

# Synthesis and Structural Characterization of Two Molybdenum-phosphate Cluster Compounds: $(C_{14}N_{14}H_{63})Na(H_2Mo_6P_4O_{31})_2 \cdot 8H_2O$ and $(C_{14}N_{14}H_{63})Na(H_2Mo_6P_4O_{31})_2 \cdot 5H_2O$

WEN, Fu-Shan(温福山)    CHEN, Wei(陈伟)    SHI, Zhan(施展)    LI, Guang-Hua(李光华)  
YU, Zhen-Tao(于振涛)    CHEN, Jie-Sheng\*(陈接胜)

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, Jilin 130023, China

$(C_{14}N_{14}H_{63})Na(H_2Mo_6P_4O_{31})_2 \cdot 8H_2O$  (1) with amine-separated sodium molybdenumphosphate clusters and  $(C_{14}N_{14}H_{63})Na(H_2Mo_6P_4O_{31})_2 \cdot 5H_2O$  (2) with H-bonded cluster layers were synthesized from hydrothermal systems. Compound 1 crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 1.27445(2)$  nm,  $b = 1.37183(3)$  nm,  $c = 1.41515(3)$  nm,  $\alpha = 100.497(1)^\circ$ ,  $\beta = 109.064(1)^\circ$  and  $\gamma = 115.498(1)^\circ$ . Whereas compound 2 has a monoclinic space group  $P2_1/n$  with  $a = 1.3418(5)$  nm,  $b = 2.7787(12)$  nm,  $c = 2.0314(10)$  nm and  $\beta = 96.571(14)^\circ$ . There exist protonated ethylenediamine cations and  $H_2O$  molecules between adjacent clusters, connecting the clusters through H-bonds.

**Keywords** molybdenumphosphate cluster, crystal structure, hydrothermal synthesis

## Introduction

The synthesis and sorption properties of open framework solids such as zeolites<sup>1</sup> and metal molybdenum phosphate<sup>2,3</sup> with large cavities provoked enormous interest because of their potential application in catalysis. One-, two- and three-dimensional solid compounds consisting of organic and inorganic components, especially transition metal oxides, have recently attracted considerable attention since these materials possess not only unusual catalytic but also magnetic, electric and biochemical properties.<sup>4-6</sup> Many of the two-dimensional compounds allow chemical reactions to take place in the interlamellar region

serving as inert nanoscale reactors. Typical examples are transition metal oxides including reduced molybdenum phosphates,<sup>7</sup> vanadium oxides<sup>8</sup> and alkali metal molybdenum organophosphates.<sup>9</sup> To date, a large number of structures of molybdenum-containing compounds including 3-D frameworks,<sup>2,7</sup> 2-D layers,<sup>10,11</sup> 1-D polymers<sup>12,13</sup> and clusters<sup>14,15</sup> have been obtained by high temperature solid-state synthetic methods<sup>5,16,17</sup> and hydrothermal techniques.<sup>14,15,18</sup>

Hydrothermal synthesis combines the advantages of both high temperature solid-state synthesis and synthesis in a solution, and has been proven to be an excellent mild synthetic means for novel solid-state materials. A combination of the hydrothermal technique and the structure directing properties of certain organic amines and/or other species can lead to the formation of compounds with versatile structures.<sup>19-21</sup> Many molybdenum phosphates have been obtained in the hydrothermal systems with tetramethylammonium and other amines as the structure directing agents.<sup>2,7,22,23</sup> And by changing the amine species, compounds with different structural features can be obtained. In this article, we describe the hydrothermal syntheses and structural characterizations of two new amine/sodium hydrogen molybdenum phosphates  $(C_{14}N_{14}H_{63})Na(H_2Mo_6P_4O_{31})_2 \cdot 8H_2O$  (1) and  $(C_{14}N_{14}H_{63})Na(H_2Mo_6P_4O_{31})_2 \cdot 5H_2O$  (2) directed by ethylenediamine, a typical aliphatic diamine molecule.

\* E-mail: chemcej@mail.jlu.edu.cn; Tel.: 0431-5670650; Fax: (+86)-0431-5671974

Received December 17, 2001; revised May 20, 2002; accepted June 5, 2002.

Project supported by the National Natural Science Foundation of China (No. 29931010) and the Education Ministry of China.

