesized with the classical Keggin and/or Dawson heteropolymolybdophosphates and PCl_5 in acetonitrile-water solutions via hydrothermal treatment. The three compounds were characterized by different analyses including IR, ^{31}P NMR spectroscopy, elemental analysis, electrochemistry, thermogravimetric analysis (TGA) and powder X-ray diffraction (XRD). Single crystal X-ray analyses were carried out on $Na_7[PMo_8O_{30}]$ (1) and $(NH_4)_7[PMo_8O_{30}]$ (3). Compound 1 and 3 crystallize in the orthorhombic system. The structure of compound 2 was confirmed by the IR spectra and powder XRD. All the three compounds contain the same octamolybdophosphate polyoxoanion $[PMo_8O_{30}]^{7-}$, which consists of two Mo_4O_{15} moieties linked by one central PO_4 tetrahedron, leading to a remarkable sandglass-like structure.

1. Introduction

Polyoxometalates (POMs) are metal-oxygen cluster [1,2] species with versatile structures and interesting properties in medicine [3], catalysis [4], and materials science [5]. Although POMs have been known for almost 200 years since the time of Berzelius, their multiple potential applications have led to significant interest in them over the recent years. Numerous POMs with novel structures have been synthesized, which induces the rising study in their fascinating topologies and important applications [6–8] in electronic [9,10], optical [11,12], magnetic [13–15] and catalytic [16–18] properties.

An additional beauty of the POMs is their structural features, which have attracted so much attention. Especially, Müller's group has reported several giant mixed-valence polyoxomolybdates [19–22]. In polyoxotungstate chemistry, Pope et al. reported quite different structures [23]. It has been realized that the formation of polyanions in hydrothermal treatment is a self-assembly process, which relies more on the reaction conditions (e.g. pH value, concentration and ratio of reagents) than on the type of polyanion precursors employed [24]. Therefore, the systematic design and synthesis of novel POMs remain a challenge for synthetic chemists, and the discovery of new POMs with fundamentally novel structures and properties is still a focus of considerable ongoing research [25–27].

POMs are known to form original molecular and supramolecular structures of impressive size and complexity. One of the challenging tasks in POM chemistry is to find some novel structural units and then to link them up into larger clusters, or to one-, two-, and even three-dimensional extended frameworks in appropriate ways. So far, a number of mono-, di-, and trilacunary tungstosilicates have been known for many years, and the synthetic procedures for all these species have been developed by the groups of Hervé and Tezé [28]. Recently, several polyoxomolybdates possessing novel structures, $Cs_5Mo_8O_{24}AsO_4 \cdot 2H_2O$, $Cs_7Mo_8O_{26}AsO_4$ [29] and $Cs_5P[Mo_4O_{14}(OH)]_2 \cdot 2H_2O$ [30], have been synthesized by Hsu and Wang, Dumas and Sevov, respectively.

Further, unprecedented (β-SiW_8O_{31}) fragment has been observed in the trimeric satellite-shaped Co-15 polyoxotungstate anion $[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_{9-}(\beta\text{-}SiW_8O_{31})_3\}]^{5-}$ [31]. In our research on POMs, we have been trying to synthesize novel polyoxoanions as the architectural units to form multidimensional structure with a new simple strategy. During the synthesis, phosphorus pentachloride (PCl_5) was introduced into the reaction system to react with Keggin or Dawson polyanions via the hydrothermal technique, which surprisingly played a very important role to obtain the accidentally new sandglass-like heteropolyanions $[PMo_8O_{30}]^{7-}$ (PMo_8) in a very high yield. The structure of PMo_8 is quite different from those of Keggin, Dawson and other "defect" polyanions. The synthetic route is also different from those of the reported compounds $Cs_5Mo_8O_{24}AsO_4 \cdot 2H_2O$, $Cs_7Mo_8O_{26}AsO_4$ [17] and $Cs_5P[Mo_4O_{14}(OH)]_2 \cdot 2H_2O$ [31].

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2. Experimental section

2.1. Preparation of compounds

All organic solvents and materials used for synthesis were purchased without further purification. The precursor α-$H_6P_2Mo_{18}O_{62} \cdot nH_2O$ was synthesized according to the published procedure [32,33].

