

Three-Dimensional open-framework cobalt–molybdenum phosphate by hydrothermal synthesis: $(\text{C}_2\text{H}_9\text{N}_2)_4(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Co}_3\text{Mo}_4\text{P}_4\text{O}_{28}]$

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Abstract

The new three-dimensional open-framework cobalt(II) molybdenum(VI) phosphate, $(\text{C}_2\text{H}_9\text{N}_2)_4(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Co}_3\text{Mo}_4\text{P}_4\text{O}_{28}]$ **1**, has been prepared by the reaction of sodium molybdate, phosphoric acid and ethylenediamine with Co_3^{2+} salts. The crystal data for **1** are as follows: Tetragonal, space group $I4(1)/a$, $a = 17.088(2)$ Å, $c = 10.745(2)$ Å $V = 3137.7(9)$ Å³, $Z = 4$. The structure of **1** is constructed from CoMo_2P tetrahedral units connected by CoO_4 tetrahedra through sharing corners. The connectivity leads to the formation of intersecting channels in all three crystallographic directions, resembling an aluminosilicate zeolite, and the channels are filled with charge-compensating ethylenediamine ions.

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1. Introduction

Microporous compounds such as zeolites and aluminophosphates have been received a lot of interest in research because of their potential applications in sorbents, ion exchangers, and catalysts. Among the vast family of open-framework metal phosphates, the transition metal phosphates constitute an important group. The synthesis and structure of several open-framework iron phosphates have been reported in the recent literatures [1–8]. However, there are very few reports of open-framework phosphates of cobalt and molybdenum. The first three-dimensional (3-D) cobalt–molybdenum phosphate with open architecture has just been reported by Xu et al. [9]. Several cobalt phosphates with open-framework structures using alkali and alkaline-earth metals as counterions have been prepared by Feng et al. and others [10–13]. Cobalt phosphate structures stabilized by incorporation of aluminum as a part of the

framework have been prepared in the presence of structure-directing amines. Herein are described the synthesis and characterization of a new open-framework cobalt–molybdenum phosphate with intersecting channels, $(\text{C}_2\text{H}_9\text{N}_2)_4(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Co}_3\text{Mo}_4\text{P}_4\text{O}_{28}]$. Its structure contains a novel open framework structure built from four- and six-coordinated cobalt atoms, MoO_6 octahedra and PO_4 tetrahedra.

2. Experimental

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Co, Mo, and P were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an FT/IR Spectrophotometer using KBr pellets. EPR spectrum was recorded on Bruker ER 200D-SRC spec-

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

Empirical formula	(C ₂ H ₉ N ₂) ₄ (C ₂ H ₁₀ N ₂)[Co ₃ Mo ₄ P ₄ O ₂₈]
Crystal system, space group	Tetragonal, <i>I4</i> (1)/ <i>a</i>
Unit cell dimensions	<i>a</i> = 17.088(2) Å α = 90° <i>b</i> = 17.088(2) Å β = 90° <i>c</i> = 10.745(2) Å γ = 90°
Volume	3137.7(9) Å ³
Z, Calculated density	4, 3.046 Mg/m ³
Absorption coefficient	3.432 mm ⁻¹
<i>F</i> (000)	2836
Crystal size	0.355 × 0.350 × 0.173 mm ³
θ range for data collection	2.24–27.48°
Limiting indices	0 ≤ <i>h</i> ≤ 22, 0 ≤ <i>k</i> ≤ 22, 0 ≤ <i>l</i> ≤ 13
Reflections collected/unique	1801/1801 [<i>R</i> (int) = 0.02098]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.119
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0344, <i>wR</i> 2 = 0.0984
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0368, <i>wR</i> 2 = 0.0998
Largest diff. peak and hole	1.228 and -1.797 e Å ⁻³

trometer at room temperature. XPS analysis was performed on an EASY ESCA spectrometer with a Mg-K α achromatic X-ray source. Variable-temperature magnetic susceptibility measurements for **1** were performed on MPMS-XL magnetometer in 2–300 K and under an applied field of 5000 Oe. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.83(\chi_{\text{M}}T)^{1/2}$, where χ_{M} is the molar magnetic susceptibility. TG analysis was performed on a Perkin–Elmer TGA7 instrument in air with a heating rate of 5 °C min⁻¹.

