Full paper / Mémoire

Hydrothermal synthesis and crystal structure of a novel two-dimensional molybdenum(V) phosphate with manganese coordination cations

Dan Wu [a,b], Shen Lin [a,c,*], En Tang [c], Guiyang Yan [a]

[a] *College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 35007, China*
[b] *Biology Science College of Fujian Agricultural and Forest University, Fuzhou 35002, China*
[c] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

Abstract

A novel two-dimensional network structure formed by molybdenum(V) phosphate and manganese coordination cations, $[Mn_2Mo_{12}O_{30}(HPO_4)_8(H_2O)] \cdot (NH_3CH_2CH_2NH_3)_6 \cdot 3.5H_2O$ (**1**), was synthesized hydrothermally and characterized by single-crystal X-ray diffraction. It crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 12.006(2)$ Å, $b = 14.582(3)$ Å, $c = 21.270(4)$ Å, $\alpha = 86.00(3)°$, $\beta = 88.00(3)°$, $\gamma = 78.00(3)°$, the final R converged to the value 0.0604 for 12 917 observed reflections with $I > 2\sigma(I)$. In this compound, the poly(oxomolybdophosphate) anions are interconnected by transition-metal manganese cations to form an extended two-dimensional framework where the uncoordinated ethylenediamine cations and lattice water molecules are located. ***To cite this article: D. Wu et al., C. R. Chimie 11 (2008).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Keywords: Molybdenum(V) phosphate; Hydrothermal synthesis; Two-dimensional network; Inorganic−organic hybrid; Manganese

1. Introduction

The rational design and synthesis of metal oxide-based organic−inorganic hybrid materials with a two-dimensional or three-dimensional structure are receiving increasing interests in solid-state chemistry owing to their fascinating properties and great potential applications in many fields (such as catalysis, material science and medicine) as well as their unusual topological properties [1−4].

Many reduced molybdenum phosphates with transition-metal complexes have been synthesized and characterized in the past decade. These compounds include one-dimensional (1D) polymers, two-dimensional (2D) layer structures and three-dimensional (3D) microporous solids containing the $Na[Mo_6P_4]_2$ [5], $Fe[Mo_6P_4]_2$ [6], $Cr[Mo_6P_4]_2$ [7], $Cd[Mo_6P_4]_2$ [8], $Co[Mo_6P_4]_2$ [9], and $Ni[Mo_6P_4]_2$ [10] structure units. Only a few molybdenum phosphates containing the manganese element,

* Corresponding author.
E-mail address: shenlin@fjnu.edu.cn (S. Lin).

such as $(NH_3CH_2CH_2NH_3)_{10}(H_3O)_3(H_5O_2)Na_2$ $[MnMo_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4][MnMo_{12}O_{24}(OH)_6$ $(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$ and $Na_2[\{Mn(phen)_2(H_2O)\}$ $\{Mn(phen)_2\}_3\{MnMo_{12}O_{24}(HPO_4)_6(PO_4)_2(OH)_6\}]\cdot 4H_2O$ have been reported [11]. Two $[Mo_6O_{12}(OH)_3$ $(PO_4)_2(HPO_4)_2]^{7-}$ units are bonded together by a manganese ion while several P−O groups are not protonated on account of coordination to a Na^+ cation in the former compound. The latter compound may be considered to be based on $\{Mo_6O_{12}(HPO_4)_3(PO_4)(OH)_3\}$ units bonded together with $\{Mn(phen)_2\}$ subunits.

Herein we wish to report the hydrothermal synthesis and structural characterization of a novel manganese molybdenum(V) phosphate, $[Mn_2Mo_{12}O_{30}(HPO_4)_8$ $(H_2O)]\cdot(NH_3CH_2CH_2NH_3)_6\cdot 3.5H_2O$ (**1**). To our knowledge, the two-dimensional network structure which is constructed from molybdenum(V) phosphate interconnected only with manganese cations has not been reported up to date.

2. Experimental

2.1. Hydrothermal synthesis and characterization

$Na_2MoO_4\cdot 2H_2O$ (1.20 g, 4.96 mmol), $MnSO_4$ (0.38 g, 2.50 mmol), ethylenediamine (0.40 ml, 3.03 mmol), H_3PO_4 (0.5 ml) and H_2O (15 ml) were mixed and transferred into a 30-ml Teflon-lined stainless steel autoclave and heated at 160 °C for 6 days. Then, the autoclave was cooled to room temperature at 5 °C h^{-1}. The black crystals of compound **1** were filtered off, washed with water and dried in a desiccator at ambient temperature (yield 37% based on Mo). Infrared spectrum was measured on a Nicolet AVATAR 360 FT-IR spectrometer on KBr pellets in the 4000−400 cm^{-1} region.

