

A Novel Three-dimensional Framework with Tunnels Based on the Cobalt-containing Molybdenum Phosphate Moieties

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A novel compound $(\text{H}_2\text{en})_5[\text{CoMo}_{12}\text{O}_{50}\text{P}_8(\text{OH})_{12}] \cdot 2\text{H}_2\text{O}$ (**1**) ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) has been hydrothermally synthesized and characterized by elemental analyses, IR, EPR, XPS spectra and single-crystal X-ray diffraction analyses. Compound **1** crystallizes in a triclinic system, space group $P\bar{1}$, with $a = 1.1863(2)$ nm, $b = 1.3361(3)$ nm, $c = 1.3783(3)$ nm, $\alpha = 88.13(3)^\circ$, $\beta = 70.09(3)^\circ$, $\gamma = 65.24(3)^\circ$, $V = 1.8497(6)$ nm³, and $R = 0.0417$. The basic building blocks of compound **1** are $\{\text{Mo}_6\text{P}_4\}$ clusters forming dimers through the $\{\text{CoO}_6\}$ octahedra. Compound **1** exhibits an unusual three-dimensional framework with tunnels owing to the extensive hydrogen bonding interactions between the dimers and H_2en .

Keywords hydrothermal synthesis, molybdenum phosphate, dimer, hydrogen bond

Introduction

The design and synthesis of organic-inorganic hybrid materials are of great interest in material science owing to their extensive applications in catalysis, sorption and electrical conductivity.¹⁻⁴ Exploitation of hydrothermal techniques and use of organic structure-directing agents have been proved fruitful methods in the production of organic-inorganic hybrid materials.^{5,6} Metal oxide clusters based on anionic molybdenum phosphates are one of excellent subfields with abundant structures. It is well known that molybdenum phosphates at hydrothermal environment and autogenous pressure have exhibited various structures, however, many of them possess the identical clusters with the unit of $\{\text{Mo}_6\text{P}_4\}$ ($\text{Mo}_6\text{P}_4\text{X}_{31}$, X = O, OH).⁷ Based on this building blocks, molybdenum phosphates exhibit diversified structures including examples of one-dimensional (1-D) chains, two-dimensional (2-D) layered networks and three-dimensional (3-D) frameworks.⁸⁻¹⁴ However, discrete molybdenum phosphates based on $\{\text{Mo}_6\text{P}_4\}$ units with nitrogen-rich organic groups have rarely been reported. The nitrogen-rich organic groups can be easily linked

to the inorganic clusters by hydrogen bonds leading 3-D structures with tunnels. Unlike the traditional 2-D and 3-D anionic structures formed by covalence bond based on $\{\text{Mo}_6\text{P}_4\}$ units,^{9,13} the sizes of the tunnels constructed by hydrogen bonds up to not the lengths of covalence bond of metals and oxygen atoms but the characteristic of the organic groups. According to this point, the sizes of the tunnels in compounds can be easily modified for the diversity and flexibility of the organic groups, so that the compounds with similar structures are significative to catalysis for the controllable tunnels. Based on the discussion of above, herein, paper reports the hydrothermal synthesis and structural characterization of a novel cobalt-containing molybdenum phosphate $(\text{H}_2\text{en})_5[\text{CoMo}_{12}\text{O}_{50}\text{P}_8(\text{OH})_{12}] \cdot 2\text{H}_2\text{O}$ (**1**). Compound **1** exhibits a novel 3-D framework with tunnels, which is based on the $\{\text{Co}(\text{Mo}_6\text{P}_4)_2\}$ building blocks linked by the diprotonated ethylenediamine counter cations via hydrogen bonds. To our knowledge, **1** represents the first example of three-dimensional assembly with tunnels constructed through hydrogen bonds in the system of cobalt-containing molybdenum phosphates.

Experimental

Physical measurements

Elemental analyses (C and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. P, Mo and Co were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range of 400—4000 cm^{-1} on an Alpha Centaur FT/IR Spectrophotometer using KBr pellets. EPR spectra were recorded on a Japanese JES-FE3AX spectrometer at 293 K. XPS analyses were performed on a VG ESCALAB MK II spectrometer with a Mg $\text{K}\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis.

