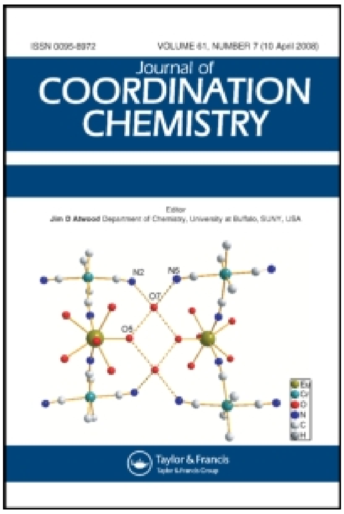

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# Hydrothermal syntheses and crystal structures of two new phosphomolybdates based on an organoamine template

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# Hydrothermal syntheses and crystal structures of two new phosphomolybdates based on an organoamine template

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Two new compounds of disphosphopentamolybdate (VI), $(C_6H_{18}N_2)_2[H_2P_2Mo_5O_{23}]\cdot 2(H_2O)$ (**1**) and $(C_6H_{18}N_2)_{4.5}H_3[P_2Mo_5O_{23}]_2\cdot 6(H_2O)$ (**2**), have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.0863(9)$ Å, $b = 11.9562(9)$ Å, $c = 14.2291(19)$ Å, $\alpha = 103.0410(10)^\circ$, $\beta = 100.3530(10)^\circ$, $\gamma = 103.7390(10)^\circ$, $V = 1729.8(2)$ Å$^3$, $Z = 2$; compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.6440(13)$ Å, $b = 15.9168(13)$ Å, $c = 17.9795(13)$ Å, $\alpha = 80.4270(10)^\circ$, $\beta = 86.1180(10)^\circ$, $\gamma = 64.1890(10)^\circ$, $V = 3720.1(5)$ Å$^3$, $Z = 2$. Characterizations by elemental analysis, infrared analysis, and thermal analysis are also given. Formation of **1** and **2** indicates that pH of solution plays an important role during the synthesis.

*Keywords*: Polyoxomolybdate-phosphorus; Hydrothermal synthesis; Crystal structure

## 1. Introduction

Polyoxomolybdate-phosphorus, as a part of polyoxometalates (POMs), has structural diversity and potential applications in catalysis, photochemistry, electrochemistry, magnetochemistry, and materials science [1–8]. There are several classical ployanion structures derived from the ratio of Mo/P, for example, Keggin cluster $[PMo_{12}^{VI}O_{40}]^{3-}$, Wells–Dawson cluster $[P_2Mo_{18}^{VI}O_{68}]^{18-}$, fully reduced $[P_4Mo_6^{V}O_{31}]^{12-}$, and fully oxidized $[P_2Mo_5^{VI}O_{23}]^{6-}$. Among these classical anions, pentamolybdodiphosphate, which was structurally characterized by Strandberg [9] in 1973, has a vital role in polyoxomolybdate-phosphorus. Zubieta and coworkers [10–16] reported a series of new hybrid compounds based on organophosphonate, Wang and coworkers [17–20] synthesized new crystals using phosphoric acid and others [21–27].

With the development of hydrothermal technique, organoamines were added to the reaction system, not only acting as charge-compensating cations, but also establishing stable structures through hydrogen bonds. The pH of the reaction system affects

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the formation of final products. Some Strandberg-type pentamolybdodiphosphate salts based on organoamine and protonated crystal waters have been reported [17, 28–41]. Here, we successfully synthesize two new compounds $(C_6H_{18}N_2)_2H_2[P_2Mo_5O_{23}]\cdot 2(H_2O)$ (**1**) and $(C_6H_{18}N_2)_{4.5}H_3[P_2Mo_5O_{23}]_2\cdot 6(H_2O)$ (**2**), using the same organic amine but different pH levels.

## 2. Experimental

### 2.1. *Materials and methods*

All chemicals purchased are of reagent grade and used without purification. The element analyses (C, H, N) were performed on a Perkin-Elmer 2400 elemental analyzer. Infrared (IR) spectra of **1** and **2** were recorded with a Nicolet Impact 410 FTIR spectrometer with pressed KBr pellets from 4000 to 450 $cm^{-1}$. Thermogravimetric (TG) measurement was carried out on a Diamond TG analyzer in flowing $N_2$ from 40°C to 700°C with a heating rate of 10°C $min^{-1}$.