## Experimental

### Synthesis

Compounds **1** and **2** were hydrothermally synthesized with empirical molar compositions of  $\text{Na}_2\text{MoO}_4:5.8 \text{ H}_3\text{PO}_4:4.3 \text{ NH}_2\text{CH}_2\text{CH}_2\text{NH}_2:165.4 \text{ H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4:8.7 \text{ H}_3\text{PO}_4:6.9 \text{ NH}_2\text{CH}_2\text{CH}_2\text{NH}_2:255.5 \text{ H}_2\text{O}$ , respectively. The final reaction mixtures were separately sealed in two Teflon-lined stainless steel autoclaves and heated at 160 °C for 5 d and 9 d, respectively. The resulting red large single crystals were collected by filtration, washed with distilled water, and dried in air at ambient temperature.

### General characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). The elemental analysis for C, H and N was performed on a Perkin-Elmer 2400 elemental analyzer and the inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 DV spectrometer. A Netzsch STA 449 C analyzer was employed to obtain the differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) curves.

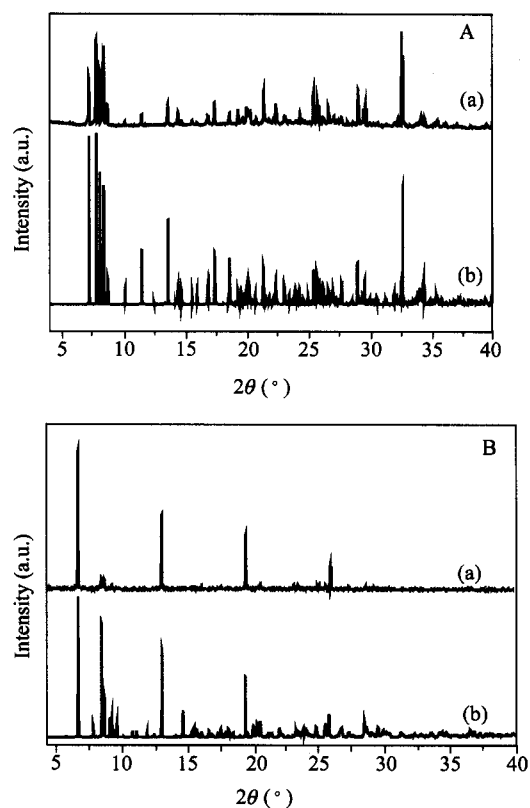
### X-Ray structure determination

The suitable crystals of **1** and **2** with dimensions of  $0.8 \text{ mm} \times 0.6 \text{ mm} \times 0.4 \text{ mm}$  and  $0.8 \text{ mm} \times 0.4 \text{ mm} \times 0.4 \text{ mm}$  were respectively selected for single-crystal X-ray analysis. The crystal was glued to a thin glass fiber and mounted on a Bruker-AXS Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source operating at 50 kV and 40 mA. Intensity data were collected using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.071073 \text{ nm}$ ) at  $20(2) \text{ }^\circ\text{C}$ . The structures of the two compounds were solved by Patterson function methods. All non-hydrogen atoms were refined anisotropically. Crystal data and structure refinement details are given in Table 1. Selected bond lengths for **1** and **2** are given in Tables 2, 3. Refinements were performed using the SHELXTL (version 5.1, Siemens Automation, Inc., Madison, WI 53719, USA, 1997) crystallographic software package.

## Results and discussion

### Characterization

The experimental and simulated powder X-ray diffraction (XRD) patterns for **1** and **2** are shown in Fig. 1. They are in good agreement with each other in main peak position, suggesting that both the products are pure. The difference in reflection intensity between the simulated and experimental patterns of each product is due to a certain degree of preferred orientation of the powder sample during data collection.



**Fig. 1** Experimental (a) and simulated (b) powder X-ray diffraction patterns of A: compound **1**, and B: compound **2**.

The elemental analysis indicates that the contents of C, H and N for **1** and **2** are 5.58, 2.85, 6.62 (calculated: 5.62, 2.80, 6.56) and 5.68, 2.66, 6.70 (calculated: 5.73, 2.64, 6.68), respectively. The ICP analysis shows that there exist Mo 38.12, P 8.35, Na 0.79 for **1**, close to the calculated values (Mo 38.50, P 8.29,

