A two-dimensional molybdenum (V) phosphate with covalently bonded transition metal coordination complexes: hydrothermal synthesis and structure characterization of Na$_2$[{Mn(phen)$_2$(H$_2$O)}{Mn(phen)$_2$}$_3${Mn Mo$_{12}^{\text{v}}$O$_{24}$ (HPO$_4$)$_6$(PO$_4$)$_2$(OH)$_6$}] · 4H$_2$O (phen = 1, 10-phenanthroline)

Mei Yuan,[a] Enbo Wang,[a,b,*] Ying Lu,[a] Yangguang Li,[a] Changwen Hu,[a] Ninghai Hu,[c] and Hengqing Jia[c]

[a] Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China
[c] Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, People's Republic of China

Abstract

An organic–inorganic hybrid molybdenum phosphate, Na$_2$[{Mn(phen)$_2$(H$_2$O)} {Mn(phen)$_2$}$_3${MnMo$_{12}^{\text{v}}$O$_{24}$ (HPO$_4$)$_6$(PO$_4$)$_2$(OH)$_6$}] · 4H$_2$O (phen = 1,10-phenanthroline), involving molybdenum present in V oxidation state and covalently bonded transition metal coordination complexes, has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Deep brown–red crystals are formed in the triclinic system, space group $P\bar{1}$, $a = 16.581(1)$ Å, $b = 18.354(1)$ Å, $c = 24.485(2)$ Å, $\alpha = 80.589(1)°$, $\beta = 71.279(1)°$, $\gamma = 67.084(1)°$, $V = 6493.8(8)$ Å^3, $Z = 2$, $\lambda(\text{Mo}K\alpha) = 0.71073$ Å ($R(F) = 0.0686$ for 29,053 reflections). Data were collected on a Bruker Smart Apex CCD diffractometer at 293 K in the range of $1.76 < \theta < 28.06°$ using ω–2θ scans technique. The structure of the title compound may be considered to be based on {Mo$_6$O$_{12}$(HPO$_4$)$_3$(PO$_4$)(OH)$_3$} units bonded together with {Mn(phen)$_2$} subunits into a two-dimensional network. Two types of tunnels are observed in the solid of the title compound.

Keywords: Organic–inorganic hybrid; Molybdenum (v) phosphate; Transition metal coordination complexes; Tunnel structure; Hydrothermal synthesis

1. Introduction

The rational design and synthesis of metal-oxides-based organic–inorganic hybrid materials are receiving increasing interest in solid state chemistry owing to their potential applications in catalysis, sorption and electrical conductivity [1–3]. Exploitation of hydrothermal techniques and the use of organic structure-directing agents have proved fruitful in the production of numerous organic–inorganic hybrid materials, including zeolites [4], transition metal phosphates [5] and vana-dium or molybdenum oxides [6]. Typically, the organic components have been presented as charge-compensating cations, such as [H$_3$N(CH$_2$)$_6$NH$_3$][Mo$_4$O$_{13}$] [7] and [HN(C$_2$H$_4$)$_3$NH][V$_6$O$_{14}$ · H$_2$O] [8], and have been introduced as ligands covalently bonded to the backbones of metal oxides, such as [V$_4^{\text{v}}$O$_{10}$(phen)$_2$] [9], [MoO$_3$(2,2'-bpy)] (bpy = bipyridine) [10] and [MoO$_3$(4,4'-bpy)$_{0.5}$] [11]. Furthermore, the introduction of amine-ligated transition metal complex cations is considered as another effective strategy to obtain various hybrid materials, for example, [(en)$_2$Zn][V$_6$O$_{14}$], [(en)$_2$Cu] [V$_6$O$_{14}$] and [(en)$_2$Cu]$_2$[V$_{10}$O$_{25}$] (en = ethylenediamine) [12]. Most recently, a number of materials in which transition metal coordination complexes are directly

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*Corresponding author. Fax: +86-431-568-4009.
E-mail address: wangenbo@public.cc.ji.cn (E. Wang).