### 2.2. *Syntheses of the complexes*

**2.2.1. $(C_6H_{18}N_2)_2H_2[P_2Mo_5O_{23}]\cdot 2(H_2O)$.** A mixture of $Na_2MoO_4\cdot 2H_2O$ (1.0326 g), 1,6-diaminehexane (0.9905 g), and deionized water (4 mL) in molar ratio 2 : 4 : 103 was stirred for 20 min in open air; 50% $H_3PO_4$ was added to the mixture (final pH was 4) and the solution was stirred for another 20 min. Then, the mixture was transferred to a 20 mL Teflon-lined autoclave and heated to 160°C for 7 days. After cooling to room temperature, light green block-like crystals were filtered, washed with deionized water and dried in air (0.4674 g, yield 37% based on Mo). Elemental analysis: found C 12.2%, H 3.6%, and N 4.78% (Calcd C 12.16%, H 3.55%, and N 4.73%).

**2.2.2. $(C_6H_{18}N_2)_{4.5}H_3[P_2Mo_5O_{23}]_2\cdot 6(H_2O)$.** Compound **2** was prepared similarly; ($Na_2MoO_4\cdot 2H_2O$ (0.2065 g), 1,6-diaminehexane (0.3966 g), and deionized water (7 mL) in molar ratio 2 : 8 : 901). The pH was adjusted to 5 by 50% phosphoric acid. After cooling to room temperature, 0.0647 g yellow block-like crystals were obtained; yield 31% (based on Mo). The elemental analysis: found C 13.21%, H 4.03%, and N 5.17% (Calcd C 13.15%, H 3.98%, and N 5.11%).

### 2.3. *X-ray crystallography*

Single crystals of **1** and **2** were selected under the microscope and glued at the top of a thin glass fiber with epoxy glue for data collection; crystallographic data were collected on a Bruker Apex II CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296 K using $\omega$–$2\theta$ scan method. The crystal structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares using the SHELX-97 program package [42]. All non-hydrogen atoms were refined anisotropically. Hydrogens of organoamine were placed in calculation positions. Hydrogens of water and OH were located from the difference

Table 1. Crystal data and structure refinement for **1** and **2**.

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{12}H_{42}N_4O_{25}P_2Mo_5$ | $C_{27}H_{96}N_9O_{52}P_4Mo_{10}$ |
| Formula weight | 1184.14 | 2462.41 |
| Temperature (K) | 296(2) | 296(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 11.0863(9) | 14.6440(13) |
| $b$ | 11.9562(9) | 15.9168(13) |
| $c$ | 14.2291(11) | 17.9795(13) |
| $\alpha$ | 103.041(10) | 80.4270(10) |
| $\beta$ | 100.353(10) | 86.1180(10) |
| $\gamma$ | 103.739(10) | 64.1890(10) |
| Volume ($Å^3$), $Z$ | 1729.8(2), 2 | 3720.1(5), 2 |
| Calculated density ($g\,cm^{-3}$) | 2.274 | 2.198 |
| Absorption coefficient ($mm^{-1}$) | 1.951 | 1.821 |
| $F(0\,0\,0)$ | 1164 | 2434 |
| Crystal size ($mm^3$) | 0.14 × 0.13 × 0.12 | 0.14 × 0.10 × 0.09 |
| Limiting indices | $-13 \le h \le 13$;<br>$-14 \le k \le 12$;<br>$-17 \le l \le 17$ | $-17 \le h \le 17$;<br>$-19 \le k \le 19$;<br>$-21 \le l \le 21$ |
| Reflections collected | 12,695 | 27,465 |
| Independent reflection | 6329[$R$(int) = 0.0182] | 13635[$R$(int) = 0.0393] |
| Max. and min. transmission | 0.7996 and 0.7718 | 0.8532 and 0.7846 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/parameters | 6329/451 | 13635/992 |
| Goodness-of-fit on $F^2$ | 1.081 | 1.097 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0232$, $wR_2 = 0.0642$ | $R_1 = 0.0668$, $wR_2 = 0.1681$ |
| $R$ indices (all data) | $R_1 = 0.0254$, $wR_2 = 0.0653$ | $R_1 = 0.1030$, $wR_2 = 0.1922$ |

map for **1** and **2**. O45, O46, O45A, O46A, C20A, and C20B are disordered with occupation factors of 0.5. The crystal data are presented in table 1 and selected bond lengths in tables 2–5.

## 3. Results and discussion

### 3.1. *Synthesis*

Many factors influence the growth of crystals, such as initial reagents, pH, temperature, and reaction time. In our research, pH was crucial. When the pH was 4, we obtained light green colored compound **1**, but when the pH was 5, yellow block-like crystals of **2** were obtained. Single crystal X-ray diffraction indicates that these two compounds have different cell parameters and structures.