2.1.1. Preparation of [$Na_7PMo_8O_{30}$] (1)

A sample of PCl_5 (0.08 g, 0.383 mmol) was added to a solution of α-$H_3PMo_{12}O_{40} \cdot nH_2O$ (0.1862 g, 0.1 mmol) in 4 mL of acetonitrile at room temperature with stirring. Then 4 mL of water was added into the stirring mixture after 30 min. The pH value was adjusted to 4.3 by adding a mixed solution of terephthalic acid and sodium hydroxide. The final mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 2 days. After the autoclave had been cooled to room temperature over 5–6 h, colorless aerofoil-like crystals were obtained by filtration, washed with distilled water, and dried at ambient temperature. Yield: 0.078 g (~62%) based on Mo analysis calculated for $Mo_8Na_7O_{30}P$ **(1)**: Na, 11.2; P, 2.2; and Mo, 33.3. Found: Na, 10.6; P, 2.3; and Mo, 34.0. Selected IR data (KBr pellet, cm^{-1}):1036 (s), 941 (vs), 909 (vs), and 721 (vs).

2.1.2. Preparation of [$K_7PMo_8O_{30}$] (2)

This compound was synthesized as colorless aerofoil-like crystals by a similar procedure described for **1** except that the pH value was adjusted to 4.2 by addition of a mixed solution of terephthalic acid and potassium hydroxide. Yield: 0.1676 g (~72%) based on Mo analysis calculated for $Mo_8K_7O_{30}P$ **(2)**: K, 17.6; P, 2.0; and Mo, 49.5. Found: K, 17.1; P, 2.3; and Mo, 49.8. Selected IR data (KBr pellet, cm^{-1}):1040 (s), 944 (vs), 915 (vs), and 725 (vs).

2.1.3. Preparation of [$(NH_4)_7PMo_8O_{30}$] (3)

A sample of PCl_5 (0.08 g, 0.383 mmol) was added to a solution of α-$H_6P_2Mo_{18}O_{62} \cdot nH_2O$ (α-P_2Mo_{18}) (0.2788 g, 0.1 mmol) in acetonitrile (5 mL) at room temperature with stirring. A 5 mL of water was added into the stirring mixture after 30 min. Then ammonium chloride (0.054 g, 0.01 mmol) was added. The final mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 130 °C for 2 days. After the autoclave had been cooled to room temperature over 5–6 h, colorless aerofoil-like crystals were recovered by filtration, washed with distilled water, and dried at ambient temperature. Yield: 0.2624 g (~83%) based on Mo analysis calculated for $N_7H_{28}O_{30}PMo_8$ **(3)**: P, 2.24; Mo, 54.73; N, 6.94; and H, 1.95. Found: P, 2.21; Mo, 54.66; N, 6.98; and H, 1.99. Selected IR data (KBr pellet, cm^{-1}):1041 (s), 947 (vs_t), 915 (vs), and 726 (vs).

2.2. Physical measurements

H and N elements were analyzed on a Heraeus CHN-Rapid elemental analyzer, and other elements were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. Infrared spectra were recorded with KBr pellets on a Nicolet 170 SXFT-IR spectrometer. ^{31}P NMR spectra were taken on a Bruker AV-400 spectrometer operating at 400 MHz, using 0.5 mol/L H_2SO_4-50% 1,4-dioxane as the mixed solvent. The thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer-7 analyzer in nitrogen atmosphere with a heating rate of 10 °C/min. The electrochemical setup was a CHI 660 (USA). Potentials were quoted against a saturated calomel electrode (SCE). The counter electrode was platinum gauze of large surface area, and the working electrodes were glassy carbon (GC, Tokai, Japan) electrodes. All experiments were performed at room temperature.