incorporated into the metal oxide scaffoldings have been synthesized, including molybdenum oxides [{Cu$_3$(4, 7-phen)$_3$}$_2$Mo$_{14}$O$_{45}$] [13] and [{Cu(2,2'-bpy)$_2$}$_2$Mo$_8$O$_{26}$] [14], vanadium oxides [M(Hdpa)$_2$V$_4$O$_{12}$] (M = Co, Ni; dpa = 4,4'-dipyridylamine) [15] and [Ni(phen)$_2$V$_4$O$_{11}$] [16], and vanadium phosphates [M(4,4'-bpy)(VO$_2$)$_2$(HPO$_4$)$_4$] (M = Co, Ni) [17] and [Cu(phen)(VO)(O$_3$PCH$_2$PO$_3$)(H$_2$O)] [18], for example. As a new class of solid state materials, molybdenum phosphates have been attracting much attention due to their particular uses in catalysis and materials science [19, 20], especially for reduced molybdenum phosphates [21]. We and others have synthesized some reduced molybdenum phosphates with organoamines as charge-compensating cations ranging from one-dimensional polymers to two- and three-dimensional microporous or tunnel materials [22–28]. However, the examples of molybdate phosphates in the presence of transition metal coordination complexes have been rarely reported [29–32].

In recent years, we have been attempting to synthesize new reduced molybdenum phosphates with transition metal coordination complexes as structure-directing reagents. Here, we report a novel organic–inorganic hybrid molybdenum (V) phosphate, Na$_2$[{Mn(phen)$_2$(H$_2$O)}{Mn(phen)$_2$}$_3${MnMo$_{12}^V$O$_{24}$(HPO$_4$)$_6$(PO$_4$)$_2$(OH)$_6$} · 4H$_2$O (phen = 1, 10-phenanthroline) **1,** which is constructed from {Mo$_6$O$_{12}$(HPO$_4$)$_3$(PO$_4$)(OH)$_3$} ($\equiv$ {Mo$_6$P$_4$}) units linked through {Mn(phen)$_2$} complexes by corner sharing in P–O–M (M = metal) mode to exhibit a two-dimensional framework with two new types of tunnels formed in the solid of **1**. To our knowledge, it is the first time for transition metal coordination complexes to be directly incorporated into the two-dimensional skeletons of reduced molybdenum phosphates.

2. Experimental

2.1. General procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. P, Mo, Mn and Na were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. XPS analysis was performed on a VG ESCALAB MK II spectrometer with an Mg$K\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis.

2.2. Hydrothermal synthesis

A mixture of Na$_2$MoO$_4$ · 2H$_2$O (0.80 g, 3.31 mmol), MnCl$_2$ · 4H$_2$O (0.33 g, 1.67 mmol), 1,10-phenanthroline (0.40 g, 2.02 mmol), and H$_2$O was neutralized to pH ≈ 4.5 with 8 M H$_3$PO$_3$ under continuous stirring and sealed in a 20 mL Teflon-lined autoclave, then heated to 160° for 6 days. After cooling to room temperature at 10°C h^{-1}, the deep brown–red crystals of compound **1** were isolated in 50% yield (based on Mo) by mechanical separation from a brown powder phase. The compound was washed with distilled water and dried at ambient temperature. The elemental analyses found: C 27.21, H 2.18, N 5.19, P 6.01, Mo 26.90, Mn 6.33, Na 1.13%; Calc. For C$_{96}$H$_{86}$Mn$_5$Mo$_{12}$N$_{16}$Na$_2$O$_{67}$P$_8$: C 27.09, H 2.04, N 5.27, P 5.82, Mo 27.05, Mn 6.46, Na 1.08%.

2.3. X-ray crystallography

The structure of compound **1** was determined by single-crystal X-ray diffraction. A single deep brown–red crystal with approximate dimensions of $0.45 \times 0.32 \times 0.24$ mm^3 was mounted inside a glass fiber capillary. Data were collected on a Bruker Smart Apex CCD diffractometer at 293 K using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and ω–2θ scans technique in the range of $1.76 < \theta < 28.06°$. Empirical absorption correction was applied. A total of 41,043 (29,053 unique, $R_{int} = 0.0853$) reflections were measured. The structure was solved by direct methods using the program SHELXS-97 [33] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 [34] program package. All of the non-hydrogen atoms were refined anisotropically except for carbon atoms. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions and those attached to oxygen atoms were not located. Structure solution and refinement based on 29053 independent reflections with $I > 2\sigma(I)$ on 0 restraint and 1378 parameters gave $R1$ (w$R2$) = 0.0686　(0.1399)　{$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; w$R_2 = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}$}. Crystal data are summarized in Table 1. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are deposited in supplementary information.