### 3.2. *Crystal structure*

Single crystal X-ray diffraction analysis shows that **1** consists of one protonated Strandberg ployoxoanion $[H_2P_2Mo_5O_{23}]^{4-}$, two protonated 1,6-diaminehexanes, and

Table 2. Selected bond distances (Å) for **1**.

| | | | | | |
|---|---|---|---|---|---|
| Mo(1)–O(7) | 1.711(2) | Mo(3)–O(4) | 1.708(2) | Mo(5)–O(14) | 1.934(2) |
| Mo(1)–O(12) | 1.725(2) | Mo(3)–O(13) | 1.929(2) | Mo(5)–O(20) | 1.946(2) |
| Mo(1)–O(13) | 1.887(2) | Mo(3)–O(14) | 1.956(2) | Mo(5)–O(21) | 2.193(2) |
| Mo(1)–O(23) | 1.922(2) | Mo(3)–O(18) | 2.251(2) | Mo(5)–O(17) | 2.388(2) |
| Mo(1)–O(16) | 2.325(2) | Mo(3)–O(21) | 2.319(2) | P(1)–O(18) | 1.502(2) |
| Mo(1)–O(19) | 2.373(2) | Mo(4)–O(1) | 1.686(3) | P(1)–O(19) | 1.539(2) |
| Mo(2)–O(11) | 1.695(2) | Mo(4)–O(6) | 1.710(2) | P(1)–O(17) | 1.544(2) |
| Mo(2)–O(3) | 1.720(2) | Mo(4)–O(15) | 1.934(2) | P(1)–O(10) | 1.561(2) |
| Mo(2)–O(15) | 1.917(2) | Mo(4)–O(23) | 1.940(2) | P(2)–O(16) | 1.518(2) |
| Mo(2)–O(20) | 1.918(2) | Mo(4)–O(19) | 2.218(2) | P(2)–O(22) | 1.525(2) |
| Mo(2)–O(22) | 2.333(2) | Mo(4)–O(22) | 2.423(2) | P(2)–O(21) | 1.544(2) |
| Mo(2)–O(17) | 2.376(2) | Mo(5)–O(2) | 1.700(2) | P(2)–O(9) | 1.561(2) |
| Mo(3)–O(5) | 1.702(2) | Mo(5)–O(8) | 1.723(2) | | |

Table 3. Selected bond distances (Å) for **2**.

| | | | | | |
|---|---|---|---|---|---|
| Mo(1)–O(11) | 1.693(5) | Mo(5)–O(2) | 1.916(6) | Mo(9)–O(32) | 2.198(4) |
| Mo(1)–O(3) | 1.720(6) | Mo(5)–O(13) | 1.949(6) | Mo(9)–O(23) | 2.359(6) |
| Mo(1)–O(18) | 1.926(4) | Mo(5)–O(9) | 2.223(4) | Mo(10)–O(46A) | 1.698(9) |
| Mo(1)–O(17) | 1.931(4) | Mo(5)–O(5) | 2.321(5) | Mo(10)–O(39) | 1.712(7) |
| Mo(1)–O(12) | 2.178(5) | Mo(6)–O(27) | 1.695(6) | Mo(10)–O(42) | 1.884(6) |
| Mo(1)–O(20) | 2.455(4) | Mo(6)–O(43) | 1.712(5) | Mo(10)–O(24) | 1.954(6) |
| Mo(2)–O(36) | 1.698(5) | Mo(6)–O(29) | 1.922(5) | Mo(10)–O(23) | 2.277(7) |
| Mo(2)–O(30) | 1.700(6) | Mo(6)–O(42) | 1.955(5) | Mo(10)–O(33) | 2.280(4) |
| Mo(2)–O(29) | 1.910(5) | Mo(6)–O(35) | 2.197(5) | P(1)–O(19) | 1.519(5) |
| Mo(2)–O(28) | 1.928(5) | Mo(6)–O(33) | 2.382(5) | P(1)–O(20) | 1.527(5) |
| Mo(2)–O(34) | 2.296(5) | Mo(7)–O(1) | 1.695(6) | P(1)–O(9) | 1.535(5) |
| Mo(2)–O(35) | 2.360(4) | Mo(7)–O(4) | 1.709(5) | P(1)–O(21) | 1.567(5) |
| Mo(3)–O(15) | 1.700(5) | Mo(7)–O(16) | 1.911(5) | P(2)–O(34) | 1.513(5) |
| Mo(3)–O(14) | 1.714(6) | Mo(7)–O(2) | 1.930(5) | P(2)–O(31) | 1.521(5) |
| Mo(3)–O(13) | 1.909(5) | Mo(7)–O(10) | 2.262(4) | P(2)–O(32) | 1.539(5) |
| Mo(3)–O(18) | 1.925(5) | Mo(7)–O(9) | 2.390(5) | P(2)–O(33) | 1.545(5) |
| Mo(3)–O(20) | 2.323(4) | Mo(8)–O(40) | 1.705(7) | P(3)–O(22) | 1.503(4) |
| Mo(3)–O(5) | 2.352(6) | Mo(8)–O(26) | 1.724(6) | P(3)–O(10) | 1.521(6) |
| Mo(4)–O(8) | 1.711(5) | Mo(8)–O(28) | 1.890(5) | P(3)–O(5) | 1.532(6) |
| Mo(4)–O(7) | 1.715(5) | Mo(8)–O(41) | 1.932(7) | P(3)–O(12) | 1.558(4) |
| Mo(4)–O(16) | 1.879(5) | Mo(8)–O(44) | 2.202(6) | P(4)–O(25) | 1.522(6) |
| Mo(4)–O(17) | 1.917(5) | Mo(8)–O(32) | 2.364(5) | P(4)–O(44) | 1.537(6) |
| Mo(4)–O(12) | 2.328(4) | Mo(9)–O(45A) | 1.662(9) | P(4)–O(23) | 1.542(6) |
| Mo(4)–O(19) | 2.356(5) | Mo(9)–O(38) | 1.704(7) | P(4)–O(35) | 1.553(4) |
| Mo(5)–O(37) | 1.708(5) | Mo(9)–O(41) | 1.928(8) | | |
| Mo(5)–O(6) | 1.708(5) | Mo(9)–O(24) | 1.999(7) | | |