2.3. X-ray crystallography

A colorless block crystal of compound **1** with dimensions of $0.33 \times 0.28 \times 0.26\,mm^3$ was picked out from the mother liquid, mounted on a glass fiber for indexing and intensity data collection at room temperature on a Bruker SMART APEX-CCD single-crystal diffractometer using Mo Ka radiation ($\lambda = 0.71073$ Å). Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. A total of 7923 (1643 unique, $R_{int} = 0.0850$) reflections were collected ($-10 < = h < = 9$,$-28 < = k < = 22$, $-19 < = l < = 18$). The structure was solved by the direct method and refined by a full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [36]. All of the non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were not included in the structure. Structure solution and refinement based on 1643 independent reflections with $I > 2\sigma(I)$ and 127 parameters gave $R_1(wR_2) = 0.0421$ (0.1124) ($R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $wR_2 = \Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$). A final difference Fourier map was featureless with the largest peak and the deepest hole of 1.368 and $-1.606\,e\,Å^{-3}$, respectively.

A suitable crystal of compound **3** with a size of $0.28 \times 0.22 \times 0.20\,mm^3$ was mounted on a glass fiber for indexing and intensity data collection at room temperature on a Bruker SMART APEX-CCD single-crystal diffractometer using Mo Ka radiation ($\lambda = 0.71073$ Å). Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. A total of 6155 (1539 unique, $R_{int} = 0.0292$) reflections were collected ($-6 \leqslant h \leqslant 10$, $-27 \leqslant k \leqslant 23$, $-18 \leqslant l \leqslant 18$). The structure was solved by the direct method and refined by a full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [34,35]. All of the non-hydrogen atoms were refined anisotropically. In this structure, however, the H atoms on the NH_4^+ cations cannot be found from the difference Fourier map and were not included in the structure refinement. Structure solution and refinement based on 1539 independent reflections with $I > 2\sigma(I)$ and 127 parameters gave $R_1(wR_2) = 0.0381(0.0996)$ ($R_1 = ||F_0|-|F_c||/|F_0|$; $wR_2 = [w(F_0^2-F_c^2)^2]/[w(F_0^2)^2]^{1/2}$). The final difference Fourier map exists the featureless but high peak ($3.14\,e\,Å^{-3}$) near the Mo atom with the distances of 0.942 Å. Such final high peaks are usually led by the series termination errors. [36] Crystallographic data are summarized in Tables 1 and 2.

3. Results and discussion

3.1. Synthesis

We prepared three compounds **1**, **2**, and **3** with high yields (62–83%) through degrading the Keggin (α-$H_3PMo_{12}O_{40} \cdot nH_2O$) and Dawson ($\alpha$-$H_6P_2Mo_{18}O_{62} \cdot nH_2O$) POMs with PCl_5. Acetonitrile was added in the first case to make sure that PCl_5 reacted with the POMs in stead of hydrolysis. The above method is a new route and obviously different from those reported basification methods for decomposing typical POM structures. It was found that the PMo_8 polyanion cannot be obtained from the classical POMs without PCl_5 in spite of changing other conditions. Therefore, we consider that it is PCl_5 that plays a very important role in this synthetic process. Furthermore, it was noteworthy that the phosphorus atoms of PMo_8 may derive from PCl_5 because the high-yield of product PMo_8 can also be obtained by the reaction between

Table 1
Crystal data and structure refinement for $Na_7PMo_8O_{30}$ (**1**)

Empirical formula	$Na_7Mo_8O_{30}P$
F_w	1439.42
Space group (no.)	Cmcm
a (Å)	8.4590(17)
b (Å)	22.801(5)
c (Å)	15.654(3)
Volume (Å^3)	3011.8(14)
Z	4
Temperature (K)	293(2)
Wavelength (Å)	0.71073
D_{calcd} (g cm^{-3})	1.486
Abs. coeff. (mm^{-1})	1.690
Crystal size (mm^3)	0.33 × 0.28 × 0.26
Goodness-of-fit on F^2	1.054
R [$I>2\sigma(I)$]^a	$R_1=0.0421$, $wR_2=0.1124$
R (all data)^b	$R_1=0.0493$, $wR_2=0.1168$
Residuals (e Å^{-3})	−1.622, 1.226

[a] $R=\sum||F_0|-|F_c||/|F_0|$.
[b] $R_w=[\sum w(F_0^2-F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

Table 2
Crystal data and structure refinement for $(NH_4)_7PMo_8O_{30}$ (**3**)

