

Influence of organic amines on the self-assembly of hybrid polyoxomolybdenum(v) phosphate frameworks

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The synthesis and structural characterization of three new polyoxomolybdenum(v) phosphate frameworks have been achieved by using dimeric $\{\text{Mo}_6\}_2$ moieties as inorganic building blocks and protonated organic amines as counter ions. The structure-directing role of the organic cations was investigated and it was shown, that the geometry and the rigidity of the amines as well as their hydrogen bonding capabilities influence the formation of layered or chain-like superstructures.

Introduction

Since their first structural characterization, polyoxomolybdates (POMs) have attracted much attention from almost all fields of chemistry.¹ Their structural diversity and unique characteristics such as catalytic activity² and rich redox chemistry³ offer promising features for the design of novel functional materials with unprecedented chemical and physical properties. In recent years, a great deal of research has focussed on reduced polyoxomolybdenum(v) phosphates (POMPs) with 4d¹ molybdenum centers and in the search for new POM-based functional materials, several groups have investigated the structures and properties of crystalline organoammonium–POMP frameworks. The assembly of these materials often involves a dimeric $\{\text{Mo}_6\}_2$ species as the inorganic building block, owing to its ability to incorporate various alkali and transition metal cations such as Na, Fe, Zn, Co and Ni.^{4–11} This is because the unique coordination environment of these metal cations, provided by the POMP cluster, renders them interesting candidates for transition metal-mediated catalytic applications. In addition, the outer sphere of the $\{\text{Mo}_6\}_2$ cluster features protonated phosphate ligands and can therefore be considered as a solid acid.¹² The chemical properties of the cluster can be further fine-tuned by substitution of the inorganic phosphate groups with phosphonate moieties and thereby give access to a range of organo-functionalized structures.^{4,13} The self-assembly of these POMP anions in the presence of structure-directing protonated organic amines can result in the formation of porous frameworks with layered or channel-like structures which have potential applications as multifunctional materials in catalysis and separation processes.^{7,8,14}

However, the structure-directing effect of organic amines is not restricted to the formation of novel frameworks. In previous work we have recently reported the use of rigid organic amines to isolate new cluster types by virtue of the cations used to ‘encapsulate’ the new building blocks.^{15–20} By trapping clusters during the self-assembly process it may be

possible to restrain the cluster from reorganizing into other well-known structure types. For example, by using protonated hexamethylenetetraamine (HMTAH⁺) as counter ion, we were able to stabilize and isolate a highly charged polyoxomolybdate anion, $[\text{H}_2\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{12}\text{O}_{52}]^{10-}$, $\{\text{Mo}_{16}\}$, which represents a previously unknown structural type.^{18,19} The $\{\text{Mo}_{16}\}$ is stable in the solid state since the highly negative cluster anion is virtually completely wrapped by the organic HMTAH⁺ cations and is hence “shielded” from its environment. The extension of this approach also yielded clusters, Dawson-type mixed-valence polyoxomolybdates $[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]^{7-}$, with known structures, but with novel electronic properties.²⁰ Indeed, owing to their unprecedented structural^{18,19} or physical¹⁷ features, POM clusters have great potential for the engineering of novel functional frameworks. Therefore, in an extension to our previous work, we wished to investigate the assembly of known POM building blocks with organo-cations with the aim of manipulating the supramolecular structure types, and ultimately the physical properties of the material engineered.

In this report, we describe the synthesis and structural characterization of three new polyoxomolybdenum(v) phosphate frameworks, $[\text{CH}_6\text{N}_3]_{12}[\text{Mo}_{12}\text{O}_{62}\text{H}_{11}\text{NaP}_8] \cdot 11\text{H}_2\text{O}$ (**1**), $[\text{C}_4\text{H}_6\text{N}_3]_{14}[\text{Mo}_{12}\text{O}_{62}\text{H}_9\text{NaP}_8] \cdot 13\text{H}_2\text{O}$ (**2**) and $[\text{C}_2\text{H}_{10}\text{N}_2]_6[\text{Mo}_{12}\text{O}_{62}\text{H}_9\text{Na}_3\text{P}_8] \cdot 18\text{H}_2\text{O}$ (**3**), all comprising sodium-linked dimeric $\{\text{Mo}_6\}_2$ moieties as inorganic building blocks and guanidinium (**1**), 2-aminopyrimidinium (**2**) or protonated ethylenediamine (**3**) as structure-directing amines.