Table 1 Crystal data and structure refinement for 1 and 2

|  | 1  | 2   |
|--|--|---|
| Empirical formula  | C <sub>7</sub> H <sub>41.50</sub> Mo <sub>6</sub> N <sub>7</sub> Na <sub>0.50</sub> O <sub>35</sub> P <sub>4</sub> | C <sub>14</sub> H <sub>77</sub> Mo <sub>12</sub> N <sub>14</sub> NaO <sub>67</sub> P <sub>8</sub> |
| Formula weight   | 1494.99  | 2935.93   |
| <i>T</i> (°C)  | 20(2)  | 20(2)   |
| $\lambda$ (nm)   | 0.071073   | 0.071073  |
| Crystal system   | Triclinic  | Monoclinic  |
| Space group  | <i>P</i> $\bar{1}$   | <i>P</i> 2 <sub>1</sub> / <i>n</i>  |
| <i>a</i> (nm)  | 1.27445(2)   | 1.3418(5)   |
| <i>b</i> (nm)  | 1.37183(3)   | 2.7787(12)  |
| <i>c</i> (nm)  | 1.41515(3)   | 2.0314(10)  |
| $\alpha$ (°)   | 100.497(1)   | 90  |
| $\beta$ (°)  | 109.064(1)   | 96.571(14)  |
| $\gamma$ (°)   | 115.498(1)   | 90  |
| <i>V</i> (nm <sup>3</sup> )                                      | 1.95376(7)   | 7.524(6)  |
| <i>Z</i>   | 2  | 4   |
| <i>D</i> <sub>c</sub> (Mg/m <sup>3</sup> )                       | 2.541  | 2.592   |
| Absorption coefficient (mm <sup>-1</sup> )                       | 2.158  | 2.236   |
| <i>F</i> (000)   | 1460   | 5720  |
| Crystal size (mm)  | 0.8 × 0.6 × 0.4  | 0.8 × 0.4 × 0.4   |
| Reflections collected/unique (mm <sup>-1</sup> )                 | 9584/5589 (0.0145)   | 36417/10815 (0.0313)  |
| Absorption correction  | Sadabs   | Sadabs  |
| <i>T</i> <sub>max</sub> / <i>T</i> <sub>min</sub>                | 0.4175/0.3536  | 0.4520/0.3513   |
| Refinement method  | Full-matrix least-squares on <i>F</i> <sub>2</sub>   | Full-matrix least-squares on <i>F</i> <sub>2</sub>  |
| Data/restraints/parameters                                       | 5589/0/556   | 10815/0/1045  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                         | 1.127  | 1.062   |
| Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup> | <i>R</i> <sub>1</sub> = 0.0291, <i>wR</i> <sub>2</sub> = 0.0806  | <i>R</i> <sub>1</sub> = 0.0321, <i>wR</i> <sub>2</sub> = 0.0834                                   |
| <i>R</i> indices (all data)                                      | <i>R</i> <sub>1</sub> = 0.0307, <i>wR</i> <sub>2</sub> = 0.0816  | <i>R</i> <sub>1</sub> = 0.0465, <i>wR</i> <sub>2</sub> = 0.0929                                   |
| Largest diff. peak and hole (e/nm <sup>3</sup> )                 | 1.246 × 10 <sup>3</sup> and -1.123 × 10 <sup>3</sup>   | 1.531 × 10 <sup>3</sup> and -0.723 × 10 <sup>3</sup>  |

$$^a R_1 = \sum \| F_o \| - \| F_c \| / \sum \| F_o \| ; wR_2 = \{ \sum [ w ( F_o^2 - F_c^2 )^2 ] / \sum [ w ( F_o^2 )^2 ] \}^{1/2}$$

Na 0.77), and Mo 39.14, P 8.39, Na 0.81 for 2, corresponding to the calculated ones (Mo 39.21, P 8.44, Na 0.78).

The TGA and DTA curves for 1 and 2 appear to be similar: a continuous thermal change occurring between 50 °C and 650 °C accompanies a total weight loss of about 21%. This weight loss corresponds to the removal of the water and ethylenediamine molecules (16% in comparison with the theoretical value of about 15%). There is a marked endothermic peak in the temperature range of 650–700 °C in the DTA curves, and it could be associated with a phase transformation.<sup>15</sup>