two waters (figure 1). The polyoxoanion can be described as a ring of five edge- and corner-sharing distorted $\{MoO_6\}$ octahedra with two capped $PO_4$ tetrahedra on each side. Each phosphate shares three oxo groups with the molybdate ring. In the three oxygens, one adopts $\mu_2$-bridging (O(18) for $P(1)O_4$; O(16) for $P(2)O_4$), linking one molybdenum site and the phosphorus; the other two adopt $\mu_3$-bridging, linking two molybdenum sites and phosphorus (O(1) and O(10) for $P(1)O_4$; O(7) and O(3) for $P(2)O_4$). The Mo–O bonds can be divided into three types: (1) short terminal oxygen bonds, Mo–$O_t$ 1.686(3)–1.725(2) Å; (2) medium bridging oxygens, Mo–$O_{b1}$ (oxygens are shared by two molybdenums) 1.887(2)–1.956(2) Å; and (3) long Mo–$O_{2b}$ (oxygens are between phosphorus and molybdenum) 2.193(2)–2.423(2) Å. The bond angles of O–Mo–O range from 69.97(8)° to 173.34(10)°. P–O bond distances are between 1.502(2)

Table 4. Hydrogen bond interactions in **1**.

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| N(1)–H(1C)···O(23) | 0.8900 | 2.0500 | 2.914(4) | 164.00 |
| N(1)–H(1D)···O(5) | 0.8900 | 2.0300 | 2.886(4) | 161.00 |
| N(1)–H(1E)···O(6) | 0.8900 | 2.0800 | 2.962(4) | 173.00 |
| N(2)–H(2C)···O(18) | 0.8900 | 2.5400 | 2.847(4) | 101.00 |
| N(2)–H(2C)···O(1W) | 0.8900 | 2.1600 | 2.944(4) | 146.00 |
| N(2)–H(2D)···O(4) | 0.8900 | 2.1200 | 2.987(4) | 163.00 |
| N(2)–H(2D)···O(18) | 0.8900 | 2.4400 | 2.847(4) | 108.00 |
| N(2)–H(2E)···O(14) | 0.8900 | 1.9900 | 2.819(4) | 154.00 |
| N(3)–H(3C)···O(17) | 0.8900 | 2.0300 | 2.917(3) | 172.00 |
| N(3)–H(3D)···O(2W) | 0.8900 | 1.9800 | 2.849(5) | 167.00 |
| N(3)–H(3E)···O(3) | 0.8900 | 2.1200 | 2.921(4) | 150.00 |
| N(4)–H(4C)···O(12) | 0.8900 | 2.0800 | 2.963(4) | 171.00 |
| N(4)–H(4D)···O(2) | 0.8900 | 2.5900 | 2.936(4) | 104.00 |
| N(4)–H(4D)···O(9) | 0.8900 | 2.5400 | 3.086(4) | 121.00 |
| N(4)–H(4D)···O(20) | 0.8900 | 2.0000 | 2.831(4) | 154.00 |
| N(4)–H(4E)···O(7) | 0.8900 | 1.9900 | 2.873(4) | 174.00 |
| O(1W)–H(1WB)···O(2W) | 0.80(4) | 1.97(4) | 2.766(4) | 171(5) |
| O(1W)–H(1WA)···O(15) | 0.81(3) | 1.97(3) | 2.775(3) | 173(4) |
| O(2W)–H(2WB)···O(12) | 0.82(3) | 1.99(3) | 2.788(4) | 166(4) |
| O(2W)–H(2WA)···O(8) | 0.82(4) | 2.04(4) | 2.836(4) | 165(4) |
| O(9)–H(9)···O(16) | 0.78(3) | 1.89(3) | 2.662(3) | 176(5) |
| O(10)–H(10)···O(1W) | 0.81(4) | 1.84(4) | 2.643(4) | 175(5) |
| C(2)–H(2A)···O(15) | 0.9700 | 2.5700 | 3.491(5) | 158.00 |
| C(5)–H(5A)···O(8) | 0.9700 | 2.4800 | 3.432(5) | 165.00 |
| C(7)–H(7B)···O(1) | 0.9700 | 2.4100 | 3.143(5) | 132.00 |
| C(8)–H(8A)···O(11) | 0.9700 | 2.4700 | 3.315(5) | 145.00 |