Empirical formula	$H_{28}Mo_8N_7O_{30}P$
F_w	1404.78
Space group (no.)	Cmcm
a (Å)	8.5106(17)
b (Å)	22.822(5)
c (Å)	15.499(3)
Volume (Å^3)	3010.3(10)
Z	4
Temperature (K)	293(2)
Wavelength (Å)	0.71073
D_{calcd} (g cm^{-3})	3.100
Abs. coeff. (mm^{-1})	3.394
Crystal size (mm^3)	0.28 × 0.22 × 0.20
Goodness-of-fit on F^2	1.076
R [$I>2\sigma(I)$]^a	$R_1=0.0381$, $wR_2=0.0996$
R (all data)^b	$R_1=0.0440$, $wR_2=0.1044$
Residuals (e Å^{-3})	−0.668, 3.140

[a] $R=\sum||F_0|-|F_c||/|F_0|$.
[b] $R_w=[\sum w(F_0^2-F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

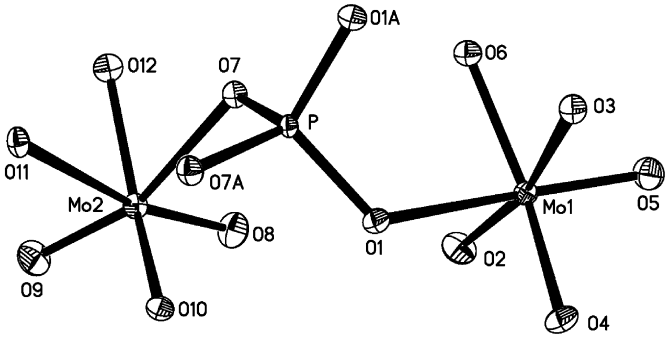

Fig. 1. Crystallographic unit cell of $[PMo_8O_{30}]^{7-}$ (PMo_8).

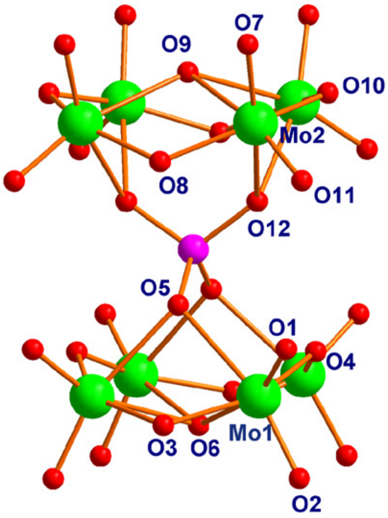

Fig. 2. Ball-and-stick representation of the PMo8 polyanion: O, red; Mo, green; and P, purple.

α-$H_3SiMo_{12}O_{40}\cdot nH_2O$ and PCl_5. Furthermore, we cannot obtain very well qualified crystal for the X-ray diffraction (XRD) without addition of terephthalic acid. So we think the role of terephthalic acid is not only to adjust the value of pH, but perhaps to work as the template in the processes of one-pot synthesis.

3.2. Description of the crystal structures

The structural analysis for compounds **1** and **3** reveal a highly symmetrical and compact heteropolyanion. As the coordination of P{Mo_4O_{15}} moieties shown in Fig. 1, the coordination number of P atom, Mo atom and O atoms in the $[PMo_8O_{30}]^{7-}$ polyanion is 4, 6 and 2, respectively.

Based on the above coordination mode, the $[PMo_8O_{30}]^{7-}$ polyanion exhibits a D_{2h} symmetry and consists of the association of two {Mo_4O_{15}} moieties with one central {PO_4} tetrahedron, leading to a sandglass-like structure. Each {Mo_4O_{15}} moiety contains two face-shared {Mo_2O_9} units, coordinating to each other by the edge-sharing mode. There are four kinds of oxygen atoms exist in the polyanion: terminal oxygen O_{term}, double-bridging oxygen atoms O_{bi}, triple-bridging oxygen atoms O_{tri}, and tetra-bridging oxygen atoms O_{tetra}. The Mo–O bond lengths can also be divided into four different classes correspondingly. As shown in Fig. 2, the octahedral geometry around each molybdenum in the {PMo_8O_{30}} unit is defined by two O_{term} (O1, O2 or O7, O11) with Mo–O distances within 1.699(3)–1.719(2) Å, two O_{bi} (O3, O4 or O8, O10) with Mo–O of 1.9101(2)–1.9238(2) Å, one O_{tri} (O5 or O12) with Mo–O of about 2.321(2)–2.368(2) Å, and only one O_{tetra} (O6 or O9) that is simultaneously shared by all four Mo atoms with Mo–O distances of about 2.3618(1)–2.4382(2) Å. In addition, there are two terminal oxygen atoms linking to one molybdenum atom in each $[PMo_8O_{30}]^{7-}$ while there is only one in the Keggin and Dawson polyanions. Depending upon the above analysis, we can draw a conclusion that the ratio of the terminal oxygen atoms number to that of the molybdenum atoms in each $[PMo_8O_{30}]^{7-}$ is much more than those of Keggin and Dawson polyanions, which provides a possibility of constructing novel multidimensional POMs with PMo_8 as a basic building block.