2.2. X-ray crystallography

A black single crystal with dimensions of $0.40 \times 0.10 \times 0.40$ mm was mounted on a glass fibre. Data collection was performed on a Rigaku Weissenberg IP diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct method using SHELXS-86 and refined by full-matrix least squares calculations using SHELXL-97 software. All non-hydrogen atoms were refined with anisotropic thermal parameters. Most of the hydrogen atoms were located in calculated positions and/or in the positions from difference Fourier map. The crystallographic data are given in Table 1.

Table 1
Crystallographic data for compound **1**

Formula	$H_{77}C_{12}Mn_2Mo_{12}N_{12}O_{66.5}P_8$
Fw	2962.78
Color	Black
Crystal system	Triclinic
Space group	$P\bar{1}$
F (000)	2878
a (Å)	12.006(2)
b (Å)	14.582(3)
c (Å)	21.270(4)
α (°)	80.96(3)
β (°)	83.24(3)
γ (°)	76.33(3)
V (Å^3)	3560.8(1)
Z	2
$D_{calc.}$ (g cm^{-3})	2.763
μ (mm^{-1})	2.691
θ Range (°)	3.02−27.48
$h_{\min\to\max}$	$-15 \to 15$
$k_{\min\to\max}$	$-18 \to 18$
$l_{\min\to\max}$	$-27 \to 26$
No. of unique data	15 522
No. of observed	12 917
Parameter	1019
GOF	1.146
R/R_w	0.0604/0.1715
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e/Å^3)	2.409/(-1.662)

Selected bond lengths and angles are provided in Tables 2 and 3.

3. Results and discussion

3.1. The crystal structure of complex **1**

The single-crystal X-ray analysis revealed that compound **1** consists of $\{Mo_6P_4\}$ hexamers, manganese cations and lattice water molecules. As shown in Figs. 1 and 2, in each $\{Mo_6P_4\}$, there is a six-membered ring of oxo-bridged Mo atoms with alternating Mo−Mo single bonds (2.5870(2)−2.6053(2) Å), and there are four phosphate groups. The phosphorous atoms have P−O bond lengths in the range 1.492(1)−1.586(9) Å, while the O−P−O bond angles are in the range 105.9(5)°−112.6(5)°. As illustrated in Fig. 3, the Mn(1) and Mn(2) atoms are located at the octahedral MnO$_6$ center, the Mn−O distances are ranging from 2.103(9) to 2.236(2)Å, and the O−Mn−O angles vary from 78.31(6)° to 180.0(1)°, while Mn(3) atoms adopt a five-coordinated geometry.

The structure of **1** was constructed from molybdenum hexamers bonded together with octahedral Mn^{2+} into a two-dimensional framework (see Fig. 3). There