Results and discussion

Description of the $\{\text{Mo}_6\}_2$ dimer structure

The dimeric polyoxomolybdenum(v) phosphate anion $\text{Na}\{\text{Mo}_6\text{P}_4\text{X}_{31}\}_2^{n-}$ ($= \{\text{Mo}_6\}_2$) $\text{X} = \text{O}, \text{OH}$ has been extensively discussed in the literature.^{5,6} Briefly, the structure is based on two planar hexanuclear $\{\text{Mo}_6\}$ rings, each formed by six edge-sharing MoX_6 octahedra with alternating bonding (~ 2.6 Å) and non-bonding (~ 3.6 Å) Mo–Mo distances. The framework is therefore stabilized by three Mo–Mo single bonds, formed between the six single occupied 4d¹ orbitals of the particular Mo centers. The formation of these three metal–metal bonds can be postulated to be a major driving force in the self-assembly of the cluster, since there is no fully oxidized

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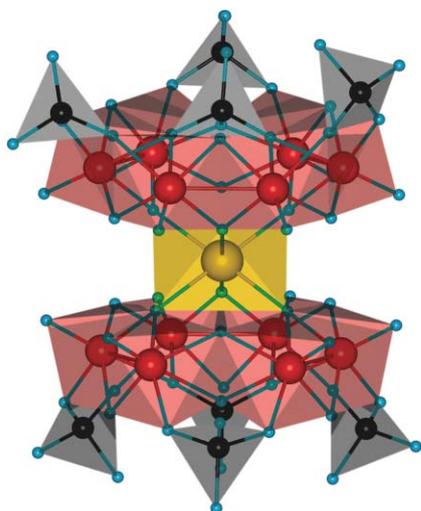
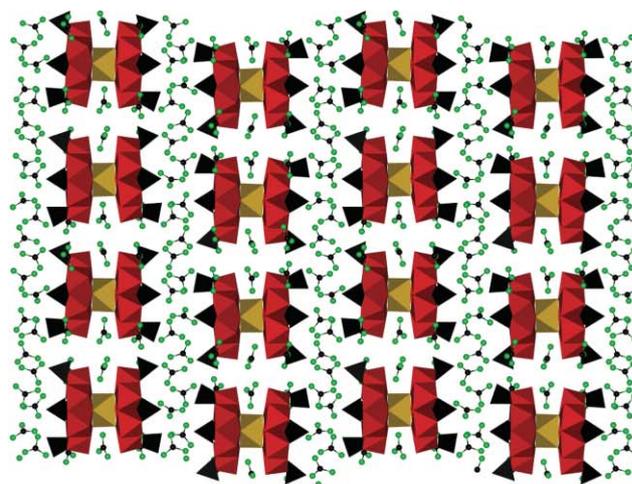


Fig. 1 Polyhedral representation of the dimeric $\{\text{Mo}_6\}_2$ sandwich anion with overlaid ball and stick drawing. Light grey: PX_4 tetrahedra, red: MoX_6 octahedra, gold: NaO_6 octahedron, blue balls: oxygen. This colour scheme will be used throughout.