and 1.561(2) Å, while O–P–O angles vary from 103.69(13)° to 111.69(13)°, consistent with the literature [21, 39]. Terminal oxygens [O(9) and O(10)] are OH groups. Two waters [O1w and O2w] are linked by O1w–H1wb···O2w hydrogen bonds with O1w···O2w 2.766(4) Å, while O1w–H1wb···O2w is 171(5)°. Adjacent polyanions are linked by water clusters using hydrogen bonds to make $[H_2(P_2Mo_5O_{23}) \cdot (H_2O)_2]_n$ chains along the a axis. These units are further connected by P–O–H···O hydrogen bonds to generate a layer shown in figure 2. Fully protonated organoamine cations are inserted between adjacent layers and involved in N–H···O hydrogen bonds with polyanion to form a 3D framework (figure 3). The N···O distances vary from 2.819(4) to 3.087(4) Å, while Ow···O range between 2.775(3) and 2.836(4) Å.

When we changed pH from 4 to 5, **2** was obtained with one $[H_2P_2Mo_5O_{23}]^{4-}$, one $[HP_2Mo_5O_{23}]^{5-}$, protonated 1,6-diaminehexane, and water (figure 4). The polyoxoanion cluster is also Strandberg type. The P–O bond lengths are 1.513(5) to 1.572(5) Å and Mo–O vary from 1.670(9) to 2.455(4) Å. The O–P–O angles range from 106.2(3)° to 113.1(2)° and O–Mo–O from 69.60(17)° to 175.0(2)°. O21, O25, and O31 are OH groups with O–H distances between 0.807(17) and 0.821(8) Å. Four waters link two $[H_2P_2Mo_5O_{23}]^{4-}$ and two $[HP_2Mo_5O_{23}]^{5-}$ units by hydrogen bonds to form a closed ring $[H_2P_2Mo_5O_{23}]_2 \cdot [HP_2Mo_5O_{23}]_2 \cdot (H_2O)_4$. Two protonated organic amines are in the center of the circle, which is further surrounded by other organic amines. All organic cations have hydrogen bonding interactions with terminal and bridging oxygens of the polyoxoanion (figure 5). The N···O distances vary from 2.750(9) to 3.471(10) Å and C···O lengths range from 3.242(11) to 3.361(11) Å. Assignment of the oxidation state

Table 5. Hydrogen bond interactions in **2**.