Table 2
Selected bond lengths (Å) of compound **1**

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
Mo(1)−O(28)	1.683(8)	Mo(1)−O(49)	1.935(8)	Mo(1)−O(50)	1.970(8)
Mo(1)−O(32)	2.033(8)	Mo(1)−O(21)#1	2.128(8)	Mo(1)−O(8)	2.289(8)
Mo(1)−Mo(9)	2.5994(16)	Mo(2)−O(2)	1.685(8)	Mo(2)−O(58)	1.948(8)
Mo(2)−O(48)	1.978(7)	Mo(2)−O(43)#2	2.053(8)	Mo(2)−O(46)#2	2.084(8)
Mo(2)−O(4)#2	2.289(7)	Mo(2)−Mo(8)	2.5884(15)	Mo(3)−O(42)	1.694(9)
Mo(3)−O(57)	1.945(8)	Mo(3)−O(54)	1.969(8)	Mo(3)−O(38)#3	2.054(8)
Mo(3)−O(31)	2.095(7)	Mo(3)−O(15)	2.291(8)	Mo(3)−Mo(5)	2.5870(16)
Mo(4)−O(1)	1.690(9)	Mo(4)−O(56)	1.961(8)	Mo(4)−O(59)	1.973(7)
Mo(4)−O(25)	2.060(8)	Mo(4)−O(46)	2.075(8)	Mo(4)−O(4)	2.263(8)
Mo(4)−Mo(10)	2.6011(16)	Mo(5)−O(6)	1.682(8)	Mo(5)−O(57)	1.946(8)
Mo(5)−O(54)	1.962(7)	Mo(5)−O(24)	2.064(7)	Mo(5)−O(37)#1	2.100(8)
Mo(5)−O(44)	2.284(8)	Mo(6)−O(41)	1.688(8)	Mo(6)−O(39)	1.947(8)
Mo(6)−O(55)	1.980(8)	Mo(6)−O(45)#1	2.042(8)	Mo(6)−O(21)	2.110(8)
Mo(6)−O(8)#1	2.282(8)	Mo(6)−Mo(12)	2.6053(14)	Mo(7)−O(12)	1.694(8)
Mo(7)−O(51)	1.932(8)	Mo(7)−O(34)	1.973(7)	Mo(7)−O(53)	2.027(8)
Mo(7)−O(35)	2.108(8)	Mo(7)−O(29)#2	2.343(7)	Mo(7)−Mo(11)	2.5903(14)
Mo(8)−O(17)	1.691(8)	Mo(8)−O(58)	1.941(7)	Mo(8)−O(48)	1.965(7)
Mo(8)−O(36)	2.087(8)	Mo(8)−O(35)	2.101(8)	Mo(8)−O(29)#2	2.241(7)
Mo(9)−O(23)	1.691(8)	Mo(9)−O(49)	1.941(8)	Mo(9)−O(50)	1.973(8)
Mo(9)−O(47)#3	2.085(8)	Mo(9)−O(31)	2.108(8)	Mo(9)−O(15)	2.308(7)
Mo(10)−O(19)	1.683(8)	Mo(10)−O(56)	1.953(8)	Mo(10)−O(59)	1.961(8)
Mo(10)−O(52)#2	2.065(8)	Mo(10)−O(30)#2	2.090(8)	Mo(10)−O(33)	2.287(7)
Mo(11)−O(9)	1.685(8)	Mo(11)−O(51)	1.935(8)	Mo(11)−O(34)	1.962(7)
Mo(11)−O(10)	2.081(8)	Mo(11)−O(30)	2.126(8)	Mo(11)−O(33)#2	2.286(7)
Mo(12)−O(20)	1.684(8)	Mo(12)−O(39)	1.939(8)	Mo(12)−O(55)	1.970(7)
Mo(12)−O(26)#1	2.080(7)	Mo(12)−O(37)	2.121(7)	Mo(12)−O(44)#1	2.233(8)
Mn(1)−O(34)	2.187(7)	Mn(1)−O(59)	2.207(7)	Mn(1)−O(48)	2.234(7)
Mn(2)−O(55)	2.192(7)	Mn(2)−O(50)	2.214(8)	Mn(2)−O(54)	2.217(8)
Mn(3)−O(62)	2.103(9)	Mn(3)−O(18)	2.162(9)	Mn(3)−O(11)	2.170(9)
Mn(3)−O(5)	2.194(10)	Mn(3)−O(1W)	2.236(15)	P(1)−O(3)	1.517(9)
P(1)−O(32)	1.540(9)	P(1)−O(40)	1.546(9)	P(1)−O(45)	1.546(9)
P(2)−O(11)	1.508(8)	P(2)−O(15)	1.538(8)	P(2)−O(44)	1.545(8)
P(2)−O(8)	1.551(8)	P(3)−O(7)	1.511(9)	P(3)−O(60)	1.526(9)
P(3)−O(53)	1.552(9)	P(3)−O(36)	1.560(9)	P(4)−O(61)	1.492(10)
P(4)−O(25)	1.535(9)	P(4)−O(43)	1.545(8)	P(4)−O(27)	1.586(9)
P(5)−O(22)	1.517(9)	P(5)−O(5)	1.525(9)	P(5)−O(47)	1.556(9)
P(5)−O(38)	1.575(9)	P(6)−O(18)	1.507(9)	P(6)−O(14)	1.542(8)
P(6)−O(24)	1.551(8)	P(6)−O(26)	1.551(8)	P(7)−O(62)	1.493(9)
P(7)−O(52)	1.518(9)	P(7)−O(10)	1.552(8)	P(7)−O(13)	1.566(9)
P(8)−O(16)	1.513(8)	P(8)−O(4)	1.545(8)	P(8)−O(29)	1.553(7)
P(8)−O(33)	1.556(8)				

are three independent Mn atoms in the compound (see Fig. 3) which may be divided into two types: (*i*) Mn(1) and Mn(2), Mn(1) bridge 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(8) Å × 2, 2.217(8) Å × 2, and 2.192(7) Å × 2 to produce a centrosymmetric [$Mn(Mo_6P_4)_2$] dimer. Mn(2) is similar to Mn(1). (*ii*) Mn(3) bridges four P−O groups from different {Mo_6P_4} (i.e. one {$Mn(1)(Mo_6P_4)_2$} unit and two {$Mn(2)(Mo_6P_4)_2$} units) and has a terminal coordinated water molecule O(1W) with the distance of Mn(3)−

O(1W) 2.237(2) Å. Two-dimensional structure of **1** can be described in terms of crosslinking among different {$Mn(Mo_6P_4)_2$} units. Interestingly,{Mn(1) $(Mo_6P_4)_2$} unit and {$Mn(2)(Mo_6P_4)_2$} unit are linked by $P(7)O_4$ and $Mn(3)O_5$, while {$Mn(2)(Mo_6P_4)_2$} unit and {$Mn(2)(Mo_6P_4)_2$} unit are linked by the oxygen atom of two $P(5)O_4$, one $P(2)O_4$, one $P(6)O_4$ and two $Mn(3)O_5$ polyhedra.