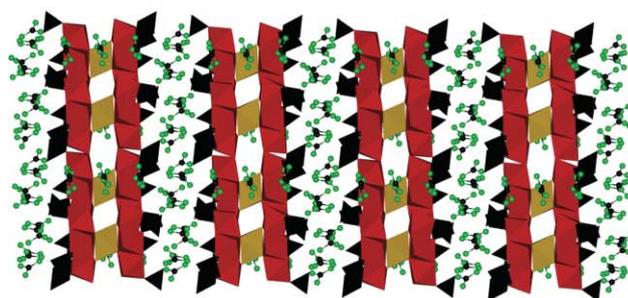
analogue known in the literature. In the outer coordination sphere of each $\{\text{Mo}_6\}$ ring, three peripheral and one central PX_4 tetrahedra are located on the same side of the ring plane (Fig. 1). These four PX_4 -tetrahedra bridge the non-bonding Mo–Mo fragments and hence shield and further reinforce the structure. The two $\{\text{Mo}_6\}$ rings are connected by a central sodium ion, which is coordinated octahedrally by three oxygen donors of each $\{\text{Mo}_6\}$ moiety, resulting in a staggered arrangement of the two rings. The $\{\text{Mo}_6\}$ units can therefore be considered as sterically demanding inorganic tridentate ligands, the complexation of which has been demonstrated with several transition metals.^{10,21–23} Characteristically for reduced Mo^{V} species, each MoX_6 octahedron in structure 1–3 features one terminally bound oxygen apex with short Mo–O distances of *ca.* 1.7 Å. In addition, two distinctive Mo–O distance ranges are observed, depending on the presence of a Mo–Mo bond or a phosphate bridge, respectively. The single-bonded Mo–Mo fragments are exclusively bridged by μ_2 -oxygen bridges (~ 1.95 Å) and by a long μ_3 -oxygen bridge from the central phosphate unit (~ 2.3 Å). The non-bonding Mo \cdots Mo moieties are bridged by μ_2 -oxygen bridges with medium bond lengths (~ 2.1 Å) and by oxygen bridges from the peripheral phosphate groups with a comparable length (~ 2.1 Å).

Description of the framework arrangement

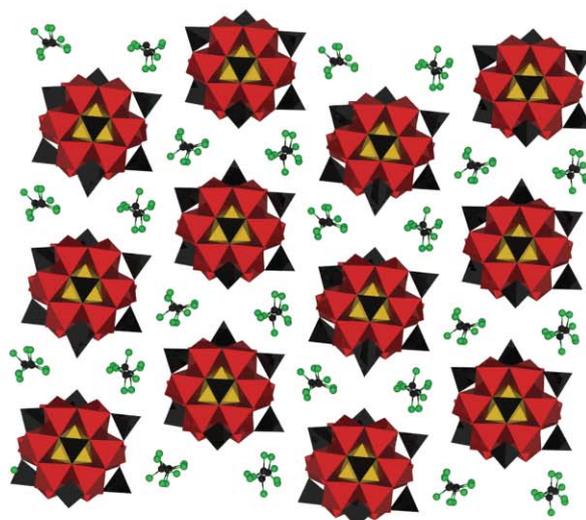
The projection of framework 1 along the crystallographic *a* axis shows that the polyoxomolybdenum phosphate dimers are arranged in layers forming ABAB motifs within the crystallographic *bc* plane, with inter-layer spacings of *ca.* 3.4 Å. All $\{\text{Mo}_6\}_2$ units show an identical orientation, their C_3 axis runs almost parallel to the crystallographic *c* axis (Fig. 2). The voids between the layers are filled with the small, 2-dimensional guanidinium cations, which can access all parts of the supramolecular framework and are densely packed between the particular cluster layers. Their planar structure and the large number of protons render them ideal acceptors for vast



(a)



(b)



(c)

Fig. 2 Projection of 1 along *a* (top), *b* (middle) and *c* (bottom). C: black spheres, N: green spheres. Water molecules and hydrogen atoms are omitted for clarity. In Fig. 2 bottom, the guanidinium cations between the layers are omitted for clarity.

hydrogen bonding networks between the metal cluster anions. Closer investigation of the distribution and arrangement of the organic cations reveals two distinctive types within the framework. The first group of guanidinium ions is located in the voids between the particular layers with the molecule plane perpendicular to the $\{\text{Mo}_6\}$ ring plane. Therefore, the cations are able to form an extensive hydrogen-bonding network

between two layers of anions, thus reinforcing the structure. The shortest N–H···O distance observed was 2.807(9) Å (N73–O44). Projection of **1** along the crystallographic *c* axis (Fig. 2 bottom) reveals the second type of guanidinium cations present in the structure.

Three of the dimeric $\{\text{Mo}_6\}_2$ clusters enclose a cavity containing three guanidinium cations. These guanidinium ions are arranged parallel to the molybdenum ring plane and form an intra-layer hydrogen bond network between the polyoxomolybdenum phosphate anions, thereby encapsulating the three surrounding cluster anions. Each anion is in turn surrounded by a hexagonal array of 18 guanidinium cations, which are arranged in six groups of three, aligned in a parallel fashion. This hexagonal supramolecular assembly of guanidinium ions induces the formation of another hexagonal superstructure of six further $\{\text{Mo}_6\}_2$ dimers, driven by attractive electrostatic and hydrogen bonding interactions (Fig. 3). This schematic might also give a useful idea about the initial steps of the self-assembly of the framework.