CCDC reference number is 183546.

3. Results and discussion

The IR result and elemental analysis data correspond to the chemical formula of compound **1**. The single-crystal X-ray analysis reveals that the compound **1** consists of {Mo$_6$P$_4$} hexamers, {Mn(phen)$_2$} complex units, sodium cations, and lattice water molecules. In {Mo$_6$P$_4$} (see Fig. 1), the six oxo-bridged molybdenum atoms are coplanar and constitute a hexameric molybdenum cluster with alternating Mo–Mo (Ca. 2.59 Å) single bonds and non-bonding Mo–Mo contacts (Ca. 3.52 Å), The μ_2–O–Mo distances between non-bonding Mo atoms are in the range 2.094(5)–2.127(5) Å, longer

Table 1
Crystal data for structure refinement for compound **1**

Empirical formula	$C_{96}H_{86}Mn_5Mo_{12}N_{16}Na_2O_{67}P_8$
Formula weight	4255.53
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	16.581(1)
b (Å)	18.354(1)
c (Å)	24.485(2)
α (deg)	80.589(1)
β (deg)	71.279(1)
γ (deg)	67.084(1)
V (Å)^3	6493.8(8)
Z	2
Calculated density/Mg (m^{-3})	2.170
$F(000)$	4138
μ(mm^{-1})	1.794
Reflections collected/unique	41043/29053[R(int) = 0.0853]
Goodness-of-fit on F^2	0.980
Final R indices [$I > 2\sigma(I)$]	$R1$[a] = 0.0686, w$R2$[b] = 0.1399
R indices (all data)	$R1$[a] = 0.1135, w$R2$[b] = 0.1497

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$;

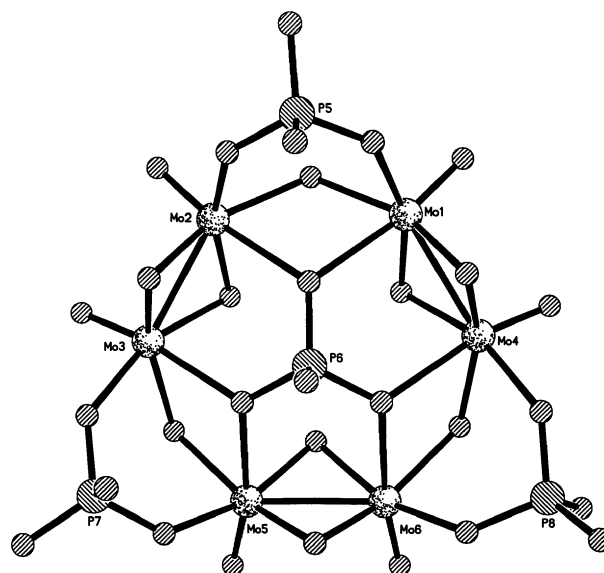[b] w$R_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

Fig. 1. Ball and stick representation of the anionic building unit $\{Mo_6P_4\}$ hexamer.