The polyanion can also be viewed as the central P atom encapsulated the eight Mo atoms forming a slightly distorted "cuboid box" As shown in Fig. S1, the four Mo atoms in the same moiety form a rectangle with average dimensions of 3.349 × 3.194 Å^2 and Mo–Mo–Mo angles of 90°. While the Mo–Mo distance between upper and lower {Mo4} moieties is 5.152(1) Å.

A similar polyanion $Mo_4O_{14}(OH)^{5-}$ has been previously identified as a monomer in some heteropolyoxomolybdates with a general formula $[(\mu_2{-}R)Mo_4O_{14}(OH)]^{n-}$ where R is an organic or organoarsenic fragment, e.g. R_2C, R_2As [37–40], PhSe or OSe [41]. Compared with the reported compounds $Cs_5Mo_8O_{24}AsO_4\cdot 2H_2O$, $Cs_7Mo_8O_{26}AsO_4$ [17], and $Cs_5P[Mo_4O_{14}(OH)]_2\cdot 2H_2O$, the former two consisting of two $Mo_4O_{14}(OH)^{5-}$ and $\{Mo_4O_{15}\}$ units connected via a central arsenate group, respectively, and being synthesized at a very high temperature of 550 °C, while the latter containing two $Mo_4O_{14}(OH)^{5-}$ units linked via a central phosphorus group [18], the Mo–O distances of the present compounds **1**–**3** are noticeably shorter owing to the difference of the heteroatoms, counter-cations or protonation.

Five quite different and interesting coordination modes of the alternating cations in the compounds **1** and **3** are clearly displayed in Fig. 3. Taking compound **1** for example, the five crystallographically independent sodium cations display five different coordination environments. Na1 shows a V-shaped coordination mode and is coordinated with two O_{bi} from two separate PMo_8, while Na2 displays a planar triangle mode and coordinates to two O_{bi} and one O_{tetra} from three various PMo_8 polyanions. The Na3 cation coordinates with four O_{term} and one O_{tetra} from three different PMo_8 and forms a pyramidal geometry, while Na4 is coordinated with one O_{bi} and four O_{term} from four PMo_8 forming a distorted tetrahedron mode and Na5 coordinates with six O_{term} and one O_{bi} of five PMo_8 and make a capped distorted octahedron coordination mode. When it comes to the compound 3 $(NH_4)_7[PMo_8O_{30}]$, according to its crystal data, we consider that there are hydrogen bonds in the crystal structure and the coordination modes of the cation in the compound 1,2,3 are quite different from those of the compound $Cs_7Mo_8O_{26}AsO_4$ reported previously.

3.3. *Powder X-ray diffraction analysis*

Powder X-ray diffraction (PXRD) analysis revealed that compound **2** has almost the same diffraction pattern (peak positions: $2\theta = 11.5°$, 12.66°, 15.74°, 19.48°, 21.08°, 22.91°, 23.02°, 23.15°, 26.35°, 28.03°, 31.4°, 35.22°, and 38.22°) as compound **1** (Fig. 4). The quite similar IR spectra and the PXRD data of compounds **1** and **2** indicate that **2** has the same crystal structure as **1** (Fig. S2. The IR spectra of 1, 2 and 3).