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Synthesis of compound 1

All chemicals were of reagent grade and used as purchased from commercial sources. Compound 1 was synthesized by employing hydrothermal method. A mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, H_3PO_4 , $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and H_2O in the molar ratio of 3:1:6:1:180 was sealed in a 18-mL Teflon-lined reactor which was kept at 180 °C for 3 days, followed by slow cooling to room temperature. Brown red crystals of 1 (yield 45% based on Mo) were isolated by filtering and washed with water. Anal. calcd for $(\text{H}_2\text{en})_5[\text{CoMo}_{12}\text{O}_{50}\text{P}_8(\text{OH})_{12}] \cdot 2\text{H}_2\text{O}$: C 4.28, N 4.99, P 8.82, Co 2.10, Mo 40.99; found C 4.15, N 4.86, P 8.93, Co 2.16, Mo 40.88.

X-Ray crystallography

The structure of compound 1 was determined by single crystal X-ray diffraction analysis. A single crystal with approximate dimensions of 0.706 mm \times 0.087 mm \times 0.073 mm was mounted in a glass capillary. Data were collected on an R-axis RAPID IP diffractometer at 293 K using graphite-monochromated Mo K α radiation ($\lambda = 0.071073$ nm) and IP technique in the range of $2.03^\circ < \theta < 27.47^\circ$. Empirical absorption correction was applied. A total of 13262 reflections (8340 unique, $R_{\text{int}} = 0.0200$) were measured. The structure was solved by direct method using the program SHELXS-97¹⁵ and refined by Full-matrix least-squares method on F^2 using the SHELXL-97¹⁶ program package. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed in the calculated positions and those attached to oxygen atoms were located inaccurately. Structure solution and refinement based on 8340 independent reflections with $I > 2\sigma(I)$ on 0 restraint and 450 parameters gave $R_1 = 0.0417$ and $wR_2 = 0.1395$ $\{R_1 = \sum \|F_o| - |F_c| \| / \sum |F_o|$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$. Crystal data are summarized in Table 1. Table 2 gives selected bond lengths and angles.

Results and discussion

Structure description

The use of lower temperature in the hydrothermal synthesis in the system of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, H_3PO_4 , $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and H_2O resulted in the formation of compound 1 in a good yield. Crystal 1 consists of $[\text{Mo}_6\text{P}_4\text{O}_{25}(\text{OH})_6]^{6-}$ as $\{\text{Mo}_6\text{P}_4\}$ anionic units, diprotonated $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and lattice water (Fig. 1). As the classical description by Haushalter,¹⁷ $\{\text{Mo}_6\text{P}_4\}$ is made up of six MoO_6 octahedra and four PO_4 tetrahedra. Each of MoO_6 contains one $\text{Mo}=\text{O}$ group and shares two edges with neighboring octahedra. The central PO_4 group provides three oxygens that bridge the bonding $\text{Mo}\cdots\text{Mo}$ contacts, while each of the remaining three PO_4 groups has two oxygens to span the non-

Table 1 Crystal data and structure refinement for compound 1

Empirical formula	$\text{C}_{10}\text{H}_{66}\text{CoMo}_{12}\text{P}_8\text{N}_{10}\text{O}_{64}$
Formula weight	2808.70
Temperature (K)	293(2)
Wavelength (nm)	0.071073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> (nm)	1.1863(2)
<i>b</i> (nm)	1.3361(3)
<i>c</i> (nm)	1.3783(3)
α (°)	88.13(3)
β (°)	70.09(3)
γ (°)	65.24(3)
<i>V</i> (nm ³)	1.8497(6)
<i>Z</i>	1
<i>D</i> _{calcd} (Mg/m ³)	2.521
Absorption coefficient (mm ⁻¹)	2.472
<i>F</i> (000)	1359
Crystal size (mm)	0.706 \times 0.087 \times 0.073
θ Range for data collection (°)	2.03 to 27.47
Index ranges (°)	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$
Reflections collected	13262
Independent reflections	8340 ($R_{\text{int}} = 0.0200$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8340/0/480
Goodness-of-fit on F^2	1.018
Final R_1 , wR_2 indices [$I > 2\sigma(I)$]	0.0417, 0.1395
R_1 , wR_2 indices (all data)	0.0491, 0.1431
Largest difference peak and hole ($e \cdot \text{nm}^{-3}$)	4830 and -1006