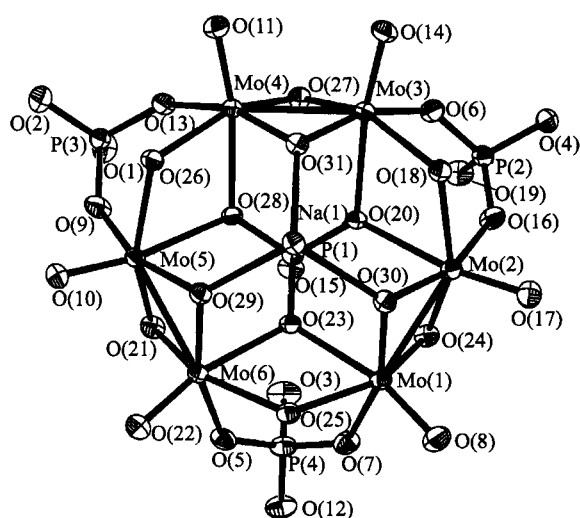
#### Structure description

The asymmetric unit of compound 1 is shown in Fig.

2. The basic structure of this unit has also been observed previously by Xu and co-workers.<sup>15</sup> There are six Mo atoms connected by twelve bridging O atoms. These Mo atoms lie in a plane and show alternate Mo—Mo bonding (average Mo—Mo distance: 0.259 nm) and non-bonding Mo—Mo contacts. There also exist four phosphate groups in the unit, and three of them are on the periphery, while the additional central phosphate has three O atoms connected with Mo atoms. Of the four phosphate groups in the unit, two P atoms form P—OH bonds (P(4)—O(3)H and P(2)—O(9)H) according to the P—O bond lengths,<sup>24</sup> whereas the other two correspond to terminal P = O bonds. The sodium atom is coordinated by six oxygen atoms at distances of 0.2227(5)—0.2325(5) nm from the opposite half clusters of (NaH<sub>4</sub>Mo<sub>12</sub>P<sub>8</sub>O<sub>62</sub>)<sup>7-</sup>.

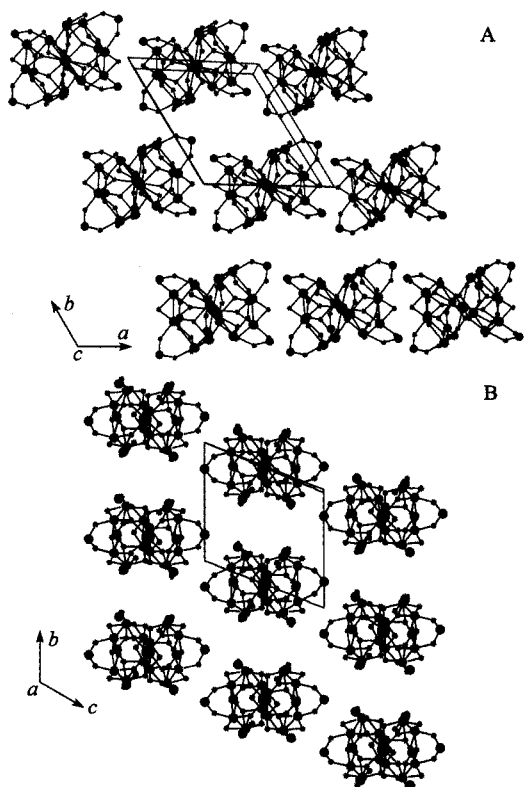
**Table 2** Selected bond lengths ( $10^{-1}$  nm) for **1**