Examination of the framework structure of **2** shows common features to the framework in **1** in so far as that the $\{\text{Mo}_6\}_2$ clusters are arranged in ABAB layers in the crystallographic *ab* plane, featuring layer spacings of *ca.* 6.4 Å. However, unlike compound **1**, the $\{\text{Mo}_6\}_2$ units within the particular layers are not grouped in a parallel fashion, but show a torsion angle of 26.3° (Fig. 4). The voids between the layers as well as the spaces in between the cluster anions are occupied by protonated 2-aminopyrimidinium cations. Similar to framework **1**, two distinct groups of organic cations are observed, one of them forming chain-like supramolecular assemblies which run along the crystallographic *b* axis (Fig. 4

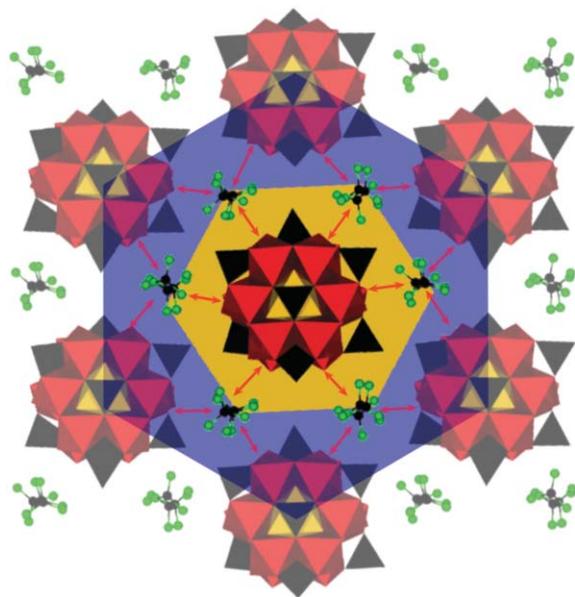
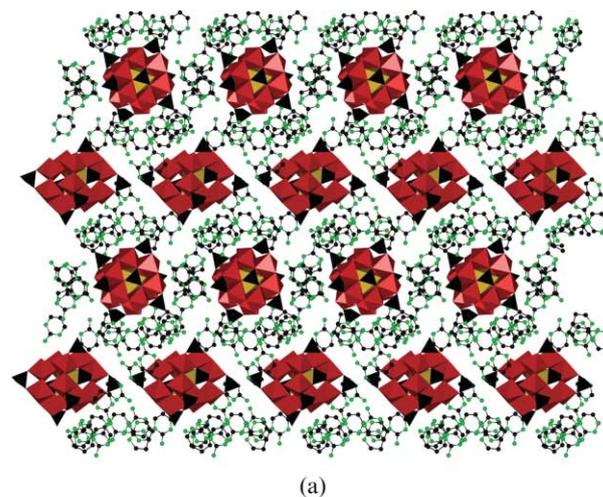
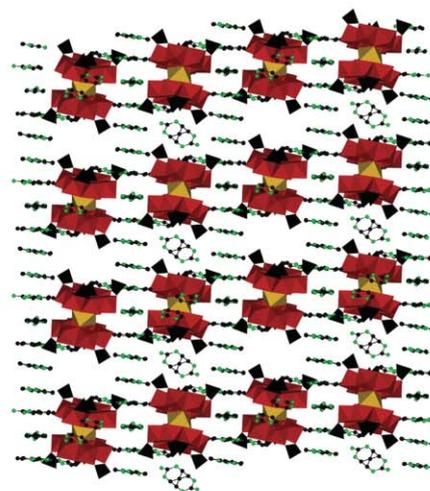