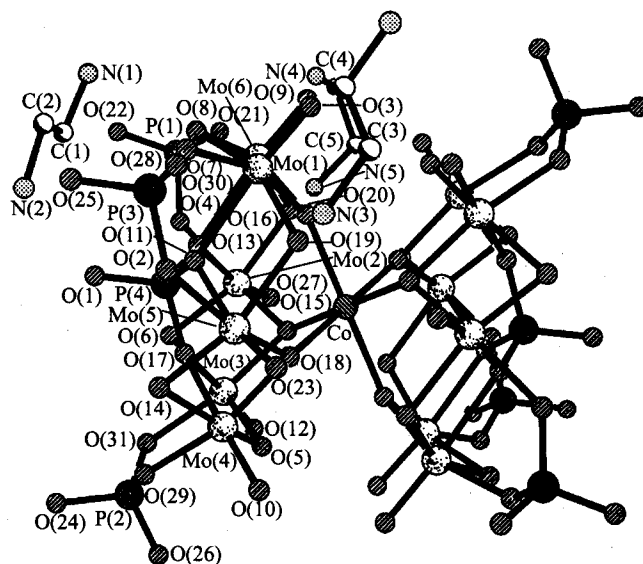


Fig. 1 View of the structure of $(\text{H}_2\text{en})_5[\text{CoMo}_{12}\text{O}_{50}\text{P}_8(\text{OH})_{12}] \cdot 2\text{H}_2\text{O}$.

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for compound **1**

Mo(1)—O(3)	0.1691(5)	Mo(1)—O(7)	0.1930(5)
Mo(1)—O(20)	0.1978(4)	Mo(1)—O(8)	2.028(5)
Mo(1)—O(16)	0.2110(4)	Mo(1)—O(13)	0.2304(5)
Mo(1)—Mo(6)	0.25807(10)	Mo(2)—O(27)	0.1686(5)
Mo(2)—O(4)	0.2064(5)	Mo(2)—O(15)	0.1979(4)
Mo(2)—O(13)	0.2246(4)	Mo(2)—O(16)	0.2112(5)
Mo(2)—O(6)	0.1930(5)	Mo(2)—Mo(3)	0.25868(11)
Mo(3)—O(5)	0.1682(5)	Mo(3)—O(6)	0.1950(5)
Mo(3)—O(12)	0.2112(5)	Mo(3)—O(17)	0.2267(4)
Mo(3)—O(15)	0.1984(4)	Mo(3)—O(31)	0.2059(5)
Mo(4)—O(10)	0.1684(5)	Mo(4)—O(14)	0.1940(5)
Mo(4)—O(12)	0.2103(4)	Mo(4)—O(29)	0.2048(5)
Mo(4)—O(18)	0.1979(5)	Mo(4)—O(17)	0.2264(5)
Mo(4)—Mo(5)	0.26034(14)	Mo(5)—O(23)	0.1687(5)
Mo(5)—O(14)	0.1938(5)	Mo(5)—O(18)	0.1971(4)
Mo(5)—O(2)	0.2029(5)	Mo(5)—O(19)	0.2122(5)
Mo(5)—O(11)	0.2233(4)	Mo(6)—O(9)	0.1682(5)
Mo(6)—O(7)	0.1942(4)	Mo(6)—O(20)	0.1970(4)
Mo(6)—O(28)	0.2058(5)	Mo(6)—O(19)	0.2113(4)
Mo(6)—O(11)	0.2293(5)	Co—O(20)	0.2119(4)
Co—O(15)	0.2160(4)	Co—O(18)	0.2182(5)
Mo(2)-O(6)-Mo(3)	83.63(18)	Mo(1)-O(7)-Mo(6)	83.59(18)
Mo(5)-O(11)-Mo(6)	100.64(17)	Mo(3)-O(12)-Mo(4)	112.2(2)
Mo(2)-O(13)-Mo(1)	99.81(18)	Mo(5)-O(14)-Mo(4)	84.33(19)
Mo(2)-O(15)-Mo(3)	81.47(16)	Mo(1)-O(16)-Mo(2)	111.1(2)
Mo(4)-O(17)-Mo(3)	101.06(17)	Mo(5)-O(18)-Mo(4)	82.46(17)
Mo(6)-O(19)-Mo(5)	110.7(2)	Mo(6)-O(20)-Mo(1)	81.64(17)