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Mo(1)—O(8)  | 1.688(4)  | Mo(5)—O(9)  | 2.042(4)  |
| Mo(1)—O(24) | 1.936(4)  | Mo(5)—O(26) | 2.103(3)  |
| Mo(1)—O(30) | 1.946(3)  | Mo(5)—O(28) | 2.326(3)  |
| Mo(1)—O(7)  | 2.098(4)  | Mo(5)—Mo(6) | 2.5864(6) |
| Mo(1)—O(25) | 2.156(4)  | Mo(6)—O(22) | 1.688(4)  |
| Mo(1)—O(23) | 2.257(3)  | Mo(6)—O(21) | 1.942(4)  |
| Mo(1)—Mo(2) | 2.5881(6) | Mo(6)—O(29) | 1.944(3)  |
| Mo(2)—O(17) | 1.682(4)  | Mo(6)—O(5)  | 2.072(4)  |
| Mo(2)—O(24) | 1.942(4)  | Mo(6)—O(25) | 2.150(3)  |
| Mo(2)—O(30) | 1.954(3)  | Mo(6)—O(23) | 2.249(3)  |
| Mo(2)—O(16) | 2.042(4)  | P(1)—O(15)  | 1.512(4)  |
| Mo(2)—O(18) | 2.115(3)  | P(1)—O(28)  | 1.551(4)  |
| Mo(2)—O(20) | 2.347(3)  | P(1)—O(20)  | 1.552(4)  |
| Mo(3)—O(14) | 1.689(4)  | P(1)—O(23)  | 1.565(4)  |
| Mo(3)—O(27) | 1.943(3)  | P(2)—O(4)   | 1.520(4)  |
| Mo(3)—O(31) | 1.952(3)  | P(2)—O(19)  | 1.525(4)  |
| Mo(3)—O(6)  | 2.049(4)  | P(2)—O(16)  | 1.542(4)  |
| Mo(3)—O(18) | 2.118(4)  | P(2)—O(6)   | 1.553(4)  |
| Mo(3)—O(20) | 2.326(3)  | P(3)—O(2)   | 1.512(4)  |
| Mo(3)—Mo(4) | 2.6017(6) | P(3)—O(1)   | 1.518(4)  |
| Mo(4)—O(11) | 1.688(4)  | P(3)—O(9)   | 1.551(4)  |
| Mo(4)—O(31) | 1.947(3)  | P(3)—O(13)  | 1.562(4)  |
| Mo(4)—O(27) | 1.953(3)  | P(4)—O(12)  | 1.505(4)  |
| Mo(4)—O(13) | 2.068(3)  | P(4)—O(5)   | 1.529(4)  |
| Mo(4)—O(26) | 2.117(3)  | P(4)—O(7)   | 1.539(4)  |
| Mo(4)—O(28) | 2.286(3)  | P(4)—O(3)   | 1.584(4)  |
| Mo(5)—O(10) | 1.692(4)  | Na(1)—O(29) | 2.264(3)  |

**Fig. 2** ORTEP drawing with thermal ellipsoids at 50% probability, of the  $[\text{Na}_{0.5}(\text{Mo}_6\text{P}_4\text{O}_{31})]^{5.5-}$  motif representing half of the cluster observed in **1** and **2**.

In the structure of compound **1**, the  $(\text{NaH}_4\text{Mo}_{12}\text{P}_8\text{O}_{62})^{7-}$  anionic cluster consists of two asymmetric units of  $(\text{Na}_{0.5}\text{H}_2\text{Mo}_6\text{P}_4\text{O}_{31})^{3.5-}$ . Each isolated  $(\text{NaH}_4\text{Mo}_{12}\text{P}_8\text{O}_{62})^{7-}$  cluster has six neighbouring clusters along the *c* axis (Fig. 3A) and the *a* axis (Fig. 3B), respectively. Thus there are ten clusters around each cluster in the compound. All the clusters are joined together through protonated ethylenediamine cations and water molecules. Differing from the situation for the structure reported by Xu *et al.*, there are no hydrogen bonds between the isolated cluster anions considering the O—O distances between different clusters, which are all over 0.411 nm. However, hydrogen bonds exist between the clusters and the protonated ethylenediamine cations, which also act as charge-balancing species in the structure of **1**. Water molecules also play a role in the hydrogen bonding with the clusters. There are 3.5  $\text{NH}_3$  protons distributed in 3.5 protonated ethylenediamine molecules, therefore the

ethylenediamine cations are monoprotonated. The hydrogen bonds connecting the anions, organic cations and water molecules together in the clusters include  $O \cdots H - O_w$  (0.238–0.283 nm),  $O \cdots H - N$  (0.278–0.289 nm),  $O_w \cdots N - H$  (0.247 nm),  $O_w \cdots H - O_w$  (0.232–0.253 nm).

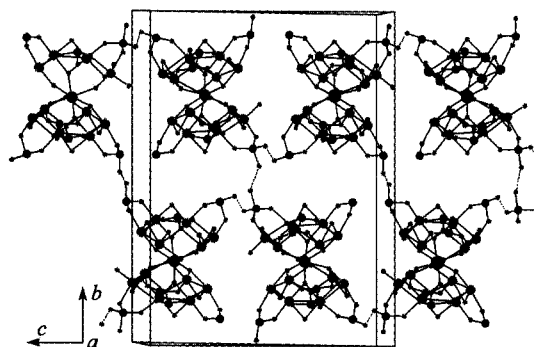


**Fig. 3** A view of (A) the  $ab$  plane along the  $c$  axis and (B) the  $bc$  plane along the  $a$  axis for compound **1** (ethylenediamine cations, water molecules and part O atoms are omitted for clarity).