Bond-valence calculations for **1** suggest that the bond-valence values for all the molybdenum and phosphorous atoms are in the ranges 5.15−5.22 and 4.89−5.05, respectively. This indicates that all

Table 3
Selected bond angles (°) of compound **1**

Angle	(°)	Angle	(°)	Angle	(°)
O(28)−Mo(1)−O(49)	106.6(4)	O(28)−Mo(1)−O(50)	101.3(4)	O(49)−Mo(1)−O(50)	95.2(3)
O(28)−Mo(1)−O(32)	97.3(4)	O(49)−Mo(1)−O(32)	86.8(4)	O(50)−Mo(1)−O(32)	159.8(3)
O(28)−Mo(1)−Mo(9)	100.9(3)	O(49)−Mo(1)−Mo(9)	48.0(2)	O(50)−Mo(1)−Mo(9)	48.8(2)
O(32)−Mo(1)−Mo(9)	134.4(3)	O(21)#1−Mo(1)−Mo(9)	134.8(2)	O(8)−Mo(1)−Mo(9)	89.43(19)
O(2)−Mo(2)−O(58)	105.0(4)	O(2)−Mo(2)−O(48)	101.4(4)	O(58)−Mo(2)−O(48)	95.6(3)
O(2)−Mo(2)−Mo(8)	100.8(3)	O(58)−Mo(2)−Mo(8)	48.2(2)	O(48)−Mo(2)−Mo(8)	48.7(2)
O(42)−Mo(3)−O(31)	98.5(4)	O(57)−Mo(3)−O(31)	155.1(3)	O(54)−Mo(3)−O(31)	84.8(3)
O(42)−Mo(3)−Mo(5)	99.3(3)	O(57)−Mo(3)−Mo(5)	48.3(2)	O(54)−Mo(3)−Mo(5)	48.7(2)
O(38)#3−Mo(3)−Mo(5)	133.8(2)	O(31)−Mo(3)−Mo(5)	132.6(2)	O(15)−Mo(3)−Mo(5)	89.74(19)
O(1)−Mo(4)−O(56)	104.3(4)	O(1)−Mo(4)−O(59)	101.9(4)	O(56)−Mo(4)−O(59)	95.4(3)
O(1)−Mo(4)−O(25)	95.6(4)	O(56)−Mo(4)−O(25)	86.3(3)	O(59)−Mo(4)−O(25)	161.3(3)
O(59)−Mo(4)−O(4)	81.4(3)	O(25)−Mo(4)−O(4)	80.2(3)	O(46)−Mo(4)−O(4)	73.7(3)
O(1)−Mo(4)−Mo(10)	100.9(3)	O(56)−Mo(4)−Mo(10)	48.2(2)	O(59)−Mo(4)−Mo(10)	48.4(2)
O(25)−Mo(4)−Mo(10)	134.1(3)	O(46)−Mo(4)−Mo(10)	134.3(2)	O(4)−Mo(4)−Mo(10)	88.45(19)
O(6)−Mo(5)−O(57)	107.1(4)	O(6)−Mo(5)−O(54)	102.6(4)	O(57)−Mo(5)−O(54)	95.3(3)
O(6)−Mo(5)−O(24)	93.3(4)	O(57)−Mo(5)−O(24)	87.5(3)	O(54)−Mo(5)−O(24)	162.2(3)
O(6)−Mo(5)−Mo(3)	101.1(3)	O(57)−Mo(5)−Mo(3)	48.3(2)	O(54)−Mo(5)−Mo(3)	49.0(2)
O(24)−Mo(5)−Mo(3)	135.8(2)	O(37)#1−Mo(5)−Mo(3)	134.5(2)	O(44)−Mo(5)−Mo(3)	87.78(19)
O(41)−Mo(6)−O(39)	105.6(4)	O(41)−Mo(6)−O(55)	101.9(4)	O(39)−Mo(6)−O(55)	94.8(3)
O(41)−Mo(6)−Mo(12)	100.6(3)	O(39)−Mo(6)−Mo(12)	47.8(2)	O(55)−Mo(6)−Mo(12)	48.6(2)
O(45)#1−Mo(6)−Mo(12)	133.1(2)	O(21)−Mo(6)−Mo(12)	133.9(2)	O(8)#1−Mo(6)−Mo(12)	87.6(2)
O(12)−Mo(7)−O(51)	106.7(4)	O(12)−Mo(7)−O(34)	101.8(4)	O(51)−Mo(7)−O(34)	94.9(3)
O(12)−Mo(7)−O(53)	97.3(4)	O(51)−Mo(7)−O(53)	87.2(4)	O(34)−Mo(7)−O(53)	159.3(3)
O(12)−Mo(7)−O(35)	98.4(4)	O(51)−Mo(7)−O(35)	154.2(3)	O(34)−Mo(7)−O(35)	85.9(3)
O(53)−Mo(7)−Mo(11)	134.9(3)	O(35)−Mo(7)−Mo(11)	133.3(2)	O(29)#2−Mo(7)−Mo(11)	87.51(18)
O(17)−Mo(8)−O(58)	104.3(4)	O(17)−Mo(8)−O(48)	102.1(4)	O(58)−Mo(8)−O(48)	96.2(3)
O(17)−Mo(8)−O(36)	93.8(4)	O(58)−Mo(8)−O(36)	86.1(3)	O(48)−Mo(8)−O(36)	162.8(3)