bonding Mo \cdots Mo contacts (Fig. 2). The average length of Mo \cdots Mo is 0.259 nm. Each of Mo $^{5+}$ cation in compound **1** has a distorted octahedral configuration with an apical Mo \cdots O bond at length of *ca.* 0.169 nm and five other Mo \cdots O bonds at lengths ranging from *ca.* 0.193 nm to *ca.* 0.230 nm. For **1**, based on the valence bond calculations,¹⁸ the bond values for all the molybdenum and phosphorous atoms are in *ca.* 5.21 and *ca.* 5.02, respectively, indicating that all Mo and P have +5 oxidation state. The bond valence values of O(12), O(16), O(19), O(21), O(24) and O(25) are in the range of *ca.* 1.13—*ca.* 1.36. It means that they are all OH oxygens. The structure of **1** consists of molybdenum hexamers which are bonded together with octahedral Co to form a dimer. The Co $^{2+}$ ion bridges two Mo $_6$ P $_4$ units via three μ -O atoms [O(15) O(18) O(20)] which link the metal-metal-bonded molybdenum atoms and the Co—O bonds lengths are 0.2160, 0.2182 and 0.2119 nm to produce centrosymmetric Co[Mo $_6$ P $_4$] $_2$. Five diprotonated diamines are present as counter-ions located around the Co[Mo $_6$ P $_4$] $_2$ dimer. It is noteworthy that compound **1** exhibits a novel 3-D structure (Fig. 3) constructed through hydrogen bonds with the lengths of *ca.* 0.2555 and *ca.* 0.2750 nm for O \cdots H \cdots O and N \cdots H \cdots O contacts, respectively. Compound **1** is stabilized by the five ethylenediamine molecules, which are nitrogen-

rich donors. Clear tunnels among Co[Mo $_6$ P $_4$] $_2$ units are observed along *c*-axis (Fig. 4).

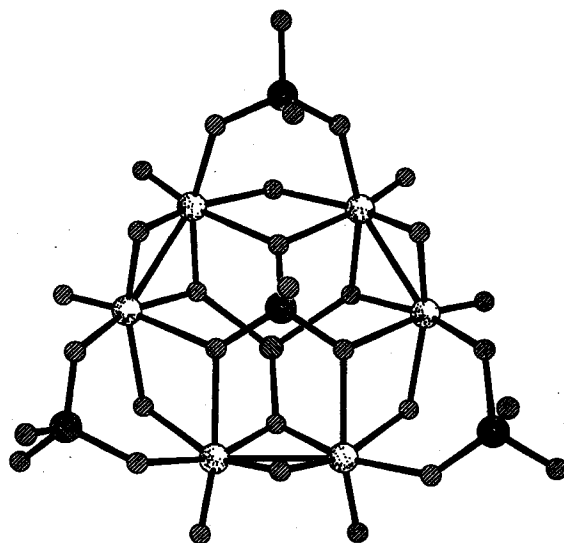


Fig. 2 View of Mo $_6$ P $_4$ O $_{31}$ cluster. P atoms are represented by black circles, Mo atoms by white circles, O atoms by gray circles.