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| N(2)–H(2C)···O(2W) | 0.8900 | 2.1400 | 2.965(10) | 154.00 |
| N(2)–H(2C)···O(31) | 0.8900 | 2.4200 | 2.715(9) | 100.00 |
| N(2)–H(2D)···O(5W) | 0.8900 | 2.3600 | 3.088(11) | 139.00 |
| N(2)–H(2D)···O(31) | 0.8900 | 2.4000 | 2.715(9) | 101.00 |
| N(2)–H(2D)···O(38) | 0.8900 | 2.5100 | 3.103(11) | 124.00 |
| N(2)–H(2E)···O(15) | 0.8900 | 2.0300 | 2.875(9) | 159.00 |
| N(3)–H(3C)···O(4) | 0.8900 | 2.1400 | 2.835(10) | 134.00 |
| N(3)–H(3C)···O(19) | 0.8900 | 2.4900 | 2.922(7) | 110.00 |
| N(3)–H(3D)···O(6) | 0.8900 | 2.0600 | 2.930(11) | 166.00 |
| N(3)–H(3E)···O(8) | 0.8900 | 2.5200 | 3.232(10) | 137.00 |
| N(3)–H(3E)···O(17) | 0.8900 | 2.2100 | 2.988(7) | 146.00 |
| N(3)–H(3E)···O(19) | 0.8900 | 2.5800 | 2.922(7) | 104.00 |
| N(4)–H(4C)···O(1W) | 0.8900 | 2.0200 | 2.855(11) | 156.00 |
| N(6)–H(6D)···O(26) | 0.8900 | 2.5400 | 3.009(10) | 114.00 |
| N(6)–H(6D)···O(41) | 0.8900 | 2.5800 | 3.458(10) | 171.00 |
| N(8)–H(8C)···O(44) | 0.8900 | 2.1300 | 2.957(7) | 154.00 |
| N(8)–H(8D)···O(25) | 0.8900 | 2.6000 | 2.992(9) | 108.00 |
| N(8)–H(8D)···O(42) | 0.8900 | 2.3800 | 3.085(9) | 136.00 |
| N(8)–H(8D)···O(46) | 0.8900 | 2.5900 | 3.338(13) | 143.00 |
| N(8)–H(8D)···O(46A) | 0.8900 | 2.3900 | 3.108(13) | 138.00 |
| N(8)–H(8E)···O(4W) | 0.8900 | 2.0500 | 2.863(10) | 152.00 |
| N(9)–H(9C)···O(25) | 0.8900 | 2.2000 | 2.899(10) | 135.00 |
| N(9)–H(9D)···O(45) | 0.8900 | 2.3600 | 3.119(15) | 143.00 |
| N(9)–H(9D)···O(45A) | 0.8900 | 2.3200 | 3.178(14) | 162.00 |
| N(9)–H(9E)···O(6W) | 0.8900 | 1.8800 | 2.762(12) | 170.00 |
| O(2W)–H(2WA)···O(37) | 0.808(12) | 2.297(11) | 3.003(7) | 146.4(10) |
| O(2W)–H(2WB)···O(26) | 0.809(13) | 2.101(19) | 2.725(8) | 134(3) |
| O(3W)–H(3WB)···O(7) | 0.809(17) | 2.07(4) | 2.833(8) | 157(10) |
| O(4W)–H(4WA)···O(41) | 0.79(2) | 2.544(18) | 2.833(9) | 103.5(15) |
| O(4W)–H(4WB)···N(9) | 0.787(13) | 2.473(13) | 2.975(11) | 122.9(12) |
| O(5W)–H(5WA)···O(24) | 0.81(2) | 1.90(3) | 2.690(9) | 164(6) |
| O(6W)–H(6WA)···O(46) | 0.818(18) | 2.21(2) | 2.822(13) | 131.8(15) |
| O(6W)–H(6WA)···O(46A) | 0.818(18) | 2.55(2) | 3.190(14) | 136.1(16) |
| O(6W)–H(6WA)···N(8) | 0.818(18) | 2.505(17) | 3.074(11) | 127.7(16) |
| O(21)–H(21)···O(19) | 0.81(2) | 1.85(2) | 2.634(7) | 163(3) |
| O(25)–H(25)···N(9) | 0.821(9) | 2.593(12) | 2.899(10) | 103.7(8) |
| O(25)–H(25)···O(25) | 0.821(9) | 2.262(9) | 2.640(5) | 108.5(8) |
| O(31)–H(31)···O(22) | 0.809(13) | 1.791(15) | 2.577(6) | 163(3) |
| C(3)–H(3B)···N(1) | 0.9700 | 2.5700 | 3.010(11) | 108.00 |
| C(23)–H(23B)···O(46A) | 0.9700 | 2.5600 | 3.291(16) | 132.00 |
| C(24)–H(24B)···O(40) | 0.9700 | 2.4900 | 3.242(11) | 134.00 |

of Mo for both **1** and **2** is based on bond valence sum calculations, which give average value 5.9919 and 6.074 for **1** and **2**, respectively. The result confirms that Mo has the oxidation state of 6, consistent with formulas of **1** and **2**. The colors of both compounds are related to charge–transfer transitions. Similarly, some reported Strandberg-type phosphomolybdates with $\mathrm{Mo^{VI}}$ are colored [38, 39].

### 3.3. *IR spectrum and solid UV spectra*

IR spectra of **1** and **2** exhibit broad bands at 3374(1) and 3447(2) due to water and a series of bands at 1384–1617 $\mathrm{cm^{-1}}$ associated with the organoamine. The compounds

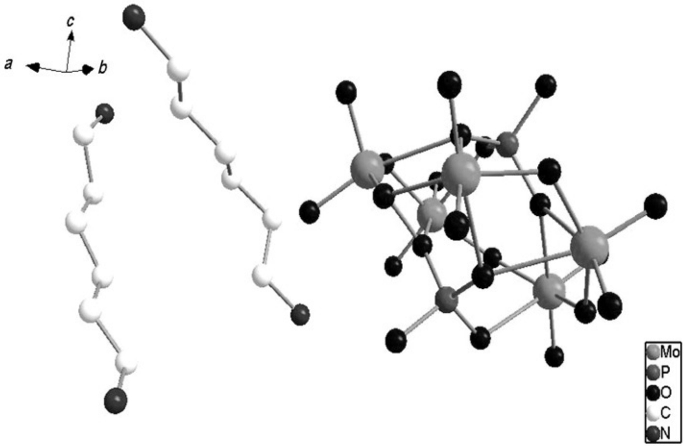

Figure 1. Structure of $(C_6H_{18}N_2)_2[H_2P_2Mo_5O_{23}] \cdot 2(H_2O)$ (**1**). Hydrogens and water are omitted for clarity.