O(17)−Mo(8)−O(35)	95.6(3)	O(58)−Mo(8)−O(35)	158.9(3)	O(48)−Mo(8)−O(35)	86.2(3)
O(36)−Mo(8)−Mo(2)	134.3(2)	O(35)−Mo(8)−Mo(2)	134.6(2)	O(29)#2−Mo(8)−Mo(2)	90.08(19)
O(23)−Mo(9)−O(49)	106.2(4)	O(23)−Mo(9)−O(50)	102.3(4)	O(49)−Mo(9)−O(50)	94.9(3)
O(50)−Mo(9)−O(15)	80.4(3)	O(47)#3−Mo(9)−O(15)	79.9(3)	O(31)−Mo(9)−O(15)	72.1(3)
O(23)−Mo(9)−Mo(1)	101.3(3)	O(49)−Mo(9)−Mo(1)	47.8(2)	O(50)−Mo(9)−Mo(1)	48.7(2)
O(47)#3−Mo(9)−Mo(1)	133.5(2)	O(31)−Mo(9)−Mo(1)	133.3(2)	O(15)−Mo(9)−Mo(1)	88.0(2)
O(19)−Mo(10)−O(56)	105.5(4)	O(19)−Mo(10)−O(59)	101.8(4)	O(56)−Mo(10)−O(59)	96.0(3)
O(19)−Mo(10)−Mo(4)	101.7(3)	O(56)−Mo(10)−Mo(4)	48.5(2)	O(59)−Mo(10)−Mo(4)	48.8(2)
O(10)−Mo(11)−O(30)	84.6(3)	O(9)−Mo(11)−O(33)#2	166.7(3)	O(51)−Mo(11)−O(33)#2	84.8(3)
O(34)−Mo(11)−O(33)#2	81.9(3)	O(10)−Mo(11)−O(33)#2	78.2(3)	O(30)−Mo(11)−O(33)#2	72.6(3)
O(9)−Mo(11)−Mo(7)	102.1(3)	O(51)−Mo(11)−Mo(7)	47.9(2)	O(34)−Mo(11)−Mo(7)	49.0(2)
O(10)−Mo(11)−Mo(7)	134.6(2)	O(30)−Mo(11)−Mo(7)	134.0(2)	O(33)#2−Mo(11)−Mo(7)	90.76(18)
O(20)−Mo(12)−O(39)	105.8(4)	O(20)−Mo(12)−O(55)	101.5(4)	O(39)−Mo(12)−O(55)	95.3(3)
O(20)−Mo(12)−O(26)#1	94.3(4)	O(39)−Mo(12)−O(26)#1	86.6(3)	O(55)−Mo(12)−O(26)#1	162.8(3)
O(20)−Mo(12)−O(37)	96.1(4)	O(39)−Mo(12)−O(37)	156.3(3)	O(55)−Mo(12)−O(37)	87.6(3)
O(26)#1−Mo(12)−Mo(6)	134.6(2)	O(37)−Mo(12)−Mo(6)	135.6(2)	O(44)#1−Mo(12)−Mo(6)	89.8(2)
O(59)#2−Mn(1)−O(48)#2	85.5(3)	O(34)−Mn(1)−O(48)	94.9(3)	O(34)#2−Mn(1)−O(48)	85.1(3)
O(59)−Mn(1)−O(48)	85.5(3)	O(59)#2−Mn(1)−O(48)	94.5(3)	O(48)#2−Mn(1)−O(48)	180.000(1)
O(50)−Mn(2)−O(54)	96.2(3)	O(55)#1−Mn(2)−O(54)#1	82.2(3)	O(55)−Mn(2)−O(54)#1	97.8(3)
O(50)#1−Mn(2)−O(54)#1	96.2(3)	O(50)−Mn(2)−O(54)#1	83.8(3)	O(54)−Mn(2)−O(54)#1	180.0(2)
O(62)−Mn(3)−O(18)	88.0(4)	O(62)−Mn(3)−O(11)	88.7(4)	O(18)−Mn(3)−O(11)	98.1(3)
O(62)−Mn(3)−O(5)	103.2(4)	O(18)−Mn(3)−O(5)	96.2(3)	O(11)−Mn(3)−O(5)	161.8(4)
O(32)−P(1)−O(40)	107.6(5)	O(3)−P(1)−O(45)	109.2(5)	O(32)−P(1)−O(45)	111.9(5)
O(40)−P(1)−O(45)	106.8(5)	O(11)−P(2)−O(15)	112.2(5)	O(11)−P(2)−O(44)	109.9(5)
O(15)−P(2)−O(44)	107.6(4)	O(11)−P(2)−O(8)	111.1(5)	O(15)−P(2)−O(8)	107.9(4)
O(53)−P(3)−O(36)	110.0(5)	O(61)−P(4)−O(25)	112.6(5)	O(61)−P(4)−O(43)	112.4(6)
O(25)−P(4)−O(43)	110.4(5)	O(61)−P(4)−O(27)	112.6(5)	O(25)−P(4)−O(27)	106.4(5)
O(47)−P(5)−O(38)	107.3(5)	O(18)−P(6)−O(14)	109.5(5)	O(18)−P(6)−O(24)	110.9(5)
O(14)−P(6)−O(24)	107.5(5)	O(18)−P(6)−O(26)	112.5(5)	O(14)−P(6)−O(26)	107.1(5)
O(10)−P(7)−O(13)	108.6(5)	O(16)−P(8)−O(4)	111.9(5)	O(16)−P(8)−O(29)	110.9(4)