2.2. Synthesis

The title compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of CoCl₂ · 6H₂O (1.0 g), Na₂MoO₄ · 2H₂O (1.8 g), H₃PO₄ (0.8 ml), and water (12 ml) was neutralized to pH 8.5 with ethylenediamine (30%) under continuous stirring and sealed in a 25 ml Teflon-lined autoclave, which was heated to 175 °C for four days. After slow cooling to room temperature, black block crystals of **1** were separated as a major phase (75% yield based on Co) together with a small amount of an unidentified black powder. Anal. Calc. For **1**: C, 8.34; H, 3.20; N, 9.73; P, 8.62; Co, 12.28; Mo, 26.66%. Found: C, 8.45; H, 3.32; N, 9.81; P, 8.55; Co, 12.17; Mo, 26.78%. The IR spectrum of **1** exhibited complex bands at 1096, 982, 952, 879, 829, and 727 cm⁻¹, ascribed to ν (P–O), ν (M–O–M), respectively. The features at 1607, 1501, 1454, 1400, and 1346 cm⁻¹ can be regarded as characteristic of ethylenediamine.

2.3. X-ray crystallography

The crystal structure determination for compound **1** was performed on a Rigaku RAXIS-RAPID diffractometer and Mo-K α (λ = 0.71073 Å) at 293 K in the range of 2.24° < θ < 27.48°. A total of 1801 (1801unique, *R*_{int} =

0.02098) reflections were measured. The structure was solved by direct methods using the program SHELXS-97 [14] and refined by full-matrix least-squares methods on *F*² using the SHELXL-97 [15] program package. Direct methods were used to locate the Co, P, and Mo atoms first, and the remaining oxygen, carbon, and nitrogen atoms were found from difference environments. All of the non-hydrogen atoms were refined anisotropically. C(3) and N(3) have only occupancy of 0.5 because of its special position, so the hydrogen atoms attached to C and N atoms were not located accurately. Crystal data are summarized in Table 1, selected bond lengths and angles are listed in Table 2 and CCDC Reference No. 200275.

3. Results and discussion

The formation of the crystal product of compound **1** depends the use of hydrothermal technique and choice of proper synthesis conditions, in which pH value is vital. No crystal product of **1** was obtained when pH value of the reaction system seriously deviated from 8.5. We attempted to prepare iron and nickel analogues of compound **1** through replacing CoCl₂ · 6H₂O with FeCl₂ · 4H₂O and NiCl₂ · 6H₂O under a similar reaction conditions, respectively, but were not successful.

Compound **1** (C₂H₉N₂)₄(C₂H₁₀N₂)[Co₃Mo₄P₄O₂₈] exhibits a novel three-dimensional framework with pores in which protonated and partially protonated ethylenediamine molecules lodge. Its structure consists of CoO₄, CoO₆, PO₄, and MoO₆ polyhedra linked through sharing vertices, forming 6-membered ring channels (Fig. 1). As shown in Fig. 2, the CoMo₂P units are linked covalently into a three-dimensional framework. Adjacent CoMo₂P units are connected through alternatively sharing Mo and Co atoms, forming 12-membered ring channels along the [001] direction. In

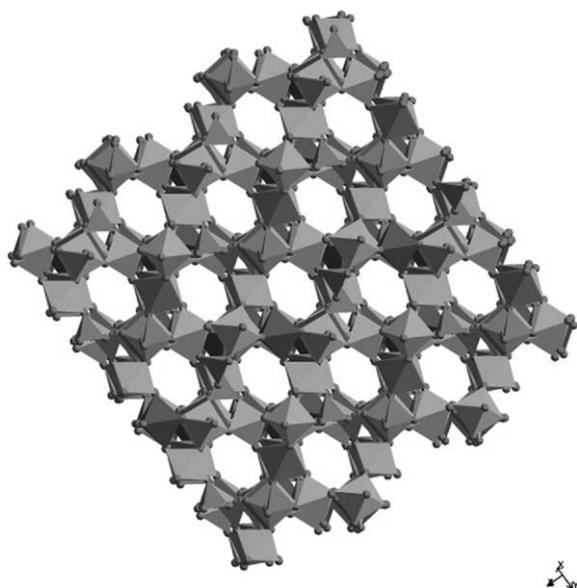


Fig. 1. Polyhedral view of the three-dimensional framework structure of showing the 6-membered ring channels.

addition, each CoO_4 tetrahedron is joined to four CoMo_2P units by sharing corner with PO_4 tetrahedron. Thus we also consider that the microporous cobalt–molybdenum phosphate is constructed from Co_2MoP units connected by CoO_4 tetrahedra through sharing vertices. Compound **1** exhibits a unique channel structure, which is quite rare in open-framework solids and there are only a few such reports in open-framework cobalt–molybdenum phosphates.