than those between bonding Mo atoms 1.912(5)–1.978(5) Å. Among four phosphate groups (dP–O: 1.480(6)–1.605(7) Å), a central one bridges the hexamer internally and three peripheral ones bridge each long Mo–Mo contact externally. Structurally, all of molybdenum octahedra are edge sharing with each other (O–Mo–O: 71.4(2)–170.2(2)°) and all of phosphate tetrahedra are corner sharing with the corresponding molybdenum octahedra (average O–P–O: 109.5°). Valence bond calculations [35] not only confirm that Mo atom is in reduced oxidation state (+5), which may be ascribed to the introduction of strong reductive reagent H_3PO_3, but also show the μ_2–O atoms between nonbonding Mo atoms (O(2), O(8), O(22), O(34), O(36), O(59)) and part of P–O groups are protonated (O(25), O(29), O(31), O(43), O(61), O(62)) with the bond valence values in the range 1.130–1.19 and 1.03–1.36, respectively. In addition, the appearance of brown–red crystals of compound **1** is the typical color of an oxide cluster containing Mo^{5+} cation. Therefore, the molybdenum hexamer should be formulated as $\{Mo_6O_{12}(HPO_4)_3(PO_4)(OH)_3\}^{6-}$ ($\equiv \{Mo_6P_4\}$). $\{Mo_6P_4\}$ units have been often encountered in reduced molybdenum phosphate [24–32], while the position and number of the protonated oxygen atoms were different from each other, such as $\{Mo_6^VO_{15}(H_2PO_4)_3(HPO_4)\}$ [26], $\{Mo_6^VO_{15}(H_2PO_4)_{1.5}(HPO_4)_2(PO_4)_{0.5}\}$ [31], $\{Mo_6^VO_{12}(H_2PO_4)_3(PO_4)(OH)_3\}$ [25] and $\{Mo_6^VO_{12}(HPO_4)(PO_4)_3(OH)_3\}$ [32].

The structure of **1** was constructed from molybdenum hexamers bonded together with octahedral Mn^{2+} into a two-dimensional framework (see Fig. 3). There are seven crystallographically independent Mn atoms in compound **1** (see Fig. 2a) which may be divided into three types: (i) Mn(3) and Mn(6), Mn(6) bridges two $\{Mo_6P_4\}$ units via three μ_3–O atoms, which link the metal–metal-bonded molybdenum atoms together with Mn–O bonds at lengths of 2.214(5) Å × 2, 2.241(5) Å × 2, and 2.239(5) Å × 2 to produce centrommetric $[Mn(Mo_6P_4)_2]$ dimers, as shown in Fig. 2b. Mn(3) is similar to Mn(6). Such dimeric species have once been observed in other molybdenum phosphates [29, 31]. (ii) Mn(1), Mn(4) and Mn(5), each of them links two P–O groups from two different $\{Mo_6P_4\}$ units, thus bridges $[Mn(Mo_6P_4)_2]$ dimers together to exhibit an extended layered framework. (iii) Mn(2), it only bridges one P–O group from $\{Mo_6P_4\}$ and has a terminal coordinated water molecule OW1 (dMn(2)–OW1 = 2.149(7) Å, dMn(2)–O(21) = 2.118(6) Å). Interestingly, the latter two types of Mn^{2+} are coordinated with two 1,10-phenanthroline molecules to form the $\{Mn(phen)_2\}$ fragments with an average length of Mn–N 2.30 Å and N–Mn–N bond angle 96.0°; thus they all finish their distorted octahedra coordination environment. Such a layered structure, with transition metal coordination complexes directly incorporated into the scaffolding in a P–O–M (M = metal) mode similar to that in Cu(en)–P–Mo^{VI} system [22], has never occurred in other reduced molybdate phosphates.