Table 3 (*continued*)

Angle	(°)	Angle	(°)	Angle	(°)
O(4)−P(8)−O(29)	107.2(4)	O(16)−P(8)−O(33)	111.4(5)	O(4)−P(8)−O(33)	106.9(4)
P(2)−O(8)−Mo(1)	126.1(4)	Mo(6)#1−O(8)−Mo(1)	101.1(3)	P(7)−O(10)−Mo(11)	137.3(5)
P(2)−O(11)−Mn(3)	118.4(5)	P(2)−O(15)−Mo(9)	125.4(4)	P(2)−O(15)−Mo(9)	127.2(5)
Mo(3)−O(15)−Mo(9)	100.1(3)	P(6)−O(18)−Mn(3)	135.0(5)	Mo(6)−O(21)−Mo(1)#1	112.8(3)
P(6)−O(24)−Mo(5)	132.0(5)	P(4)−O(25)−Mo(4)	130.7(5)	P(6)−O(26)−Mo(12)#1	133.0(5)
P(8)−O(29)−Mo(8)#2	126.4(4)	P(8)−O(29)−Mo(7)#2	126.4(4)	Mo(8)#2−O(29)−Mo(7)#2	99.5(3)

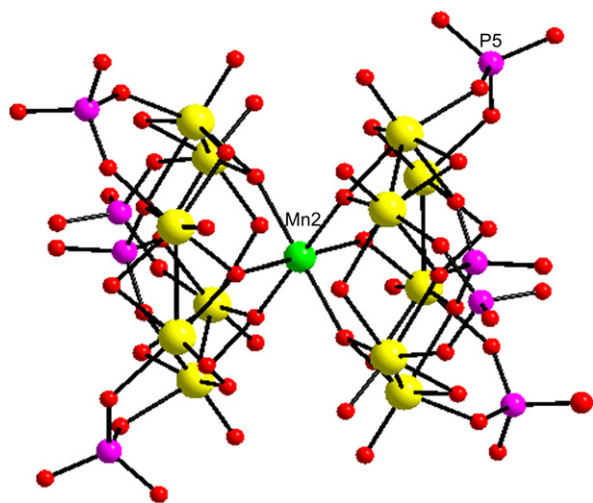Symmetry transformations used to generate equivalent atoms: #1 −x,−y,−z; #2 −x − 1,−y + 1,−z + 1; #3 −x,−y + 1,−z.