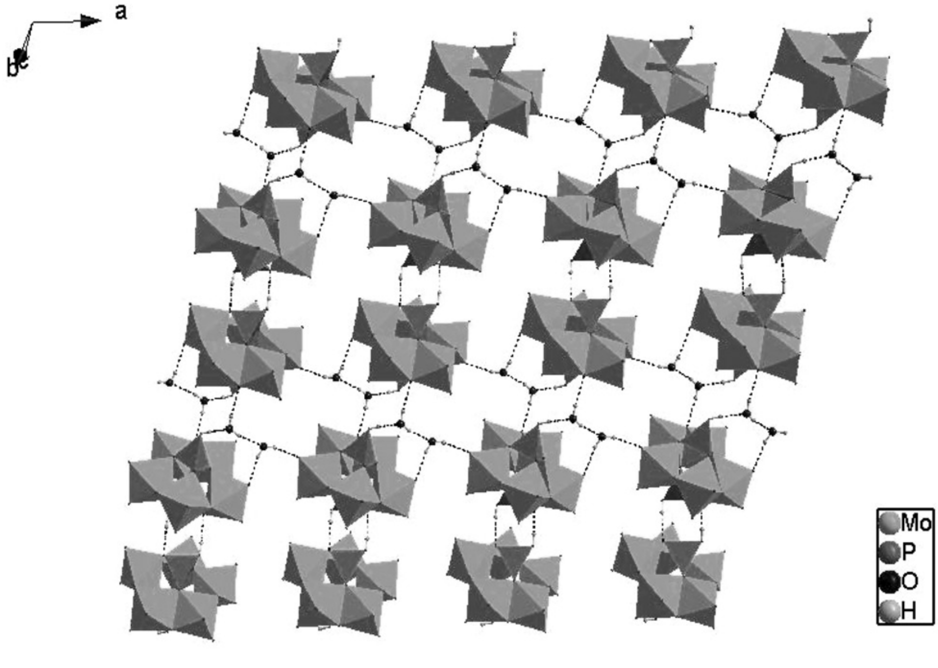

Figure 2. Polyanions are linked by O–H $\cdots$ O hydrogen bonds in **1**.

also possess bands at 1028–1122 $cm^{-1}$ attributed to $\nu$(P–O) and strong bands at 939, 895, 882, 668, 560, and 553 for **1** and 914, 693, 668, and 529 $cm^{-1}$ for **2** associated with $\nu$(Mo=O) and $\nu$(Mo–O–Mo) [17, 12–23, 38, 39, 43, 44]. In the solid ultraviolet (UV) spectra of **1** and **2**, high-energy bands are at 295 and 301 nm, respectively, categorized as metal-to-ligand (oxygen) charge–transfer transitions.

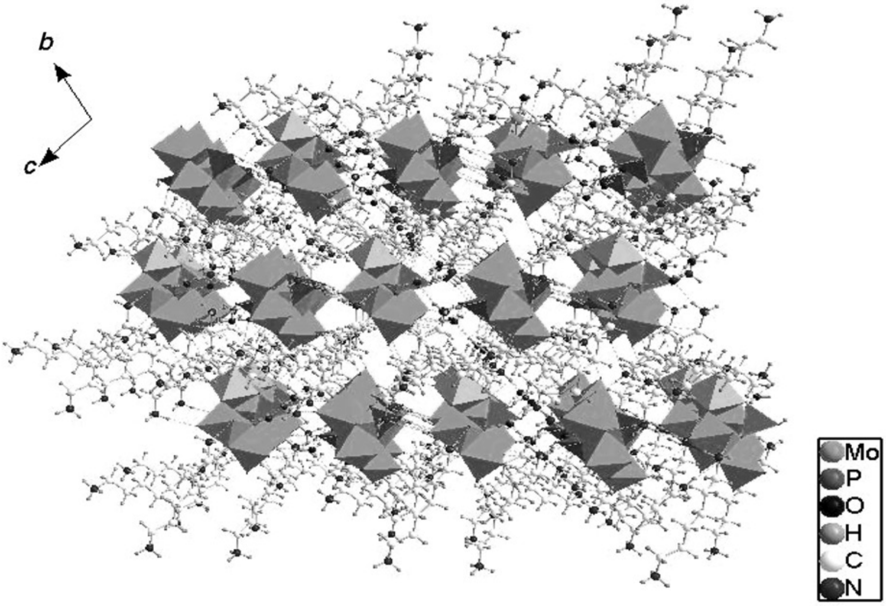

Figure 3. Packing diagram of the unit cell of **1** along the *a*-axis.