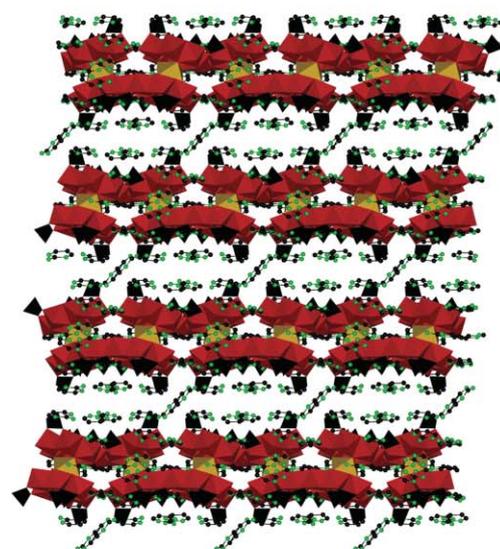
Fig. 3 Illustration of the superstructure formed around a $\{\text{Mo}_6\}_2$ dimer. The yellow hexagon illustrates the hexagonal arrangement of the guanidinium cations, the blue hexagon depicts the hexagonal superstructure formed by six further $\{\text{Mo}_6\}_2$ units. Red arrows schematically indicate the hydrogen bonding between the guanidinium cations and the POMPs groups. C: black spheres, N: green spheres, H omitted for clarity.



(a)



(b)



(c)

Fig. 4 Projection of **2** along *a* (top), *b* (middle) and *c* (bottom). C: black spheres, N: green spheres. Water molecules and hydrogen atoms are omitted for clarity.

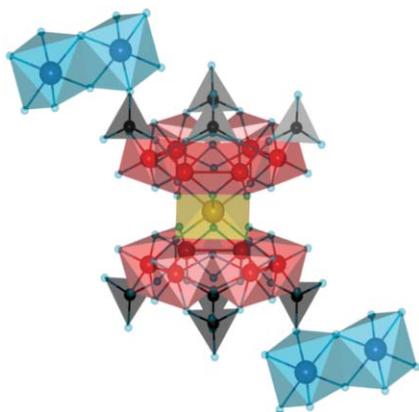


Fig. 5 Polyhedral representation of the connectivity in the polymeric chain found in **3**. Light blue octahedra: $\{\text{Na}_2\}$ di-octahedra, dark blue spheres: Na within the $\{\text{Na}_2\}$ linkers.

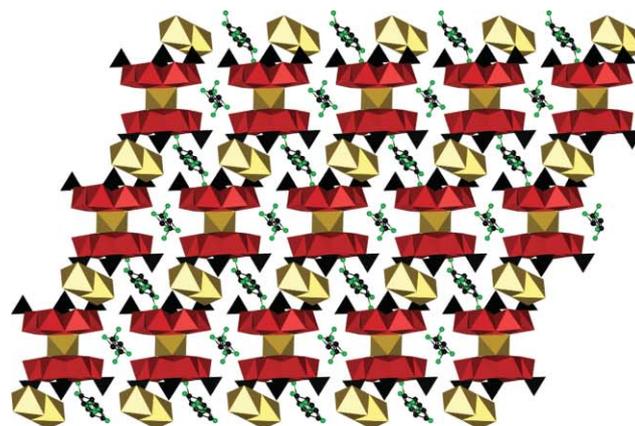
middle). The chains are held together by attractive π - π stacking interactions between the parallel aligned aromatic rings of the particular 2-aminopyrimidinium cations, resulting in a minimum distance of 3.501(4) Å between two ring centroids. In the lattice, the pyrimidinium-rings lie parallel to the ring-planes of the $\{\text{Mo}_6\}$ moieties and therefore allow for hydrogen bonding between the amine and the particular dimeric cluster units. The second group of protonated amines is found in the voids between the cluster layers and comprises a set of disordered 2-aminopyrimidinium cations with their ring planes oriented almost perpendicular to the ring planes of the first group. The cations provide further structural stability, again by electrostatic and hydrogen bonding interactions with minimum N-H \cdots O distances of 2.505(3) Å (N13-O74).

Although frameworks **1** and **2** feature non-connected $\{\text{Mo}_6\}_2$ units in a layered arrangement, the $\{\text{Mo}_6\}_2$ dimers in **3** are arranged in polymeric linear 1D chains. An edge-sharing $\text{Na}_2(\text{H}_2\text{O})_8\text{X}_2$ ($\{\text{Na}_2\}$) di-octahedron acts as a linker between two $\{\text{Mo}_6\}_2$ clusters by connecting two adjacent $\{\text{Mo}_6\}_2$ dimers. Also, the $\{\text{Na}_2\}$ unit shares two opposite apical corners with two peripheral PX_4 tetrahedra (Fig. 5), forming a purely inorganic linear chain.