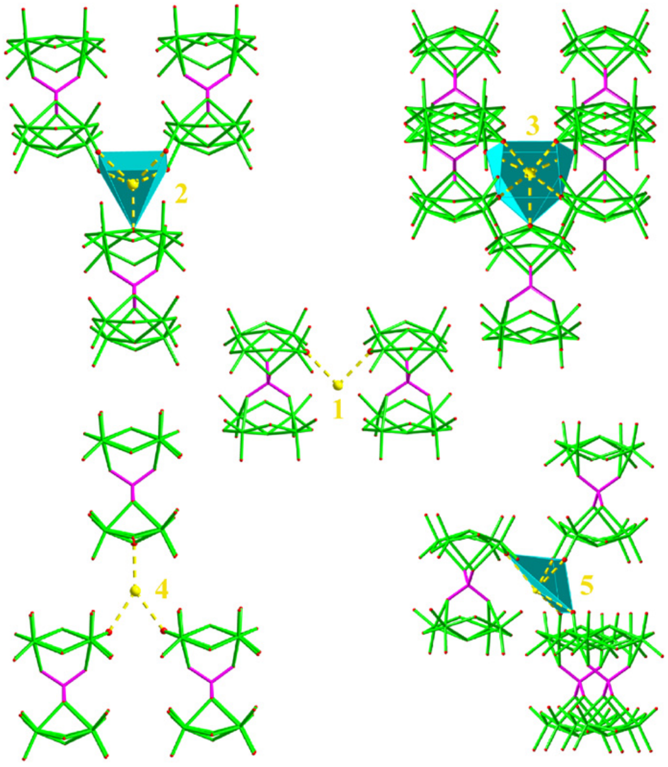

Fig. 3. The different coordination environments of Na⁺.

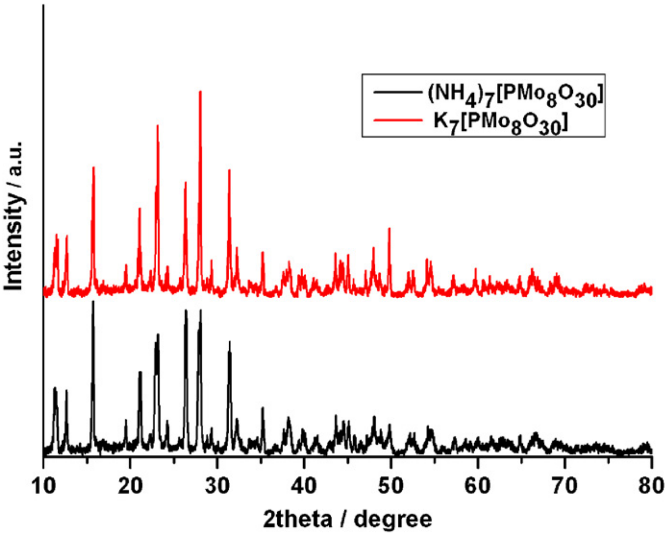

Fig. 4. PXRD patterns of compounds 1 and 2.

3.4. *^{31}P NMR analysis*

Solid-state ^{31}P NMR spectra for compound **1** exhibits the phosphorous signal at 7.317 ppm (see Fig. 5), which provides further evidence that P has only one coordination structure in the $[PMo_8O_{30}]^{7-}$ polyanion.

3.5. *Electrochemical properties*

Fig. 6 shows the cyclic voltammogram (CV) of compound **1** (2 mmol/L) in a mixed solution of 0.1 M Na_2SO_4 (10 mL) and 0.5M H_2SO_4 (8 mL) as the supporting electrolyte with Hg/Hg_2Cl_2 as the reference electrode. From the CV of compound **1** we can get the information that reduction from Mo^{VI} to Mo^{V} is an one electron reversible redox process.

3.6. *Thermal analysis*

Thermogravimetric (TG) (a Dupont thermal analyzer) was performed on the samples of **3**.