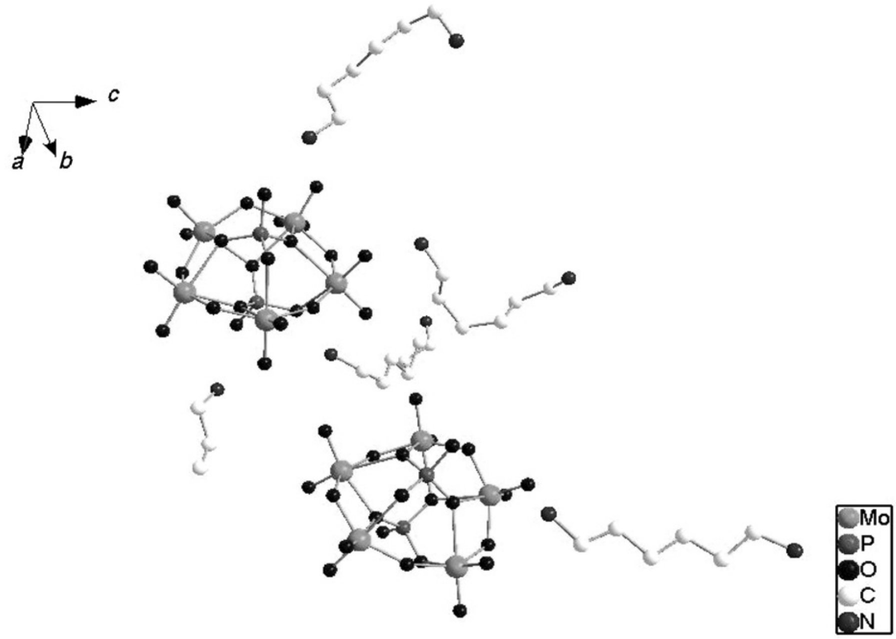

Figure 4. The structure of $(C_6H_{18}N_2)_{4.5}[HP_2Mo_5O_{23}][H_2P_2Mo_5O_{23}] \cdot 6(H_2O)$ (**2**). Hydrogens and water are omitted for clarity.

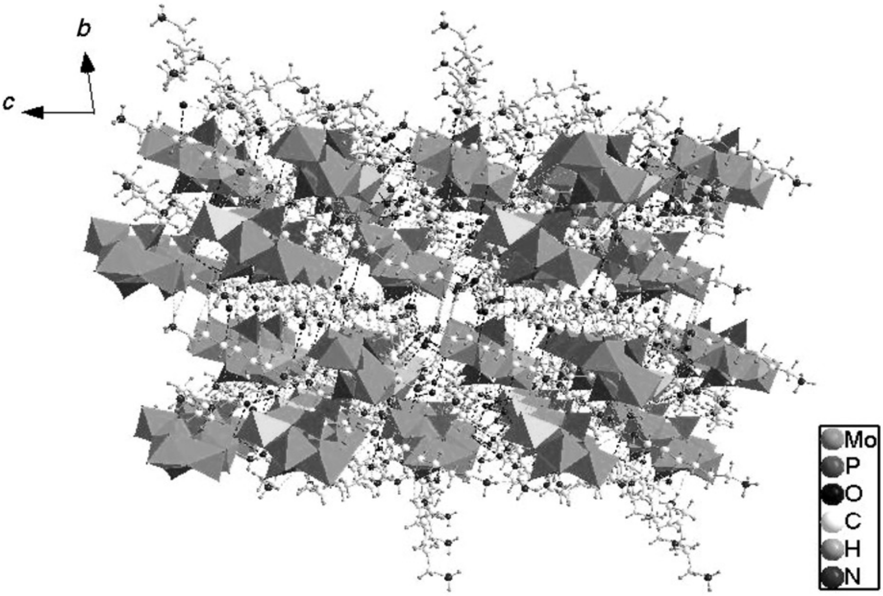

Figure 5. Packing diagram of the unit cell of **2** along the *a*-axis.

### 3.4. *Thermal analysis*

The TG curve of **1** (Supplementary material) indicates that weight loss can be divided into two distinct stages. The first weight loss of 3.37% (Calcd 3.21%) at 40–170°C corresponds to loss of water. From 170°C to 600°C, the second weight loss is attributed to the decomposition of 1,6-diaminehexane (weight loss: experimental 19.24%, Calcd 19.93%).

The TG curve of **2** (Supplementary material) indicates also two distinct stages. The first stage of 4.86% (Calcd 4.5%) at 40–140°C corresponds to loss of water. From 140°C to 700°C, the second weight loss is from decomposition of 1,6-diaminehexane (weight loss: experimental 21.78%, Calcd 21.55%).

## 4. Conclusions

Two new pentamolybdodiphosphate compounds containing protonated Strandberg polyoxoanion have been synthesized by the hydrothermal method and the pH value is vital for product formation.

## Supplementary material

CCDC-782601 and 782602 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge *via* http://www.ccdc.com.ac.uk/conts/

retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk

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