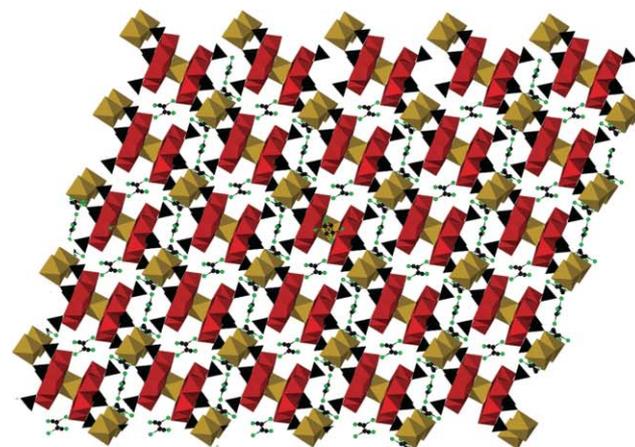
In the lattice, the polymeric chains are arranged in a parallel fashion (Fig. 6). The spaces between the chains are filled with diprotonated ethylenediamine cations which originate from the original amine, *N,N,N',N'*-tetrakis(hydroxyethyl)ethylenediamine. Further, these organo-cations stabilize the framework by both electrostatic and hydrogen bonding interactions with a minimum N-H \cdots O distance of 2.631(1) Å (N5-O22). However, it is notable that ethylenediamine does not have structure-directing properties similar to that seen for frameworks **1** and **2**, which might be due to increased flexibility of the ethyl chain.

Conclusions

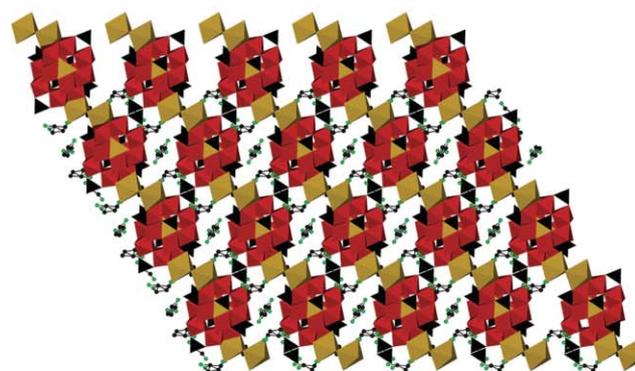
Three new hybrid polyoxomolybdenum(v) phosphate frameworks were synthesized and successfully characterized by single X-ray diffractometry. To our best knowledge, this is the first synthesis of $\{\text{Mo}_6\}_2$ units under non-hydrothermal conditions, therefore providing much greater influence on the



(a)



(b)



(c)

Fig. 6 Projection of **3** along *a* (top), *b* (middle) and *c* (bottom). C: black spheres, N: green spheres. Water molecules and hydrogen atoms are omitted for clarity.

reaction and crystallization conditions. Further, preliminary data does imply that the geometry, rigidity and hydrogen bonding ability of the organic amine can influence the overall structure of the supramolecular framework. The rigid, 2D amines in **1** and **2** induced the formation of layered arrangements, whereas the flexible amine in **3** resulted in the formation of polymeric chains (Fig. 7). It was furthermore shown, that the amines can encapsulate the POMPC clusters

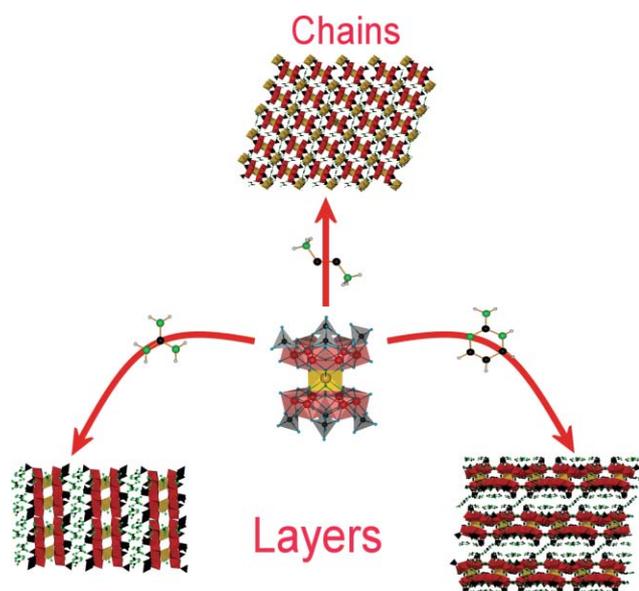


Fig. 7 Summary of the formation of layered or chain-like structures, depending on the amine used in the synthesis.