Fig. 1. Molecular structure of $[Mn_2Mo_{12}O_{30}(HPO_4)_8(H_2O)]^{12-}$.
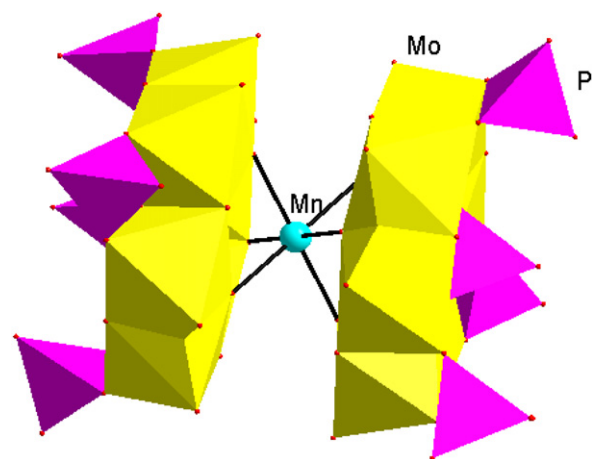
Fig. 2. Polyhedral representation of $[Mn_2Mo_{12}O_{30}(HPO_4)_8(H_2O)]^{12-}$.

Mo and P atoms exhibit a +5 oxidation state. Each Mo^{5+} cation in compound **1** has a distorted octahedral configuration with an apical Mo−O bond at a length of 1.682(8)−1.694(9) Å and five other Mo−O bonds at lengths ranging from 1.932(8) to 2.343(7) Å. The valence sums for three Mn atoms are 1.93, 1.94 and 1.79, respectively, the average value being 1.89.

3.2. IR

The IR spectrum of compound **1** exhibits a strong band at 946 cm^{-1}, characteristic of $\nu(Mo = O)$, and features at 727 and 1045 cm^{-1} associated with $\nu(Mo−O−M)$ and $\nu(P−O)$, respectively. The feature at 1517 cm^{-1} is ascribed to ethylenediamine, while the broad band at 3418 cm^{-1} is ascribed to water molecules [10].

4. Conclusion

A novel two-dimensional molybdenum(V) phosphate with manganese coordination cations has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction. It may be concluded that the microstructures of molybdenum phosphates could be 'tailored' by structure-directing function of transition-metal coordination complex.

Supplementary material. The crystallographic data have been sent to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk), with the deposited CCDC number 608620.
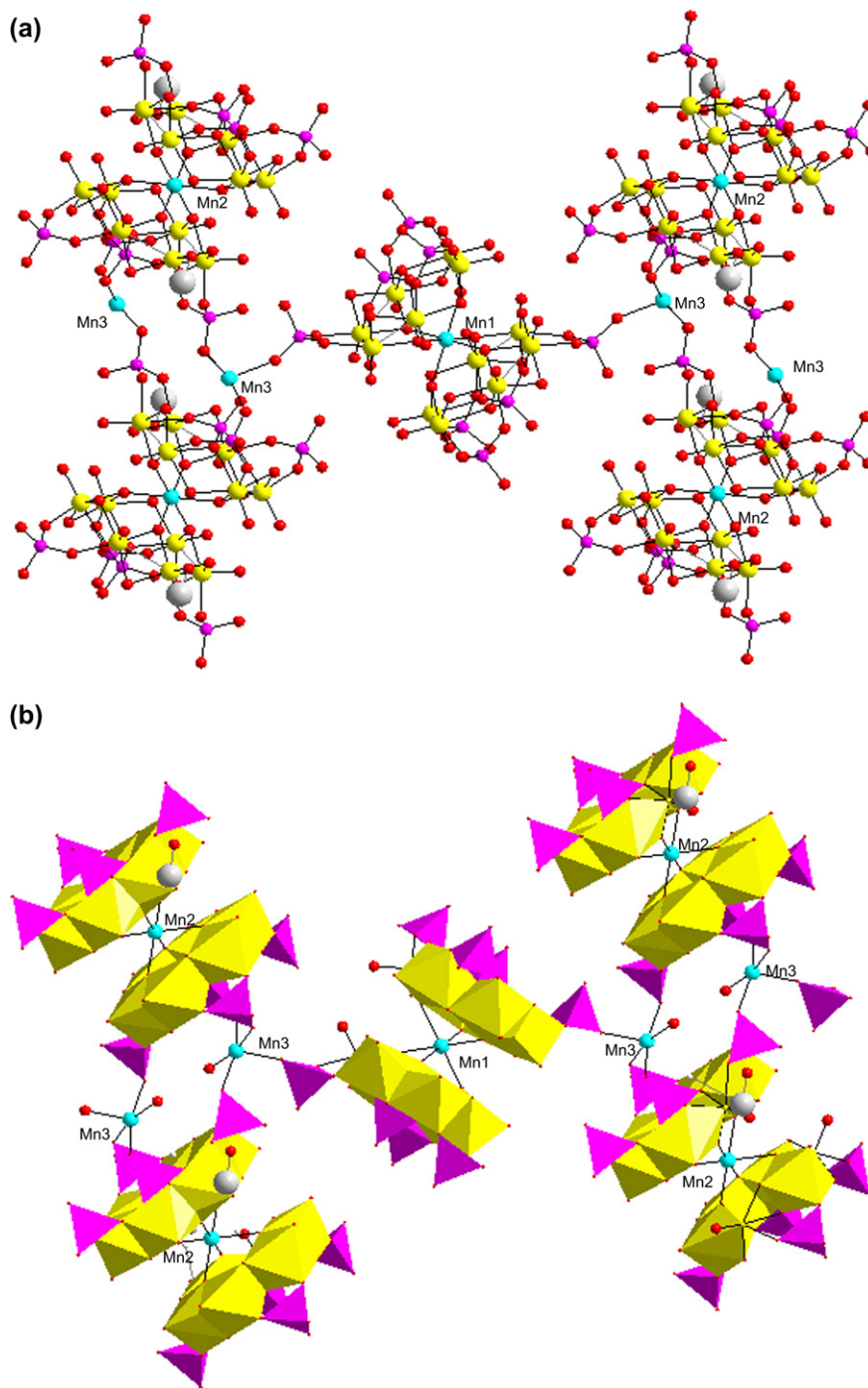
Acknowledgements