The  $(NaH_4Mo_{12}P_8O_{62})^{7-}$  cluster anion of **2** has a “sandwich” configuration similar to that of compound **1**. The difference between the cluster anions of **1** and **2** is that each of the two halves of the cluster anion in **1** contains two P—OH hydroxyl groups, while there exists one hydroxyl (P(6)—O(62)H) in one half and three (P(2)—O(53)H, P(3)—O(41)H and P(4)—O(57)H) in the other half of the cluster anion  $(NaH_2Mo_{12}P_8O_{62})^{7-}$  in **2** according to the P—O and O—O bond lengths.<sup>24</sup>

In contrast to compound **1**, the upside-down  $(NaH_2Mo_{12}P_8O_{62})^{7-}$  clusters of **2** are connected through hydrogen bonds of the type  $O - H \cdots O$  forming zigzag chains parallel to the  $b$  axis ( $O(62) - H \cdots O(62) = 0.242$  nm and  $O(41) - H \cdots O(41) = 0.240$  nm) and  $c$

axis ( $O(53) - H \cdots O(55) = 0.263$  nm), respectively. In these zigzag chains, the alternated clusters are located in one plane. The zigzag chains are connected together again through hydrogen bonds and form layers that are parallel to the  $bc$  plane (Fig. 4). Besides the hydrogen bonds between adjacent clusters, there also exist hydrogen bonds of  $O \cdots H - O_w$  (0.264–0.270 nm),  $O \cdots H - N$  (0.275–0.289 nm),  $O_w \cdots N - H$  (0.282–0.288 nm),  $O_w \cdots H - O_w$  (0.267–0.274 nm) connecting the cluster anions, water molecules and the organic cations in compound **2** in a way similar to that of compound **1**. Thus, the major difference between **1** and **2** lies in the array pattern of the cluster anions. The cluster anions are isolated in the structure of **1** but in a layered form in **2**. No hydrogen-bonds between the cluster anions are observed in **1**, but inter-cluster H-bonds are prevalent in the structure of **2**.



**Fig. 4** A view of the layer structure parallel to  $bc$  plane formed by the zigzag chains for compound **2** (ethylenediamine cations, water molecules and part O atoms are omitted for clarity).

The molybdenum phosphate building block in **1** and **2** is the  $[NaMo_{12}O_{30}(HPO_4)_4(PO_4)_4]^{7-}$  unit. Although the basic structure of this unit is similar to that reported earlier,<sup>15</sup> the array and connection patterns for **1** and **2** are different from those for the compounds described in the literature. In one of the previously reported compounds, each  $[NaMo_{12}O_{30}(HPO_4)_4(PO_4)_4]^{7-}$  cluster is joined by four adjacent clusters through strong hydrogen bonds, forming an infinite layer that parallels to the  $[010]$  direction. The layers are stacked in an ABAB sequence along the  $[100]$  direction, with naphthalene-1,5-diammonium cations and water molecules being located between the layers. In the other compound directed by naphthalene-1,