and these are therefore essential to direct the formation of the supramolecular arrangement in the crystalline state. Future work will further exploit the effects of different amines in the engineering of supramolecular POM-based structures and investigate the formation of hybrid compounds with designed structures *and* functionality.

Experimental

Materials and physical measurements

All materials were of reagent grade and were used without further purification. In opposite to the standard hydrothermal synthesis of polyoxomolybdenum(v) phosphates,^{5–11,13,14,21–24} the compounds described herein were crystallized under standard ambient conditions to allow greater control over the crystallisation conditions. Infrared spectra were obtained from samples prepared as KBr disks in the range of 4000 to 400 cm^{-1} using a Jasco FT/IR-410 spectrometer. Abbreviations used were: w = weak, m = medium, s = strong, b = broad. Elemental analyses were performed on a CE-440 Elemental Analyzer.

Synthesis of compounds 1–3

Synthesis of 1. 1.0 g (10.5 mmol) of guanidine carbonate was dissolved in 22 ml of water. After adding 0.50 g (2.07 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, the pH of the clear solution was slowly adjusted to 6.0 using a 1 : 1 (v/v) mixture of sulfuric acid (9%) and phosphoric acid (9%). After the CO_2 release ceased, 0.10 g (0.57 mmol) of $\text{Na}_2\text{S}_2\text{O}_4$ was added. The colour immediately changed to green-blue and after 15 min of stirring, the mixture was filtered and a green-blue solution was obtained. The sample was stored in a glass vial for one week and yielded 64.0 mg (0.020 mmol, 11.60% based on Mo) of **1** as red crystalline needles. Characteristic IR-bands (in cm^{-1}): 3151 (m, b), 1650 (s), 1141 (m), 1007 (m), 916 (s),

725 (s). Elemental analysis in wt% (calculated values in brackets) for $\text{C}_{12}\text{H}_{105}\text{N}_{36}\text{Mo}_{12}\text{Na}_1\text{O}_{73}\text{P}_8$: C: 4.32 (4.31), H: 2.85 (3.16), N: 14.77 (15.08%).

Synthesis of 2. 3.0 g (16.11 mmol) of 2-aminopyrimidine was dissolved in 23 ml of water. Subsequently, 0.50 g (2.07 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was added and the pH was reduced to 3.5 using phosphoric acid (9%). Then, 50 mg (0.29 mmol) of $\text{Na}_2\text{S}_2\text{O}_4$ was added to the stirred solution, resulting in an immediate colour-change to blue. After 10 min stirring, the final pH of 3.4 was adjusted using phosphoric acid (9%) and the solution was filtered. Storage at room temperature in a glass sample vial for one week gave a mixture of a few light blue needles and 52.0 mg (0.013 mmol, 7.5% based on Mo) of red-brown plates of **2**. Characteristic IR-bands (in cm^{-1}): 3394 (m, b), 1667 (s), 1626 (s), 1353 (m), 1067 (s), 959 (s), 731 (m), 492 (m). Elemental analysis in wt% (calculated values in brackets) for $\text{C}_{56}\text{H}_{119}\text{N}_{42}\text{Mo}_{12}\text{Na}_1\text{O}_{75}\text{P}_8$: C: 16.72 (16.80), H: 2.85 (3.00), N: 14.37 (14.69%).