Fig. 3. The two-dimensional framework of compound **1**: (a) Ball and stick representation; (b) polyhedral view.

References

[1] N.K. Roman, M.T. Aderson, C.J. Brinker, Chem. Mater. 8 (1996) 1683.

[2] M. Van, Y.G. Li, E.B. Wang, Y. Lu, C.W. Hu, N.H. Hu, H.Q. Jia, J. Chem. Soc., Dalton Trans. (2002) 2916.

[3] W.S. You, E.B. Wang, Y. Xu, Y.G. Li, L. Xu, C.W. Hu, Inorg. Chem. 40 (2000) 5468.

[4] R.D. Huang, F.C. Liu, Y.G. Li, M. Yuan, E.B. Wang, G.J.H. De, C.W. Hu, N.H. Hu, H.Q. Jia, Inorg. Chem. Acta 349 (2003) 85.

[5] (a) R.C. Haushalter, F.W. Lai, Inorg. Chem. 28 (1989) 2904;
(b) R.C. Haushalter, L.A. Mundi, Chem. Mater. 4 (1992) 31;

(c) M.I. Khan, Q. Chem, J. Zubieta, Inorg. Chem. Acta 206 (1993) 131.

[6] (a) L.A. Meyer, R.C. Haushalter, Inorg. Chem. 32 (1993) 1579;
(b) L. Xu, Y.Q. Sun, E.B. Wang, E.H. Shen, Z.R. Liu, C.W. Hu, Y. Xing, Y.H. Lin, H.Q. Jia, Inorg. Chem. Commun. 1 (1998) 382;
(c) Y.S. Zhou, L.J. Zhang, X.Z. You, S. Natarajan, J. Solid State Chem. 159 (2001) 209;
(d) Y.S. Zhou, L.J. Zhang, X.Z. You, S. Natarajan, Inorg. Chem. Commun. 4 (2001) 699;
(e) C.D. Peloux, P. Mialane, A. Dolbecq, J. Marrot, F. Varret, F. Secheresse, Solid State Sci. 6 (2004) 719.

[7] L. Xu, Y.Q. Sun, E.B. Wang, E.H. Shen, Z.R. Liu, C.W. Hu, Y. Xing, Y.H. Lin, H.Q. Jia, J. Mol. Struct. 519 (2000) 55.

[8] (a) L.Y. Duan, F.C. Liu, X.L. Wang, E.B. Wang, C. Qin, Y.G. Li, X.L. Wang, C.C. Hu, J. Mol. Struct. 705 (2004) 15;
(b) H.X. Guo, S.X. Liu, Inorg. Chem. Commun. 7 (2004) 1217.

[9] (a) P. Lighfoot, D. Masson, Acta Crystallogr. C 52 (1996) 1077;
(b) Y.H. Sun, X.B. Cui, J.Q. Xu, L. Ye, Y. Li, J. Lu, H. Ding, H.Y. Bie, J. Solid State Chem. 177 (2004) 1811;
(c) C. Du Peloux, P. Mialane, A. Dolbecq, J. Marrot, E. Riviereb, F. Secheresse, J. Mater. Chem. 11 (2001) 3392.

[10] W.J. Chang, Y.C. Jiang, S.L. Wang, K.H. Lii, Inorg. Chem. 45 (2006) 6586.

[11] (a) L. Xu, Y.Q. Sun, E.B. Wang, E.H. Shen, Z.R. Liu, C.W. Hu, Y. Xing, Y.H. Lin, H. Jia, New J. Chem. 23 (1999) 1041;
(b) M. Yuan, E.B. Wang, Y. Lu, Y.G. Li, C.W. Hu, N.H. Hu, H.Q. Jia, J. Solid State Chem. 170 (2003) 192.