**Table 3** Selected bond lengths ( $10^{-1}$  nm) for **2**

|             |            |               |            |
|-------------|------------|---------------|------------|
| Na(1)—O(1)  | 2.227(5)   | Mo(8)—O(45)   | 1.943(4)   |
| Na(1)—O(4)  | 2.228(5)   | Mo(8)—O(13)   | 1.956(4)   |
| Na(1)—O(11) | 2.320(5)   | Mo(8)—O(48)   | 2.056(5)   |
| Na(1)—O(14) | 2.320(5)   | Mo(8)—O(9)    | 2.141(4)   |
| Na(1)—O(12) | 2.324(5)   | Mo(8)—O(3)    | 2.294(4)   |
| Na(1)—O(13) | 2.325(5)   | Mo(9)—O(25)   | 1.681(5)   |
| Mo(1)—O(49) | 1.689(4)   | Mo(9)—O(1)    | 1.942(4)   |
| Mo(1)—O(50) | 1.940(4)   | Mo(9)—O(18)   | 1.957(4)   |
| Mo(1)—O(14) | 1.951(4)   | Mo(9)—O(42)   | 2.079(4)   |
| Mo(1)—O(32) | 2.055(4)   | Mo(9)—O(2)    | 2.136(4)   |
| Mo(1)—O(6)  | 2.131(4)   | Mo(9)—O(46)   | 2.327(4)   |
| Mo(1)—O(10) | 2.262(4)   | Mo(9)—Mo(10)  | 2.6019(11) |
| Mo(1)—Mo(7) | 2.5823(11) | Mo(10)—O(52)  | 1.679(5)   |
| Mo(2)—O(33) | 1.690(5)   | Mo(10)—O(1)   | 1.948(4)   |
| Mo(2)—O(30) | 1.931(4)   | Mo(10)—O(18)  | 1.949(4)   |
| Mo(2)—O(12) | 1.945(4)   | Mo(10)—O(54)  | 2.071(4)   |
| Mo(2)—O(23) | 2.099(5)   | Mo(10)—O(6)   | 2.147(4)   |
| Mo(2)—O(2)  | 2.138(4)   | Mo(10)—O(10)  | 2.250(4)   |
| Mo(2)—O(46) | 2.269(4)   | Mo(11)—O(36)  | 1.684(4)   |
| Mo(2)—Mo(6) | 2.5786(15) | Mo(11)—O(21)  | 1.941(4)   |
| Mo(3)—O(31) | 1.683(5)   | Mo(11)—O(4)   | 1.942(4)   |
| Mo(3)—O(29) | 1.962(4)   | Mo(11)—O(20)  | 2.028(4)   |
| Mo(3)—O(11) | 1.966(4)   | Mo(11)—O(7)   | 2.130(4)   |
| Mo(3)—O(16) | 2.038(4)   | Mo(11)—O(5)   | 2.333(4)   |
| Mo(3)—O(9)  | 2.128(4)   | Mo(11)—Mo(12) | 2.5975(11) |
| Mo(3)—O(3)  | 2.257(4)   | Mo(12)—O(58)  | 1.678(4)   |
| Mo(3)—Mo(5) | 2.6039(15) | Mo(12)—O(4)   | 1.942(4)   |
| Mo(4)—O(43) | 1.691(4)   | Mo(12)—O(21)  | 1.950(4)   |
| Mo(4)—O(45) | 1.938(4)   | Mo(12)—O(56)  | 2.082(5)   |
| Mo(4)—O(13) | 1.945(4)   | Mo(12)—O(44)  | 2.131(4)   |
| Mo(4)—O(27) | 2.057(4)   | Mo(12)—O(35)  | 2.352(4)   |
| Mo(4)—O(7)  | 2.152(4)   | P(1)—O(40)    | 1.501(5)   |
| Mo(4)—O(5)  | 2.288(4)   | P(1)—O(46)    | 1.555(5)   |
| Mo(4)—Mo(8) | 2.5788(11) | P(1)—O(8)     | 1.557(5)   |
| Mo(5)—O(39) | 1.688(4)   | P(1)—O(10)    | 1.560(4)   |
| Mo(5)—O(11) | 1.936(4)   | P(2)—O(60)    | 1.486(5)   |
| Mo(5)—O(29) | 1.951(4)   | P(2)—O(42)    | 1.539(5)   |
| Mo(5)—O(17) | 2.100(5)   | P(2)—O(23)    | 1.541(5)   |
| Mo(5)—O(44) | 2.116(4)   | P(2)—O(53)    | 1.585(5)   |
| Mo(5)—O(35) | 2.253(4)   | P(3)—O(61)    | 1.510(5)   |
| Mo(6)—O(28) | 1.688(4)   | P(3)—O(47)    | 1.531(5)   |
| Mo(6)—O(30) | 1.932(4)   | P(3)—O(41)    | 1.543(5)   |
| Mo(6)—O(12) | 1.956(4)   | P(3)—O(22)    | 1.554(5)   |
| Mo(6)—O(22) | 2.060(5)   | P(4)—O(59)    | 1.488(5)   |
| Mo(6)—O(15) | 2.130(4)   | P(4)—O(54)    | 1.524(5)   |
| Mo(6)—O(8)  | 2.289(4)   | P(4)—O(32)    | 1.532(5)   |
| Mo(7)—O(34) | 1.688(5)   | P(4)—O(57)    | 1.571(5)   |
| Mo(7)—O(50) | 1.940(4)   | P(5)—O(19)    | 1.514(5)   |
| Mo(7)—O(14) | 1.948(4)   | P(5)—O(5)     | 1.543(4)   |
| Mo(7)—O(47) | 2.074(5)   | P(5)—O(35)    | 1.552(5)   |
| Mo(7)—O(15) | 2.129(4)   | P(5)—O(3)     | 1.553(5)   |
| Mo(7)—O(8)  | 2.282(4)   | P(6)—O(55)    | 1.523(5)   |
| Mo(8)—O(51) | 1.679(5)   | P(6)—O(56)    | 1.528(5)   |