The TGA curve of compound **3** exhibits two continuous weight loss stages in the range of 250–460 °C with a total weight loss of 14.56% (calculated 14.60%) (Fig. 7). The first weight loss of 10.30% (calculated 10.39%) occurred at 250–323 °C, while the second one of 4.26% (calculated 4.21%) at 323–460 °C. Taking into account our experiments, the following decomposition path for **3** is

$$\begin{aligned}&6(NH_4)_7PMo_8O_{30}\\&\xrightarrow{250-323\,^\circ C} 42NH_3\uparrow + 9H_2O\uparrow + 3P_2O_5\cdot 48MoO_3\cdot 12H_2O\\&\xrightarrow{323-460\,^\circ C} P_2O_5\uparrow + 12H_2O\uparrow + 2P_2O_5\cdot 48Mo\end{aligned}\tag{1}$$

In addition, PXRD analysis of **3** (Fig. 8) after being heated at 320 and 500 °C for 1 h indicated that the main diffraction peaks gradually disappeared, which suggests that after being heated at 320 °C, compound **3** decomposes into the compound $3P_2O_5\cdot 48MoO_3\cdot 12H_2O$, then after the temperature enhanced, $3P_2O_5\cdot 48MoO_3\cdot 12H_2O$ further decomposed into $P_2O_5\cdot 48MoO_3$. The results of the decomposed processes probably indicate that PMo_{12} is more stable than PMo_8. Furthermore, the above residues

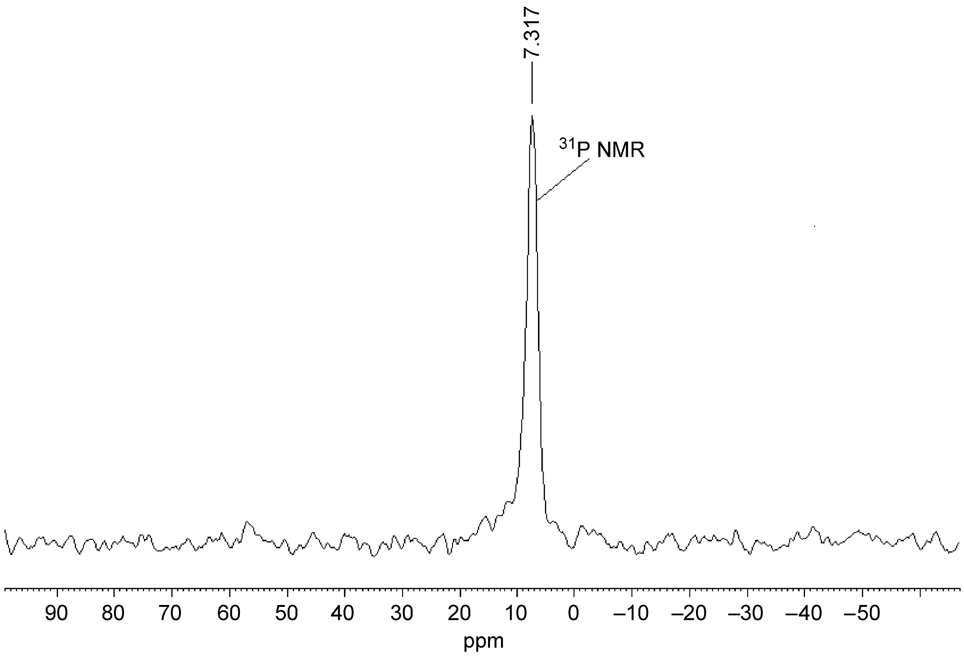

Fig. 5. ^{31}P NMR spectra of compound 1.

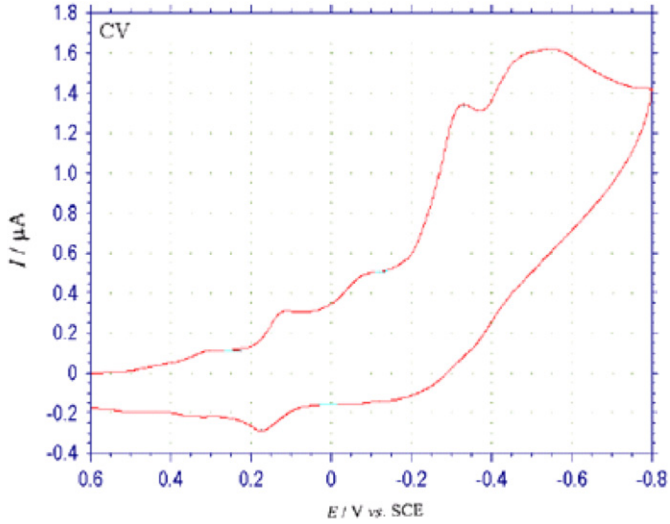

Fig. 6. Cyclic voltammogram of compound 1.