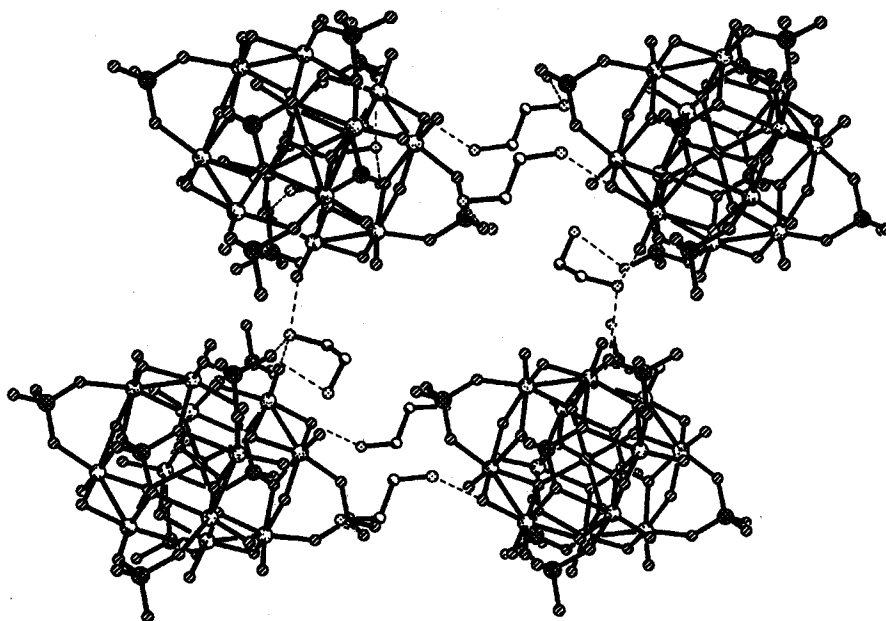


Fig. 3 View of 3-D framework with tunnels, which is based on the $\{\text{Co}(\text{Mo}_6\text{P}_4)_2\}$ building blocks linked by the diprotonated ethylenediamine counter cations via hydrogen bonds.

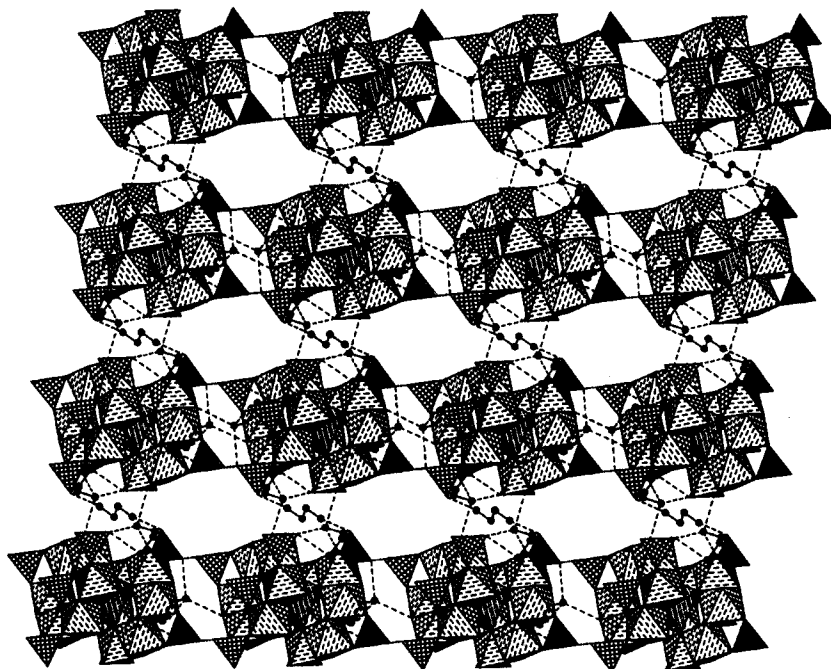


Fig. 4 View of octahedron graphical of three dimensional structure with tunnels.

IR spectrum

The IR spectra of compound **1** exhibited a strong band at 948 cm^{-1} , characteristic of $\nu(\text{Mo}=\text{O})$. Features at 735 cm^{-1} and 1015 cm^{-1} are attributed to the $\nu(\text{Mo}-\text{O}-\text{Mo})$ and $\nu(\text{P}-\text{O})$, respectively. Bands at 1041 cm^{-1} and 1534 cm^{-1} are characteristic of diprotonated ethylenediamine, while peaks at 3431 cm^{-1} and 1623 cm^{-1} are assigned to water molecules.

EPR and XPS spectra

An EPR spectrum of **1** at low temperature only shows a Mo^{5+} signal with $g = 1.9735$, in accordance with valence sum calculations. Photoelectron spectrum (XPS) measurements of compound **1** in the energy regions of $\text{Mo}_{3d}^{3/2}$ and $\text{Mo}_{3d}^{5/2}$ give one peak at 231.4 eV , which further confirms the valence of Mo^{5+} atoms,¹⁹ in good agreement with the results of valence bond calculations and EPR measurement.

Conclusion

The successful isolation of compound **1** confirms not only the strong power of hydrothermal synthesis to isolate novel organic-inorganic hybrid materials, but also the structural variety of molybdenum phosphate phase. Furthermore, the incorporation of cobalt atom into the molybdenum phosphate framework suggests that analogous complex can be derived from other first-row transition elements. The compound **1** may be used as catalyst by further modification. The catalytic activity of similar structures has been reported by our group.^{20,21}

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