As shown in Fig. 3, the network structure of **1** may also be described in terms of one-dimensional chains which consist of $\{Mn(Mo_6P_4)_2\}$ fragments linked by $\{Mn(1)(phen)_2\}$ and $\{Mn(4)(phen)_2\}$ subunits. Then each chain is connected to two other parallel chains by $\{Mn(5)(phen)_2\}$ complex to yield a plane layer. The most unusual feature of **1** is that two types of tunnels are formed in the solid of **1**. As the linkages of $\{Mn(phen)_2\}^{2+}$ cations with $\{Mn(Mo_6P_4)_2\}$ dimers are
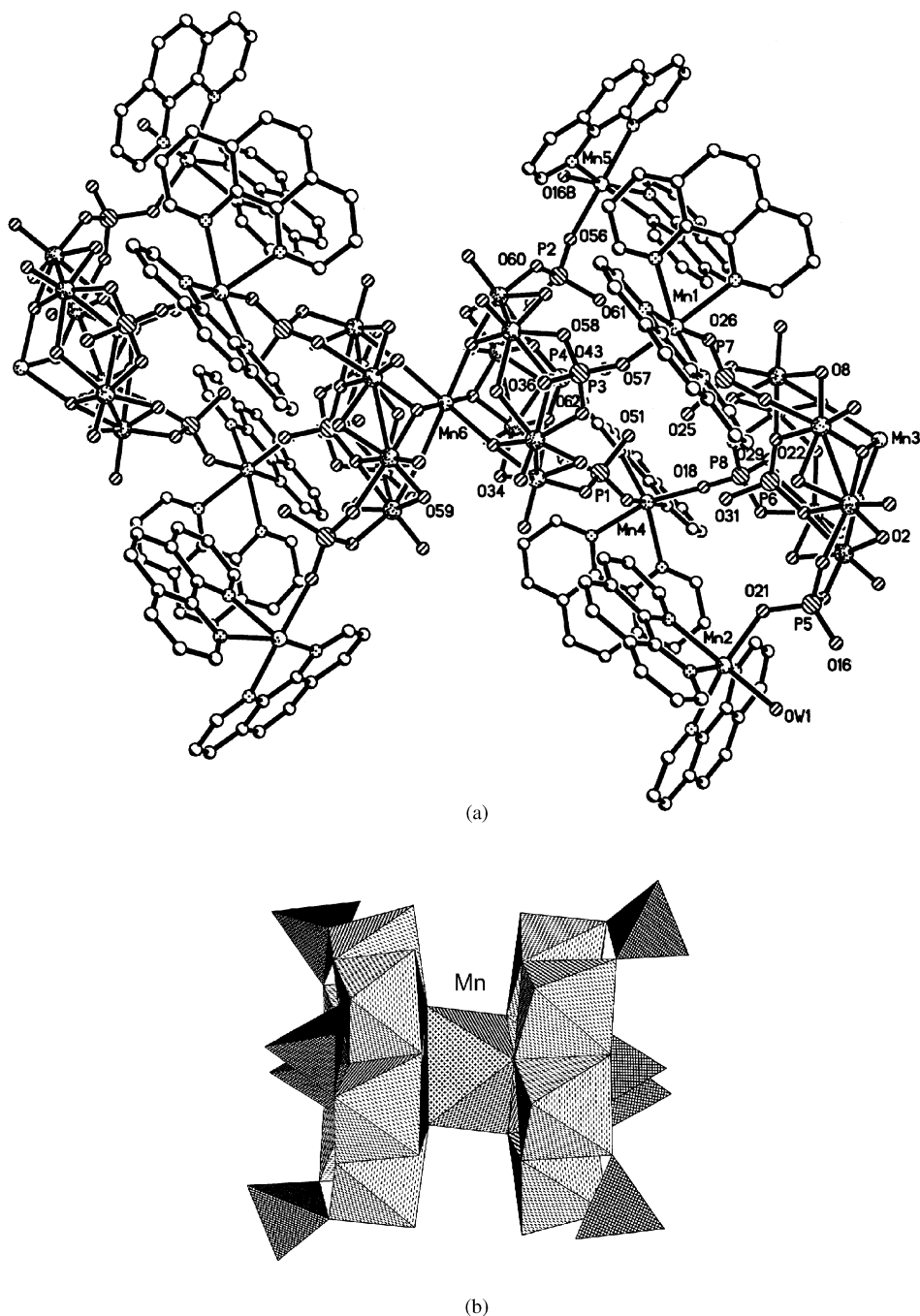
Fig. 2. (a) Coordination environment of three types of Mn atoms. (b) View of {Mn(Mo$_6$P$_4$)$_2$} dimer.

situated on the (1 0 0) plane layer, the infinite plane layers are stacked parallel along the *a*-axis to constitute a three-dimensional crystal structure, resulting in the formation of two types of one-dimensional tunnels along the *a*-axis (see Fig. 3). The small tunnel is surrounded by two {Mn(phen)$_2$}$^{2+}$ cations and two opposite {Mn(Mo$_6$P$_4$)$_2$} anions while the large tunnel in the aperture is surrounded by four {Mn(phen)$_2$}$^{2+}$ cations and four {Mn(Mo$_6$P$_4$)$_2$} anions. Furthermore,