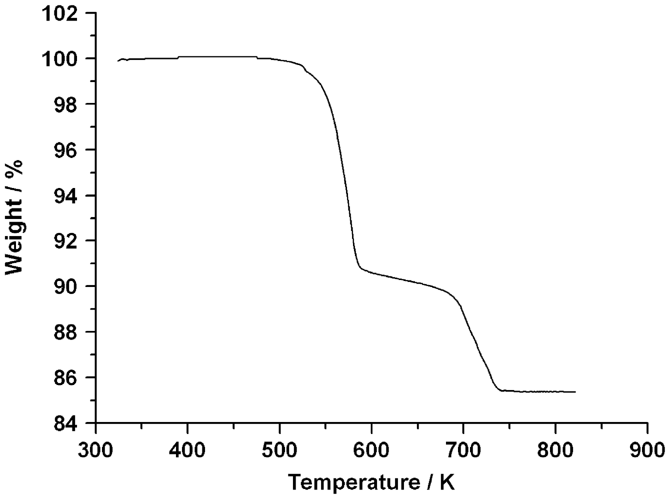

Fig. 7. TGA curve of compound 3.

were used to repeat the synthesis of PMo_8 with PCl_5 confirmed by the XRD analysis.

4. Conclusion

In summary, the successful, high-yield synthesis of compounds **1**, **2** and **3** containing heteropolyanion $[PMo_8O_{30}]^{7-}$ with a sandglass-like structure indicates that the synthetic method of adding PCl_5 into the reaction system is effective to construct novel heteropolymolybdates. Specific challenges in future include the design of versatile basic building blocks which might serve as carriers of structural and functional information to be expressed in a special target material. The present heteropolyanions $[PMo_8O_{30}]^{7-}$ may act as a building block just like $[PW_9O_{34}]^{9-}$, $[SiW_{10}O_{36}]^{8-}$ and $[SiW_{11}O_{39}]^{8-}$ and may be utilized to assemble the skeletons of the desired structures with various functionalities and dimensionalities. It might be possible to construct even heteropoly-tungstates and -vanadates with the same structure by using the strategy reported in this work, which will provide a new route to enrich polyoxometalate synthetic chemistry. Further research on the catalytic effect of synthetic light esters of this kind of polyoxometalates is in progress.

5. Supporting information available

Synthesis details and additional analytical techniques for **1** (PDF). X-ray crystallographic file in CIF format for the structural determination of **1** and **3**. (CSD number of 1 is 415332). This material is available free of charge. The Director, CCDC, 12 Union Raod, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

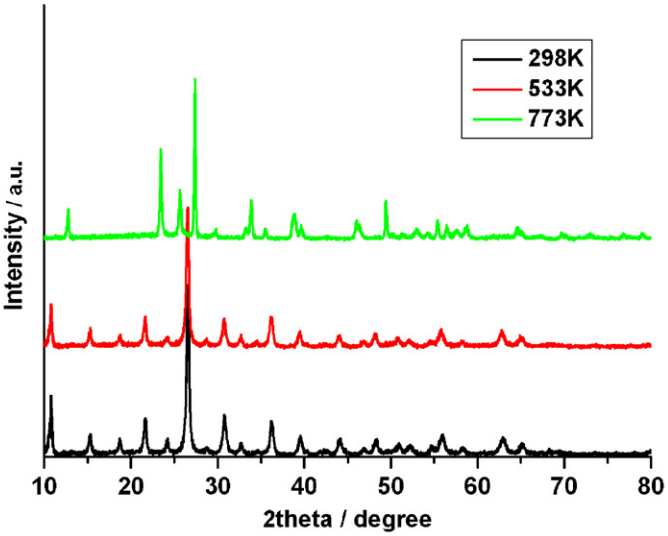

Fig. 8. PXRD patterns of samples of 3 at 25 °C and after being heated at 320 and 500 °C.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.09.025.

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