5-diammonium, the  $(\text{NaH}_6\text{Mo}_{12}\text{P}_8\text{O}_{62})^{5-}$  clusters are connected together through hydrogen bonds as well forming chains parallel to the [010] direction, and these chains are separated by a group of naphthalene-1,5-diammonium cations. In contrast to these two compounds, compound **1** from our reaction system contains sodium hydrogen phosphomolybdenum clusters isolated by protonated amine cations and water molecules. Although there also exist layers formed by the sodium hydrogen phosphomolybdenum clusters through inter-cluster H-bonds in compound **2** from our reaction system, the packing pattern of the clusters is completely different from that of the layered compound in the literature.<sup>15</sup> Another difference between compound **2** and the layered compound in the literature is that the cluster in the former has four P—OH groups whereas the one in the latter has six P—OH groups.

## Conclusions

Using ethylenediamine as the structure-directing agent, two molybdenum phosphate compounds have been crystallized through hydrothermal reaction. In one of the compounds, the isolated sodium hydrogen phosphomolybdenum clusters are packed together through H-bonds with protonated amine cations and water molecules, whereas the similar clusters are connected in the other material through inter-cluster H-bonds to form layers between which protonated amine cations and water molecules are located. The diversity of the cluster packing and connection for this type of compounds indicates that through variation of reaction conditions and amine molecules, the structural patterns can be adjusted with the basic cluster structure remaining unchanged.

## References

- Barreer, R. M. *Hydrothermal Chemistry of the Zeolites*, Academic Press, London, 1982.
- Haushalter, R. C.; Strohmaier, K. G.; Lai, F. W. *Science* **1989**, *246*, 1289.
- Mundi, L. A.; Strohmaier, K. G.; Goshorn, D. P.; Haushalter, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 8182.
- Renneke, R. F.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6885.
- Ledain, S.; Leclaire, A.; Borel, M. M.; Hervieu, M.; Provost, J.; Raveau, B. *J. Solid State Chem.* **1999**, *144*, 297.
- Luo, L. L.; Lanza, G.; Fragala, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 3111.
- Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31.
- Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1956.
- Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1995**, *34*, 4774.
- Corcoran, E. W. *Inorg. Chem.* **1990**, *29*, 157.
- Lii, K. H.; Haushalter, R. C. *J. Solid State Chem.* **1987**, *69*, 320.
- Haushalter, R. C.; Mundi, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 6340.
- Haushalter, R. C.; Lai, R. W. *Inorg. Chem.* **1989**, *28*, 2904.
- Haushalter, R. C.; Lai, F. W. *Angew. Chem.* **1989**, *101*, 802.
- Xu, Y.; Zhang, B.; Goh, N. K.; Chia, L. S. *Inorg. Chim. Acta* **1998**, *282*, 16.
- Ledain, S.; Leclaire, A.; Borel, M. M.; Provost, J.; Raveau, B. *J. Solid State Chem.* **1997**, *133*, 391.
- Ledain, S.; Leclaire, A.; Borel, M. M.; Hervieu, M.; Raveau, B. *J. Solid State Chem.* **1997**, *129*, 298.
- Wang, Y.; Chen, J. S.; Yuan, H. M.; Shi, Z.; Yu, S. F.; Chen, W. *Chin. J. Chem.* **2001**, *19*, 681.
- Liu, Y. L.; Zhu, G. S.; Chen, J. S.; Na, L. Y.; Hua, J.; Pang, W. Q.; Xu, R. R. *Inorg. Chem.* **2000**, *39*, 1820.
- Shi, Z.; Feng, S. H.; Zhang, L. R.; Yang, G. Y.; Hua, J. *Chem. Mater.* **2000**, *12*, 2930.
- Chippindale, A. M.; Cowley, A. R.; Chen, J. S.; Gao, Q. M.; Xu, R. R. *Acta Crystallogr., Sect. C* **1999**, *55*, 845.
- Linda, A. M.; Haushalter, R. C. *Inorg. Chem.* **1993**, *32*, 1579.
- Haushalter, R. C.; Lai, F. W. *Angew. Chem.* **1989**, *101*, 802.
- Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.