Synthesis of 3. 0.50 g (2.07 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was added to a stirred solution of 0.50 g (2.12 mmol) of *N,N,N',N'*-tetrakis(hydroxyethyl)ethylenediamine in 20 ml of water at 65 °C. The resulting mixture was acidified to pH 6.0 with phosphoric acid (9%). 0.10 g (0.57 mmol) of $\text{Na}_2\text{S}_2\text{O}_4$ was added under stirring. The solution instantly turned brown and the final pH of 5.9 was adjusted using phosphoric acid (9%). After the solution cooled down to room temperature, it was filtered, resulting in a brown solution and a brown precipitate. After ten days storage in a glass sample vial, 54.5 mg (0.017 mmol, 9.98%, based on Mo) of large, red crystal needles was yielded. Characteristic IR-bands (in cm^{-1}): 3380–3180 (w, b), 1617 (w), 1508 (w), 1336 (w), 1000 (w), 898 (m), 723 (m). Elemental analysis in wt% (calculated values in brackets) for $\text{C}_{12}\text{H}_{105}\text{N}_{12}\text{Mo}_{12}\text{Na}_3\text{O}_{80}\text{P}_8$: C: 4.83 (4.55), H: 3.10 (3.30), N: 5.62 (5.30%).

Crystallography

Suitable single crystals of **1–3** were prepared and the crystals were mounted on a thin glass fibre using Fomblin oil. X-Ray intensity data were measured at 150 K on a Nonius Kappa-CCD diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ \AA}$]. Structure solution and refinement for **1–3** was carried out with SHELXS-97 and SHELXL-97²⁵ via WinGX.²⁶ Corrections for incident and diffracted beam absorption effects were applied using empirical²⁷ and numerical methods.²⁸ None of the crystals showed evidence of crystal decay during data collection. Compound **1** crystallized in the space group $P2_1/c$, compounds **2** and **3** crystallized in the space group $P\bar{1}$, as determined by systematic absences in the intensity data, intensity statistics and the successful solution and refinement of the structures. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. It should be noted that in compound **3** some disorder is observed for the protonated ethylenediamine cations. In the cation involving C1 and N1, the amine group is disordered over two positions with occupancies of 0.76 (N1) and 0.24 (N1') respectively. In

Table 1 Crystallographic data for compounds 1–3

	1	2	3
Empirical formula	C ₁₂ H ₁₀₅ N ₃₆ NaMo ₁₂ O ₇₃ P ₈	C ₅₆ H ₁₁₉ N ₄₂ NaMo ₁₂ O ₇₅ P ₈	C ₁₂ H ₁₀₅ N ₁₂ Na ₃ Mo ₁₂ O ₈₀ P ₈
Formula weight/g mol ⁻¹	3344.35	4002.96	3166.09
Crystal system	Monoclinic	Triclinic	Triclinic
<i>a</i> /Å	13.3317(3)	16.9408(4)	13.4215(3)
<i>b</i> /Å	23.5623(3)	17.8534(2)	13.4228(2)
<i>c</i> /Å	29.9110(6)	26.8981(5)	14.7383(3)
α /°	90	95.992(1)	104.914(1)
β /°	93.319(1)	90.013(1)	98.443(1)
γ /°	90	113.569(1)	119.049(1)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>V</i> /Å ³	9380.0(3)	7408.1(2)	2123.7(7)
<i>Z</i> value	4	2	1
ρ_{calc} /g cm ⁻³	2.368	1.795	2.476
μ /cm ⁻¹	1.820	1.171	2.009
<i>T</i> /K	150(2)	150(2)	150(2)
Number of observations	12508	12283	8477
<i>R</i> ₁	0.0436	0.0787	0.0337
<i>wR</i> ₂ (all data)	0.1096	0.2252	0.0843

the cation involving C2 and N2, the nitrogen and the carbon atoms are disordered over 4 positions each with occupancies of 0.65 (N2, C2) and 0.35 (N2', C2'), respectively. The cation made up by C5, C6, N5 and N6 is disordered over two positions and has occupancies of 0.70 (C5, C6, N5, N6) and 0.30 (C5', C6', N5', N6'), respectively. The cations involving C1, C2, C3 and C4 are located across the crystallographic *C*₂ axis and therefore only half the cations are found in the asymmetrical unit. Due to disorders, no hydrogen atoms were added to these cations in compound **3**. For the disordered cations in compounds **1** and **2**, no hydrogen atoms were added either. Locating protons on solvent water molecules did not improve the structure quality and generated some problems like too close H...H separation and therefore these attempts were given up for all three structures. Crystal data, data collection parameters and refinement statistics for **1–3** are listed in Table 1.

CCDC reference numbers 604423–604425. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605285a

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