the small tunnel is occupied by sodium counter-ions, which form sodium dimers and are linked to lattice water molecules and to oxygen atoms of the {Mo$_6$P$_4$} anion, similar to that in Na$_{12}$Co$_3$[(PO$_4$)$_4$Mo$_6$O$_{12}$ (OH)$_3$]$_2$·44H$_2$O [32]. Another noteworthy feature in the structure of **1** is that there are two additional non-bridging {Mn(phen)$_2$}$^{2+}$ cations which project up into half of the large tunnels. It is these sodium dimers and phenanthroline molecules coordinated to Mn cen-
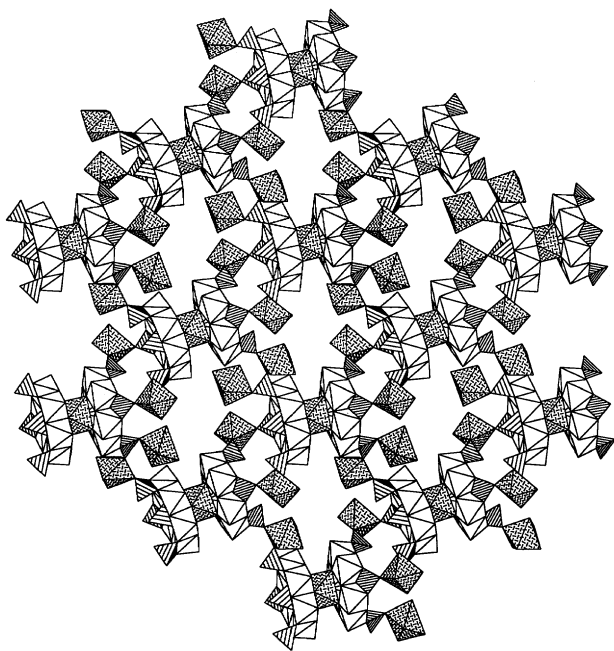
Fig. 3. Polyhedral view of the two-dimensional network of **1** along (1 0 0), showing the connectivity of {Mn(phen)$_2$}subunits and {Mn(Mo$_6$P$_4$)$_2$} dimers and two types of tunnels. All C, H, N and Na atoms are omitted for clarity.

ters that lead to an intricate network of compound **1**. In contrast to the tunnel structure in (NH$_3$CH$_2$CH$_2$NH$_3$)$_{10}$ (H$_3$O)$_3$(H$_5$O$_2$)Na$_2$[MnMo$_{12}$O$_{24}$(OH)$_6$(PO$_4$)$_4$(PO$_3$OH)$_4$] [MnMo$_{12}$O$_{24}$(OH)$_6$(PO$_4$)$_6$(PO$_3$OH)$_2$] · 9H$_2$O [30], the positions of Na atoms in the latter were replaced by {Mn(phen)$_2$} complexes and the tunnel shape, size and constitution are all distinct due to the occurrence of transition metal coordination complexes as structure-directing subunits.

The IR spectrum of compound **1** exhibited a strong band at 966 cm^{-1}, characteristic of v (Mo═O), and features at 726 and 1071 cm^{-1} associated with v (Mo–O–M) and v (P–O), respectively. The feature at 1421, 1513 and 1620 cm^{-1} is characteristic of phen group, while the broad band at 3361 cm^{-1} is ascribed to water molecules. The XPS measurement of the compound **1** in the energy region of $Mo3d_{3/2}$ and $Mo3d_{5/2}$ gives one peak at 230.9 eV, attributed to Mo^{5+} [36], in accordance with the valence sum calculations for Mo^{5+}.

In summary, a new organic–inorganic hybrid molybdenum (V) phosphate with covalently bonded transition metal coordination complexes has been obtained by hydrothermal techniques. X-ray crystallography shows that **1** consists of a novel two-dimensional layer constructed from {Mn(Mo$_6$P$_4$)$_2$} dimers and covalently bonded {Mn(phen)$_2$} fragments, which are linked by corner-sharing in P–O–M (M = metal) mode. Two unusual types of tunnels are formed in the solid of **1** with sodium dimers located in them. The successful

isolation of **1** further confirms the structure-directing function of transition metal coordination complex for "tailoring" the microstructures of molybdenum phosphates. Since manganese atoms in **1** can be replaced by other transition metal, a series of similar reduced molybdenum phosphate may be synthesized.

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