A single crystal X-ray analysis revealed that the asymmetric unit of **1** consists of a half CoO_6 octahedron, a quarter CoO_4 tetrahedron, one PO_4 tetrahedron, one MoO_6 octahedron, and one and a quarter ethylenediamine ions. The coordination geometry of the three framework atoms, Mo, P, and Co is exclusively defined by corner-shared oxo groups. The geometric parameters of the cobalt–molybdenum phosphate framework which are reasonably well determined (data: parameters ratio ca. 12:1) show that the $\text{Co}(1)\text{--O}$ contacts 1.925(3) Å (tetrahedral Co, T_{Co}), $\text{Co}(2)\text{--O}$ contacts in the range 2.066(3)–2.094(3) Å (octahedral Co, O_{Co}),

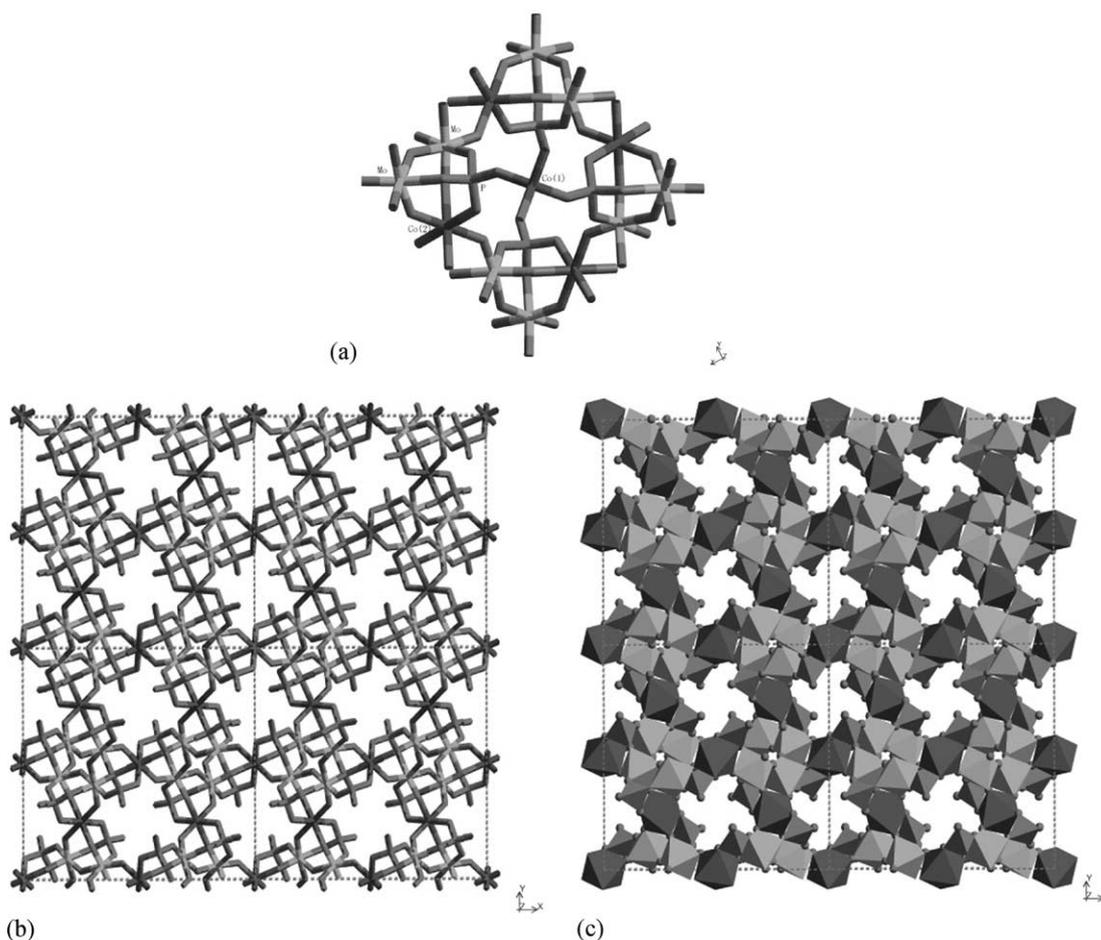


Fig. 2. (a) A view of the partial framework structure of compound **1** showing four CoMo_2P units connected by a CoO_4 tetrahedron through sharing corners. (b) A representation of the framework structure along $[001]$ direction. (c) Polyhedral view of the framework structure along $[001]$ direction showing 12-membered ring channels.

P–O contacts in the range 1.517(3)–1.554(3) Å, Mo–O contacts in the range 1.746(3)–2.208(3) Å. The P–O and Co–O (both T_{Co} and O_{Co} sites) contacts are within the expected range. The molybdenum site exhibits short-to-medium bond length pattern regardless of the absence of terminal oxo groups, which is not uncommon to Mo(VI) oxides containing unsymmetrical bridging oxo groups. This may also be attributed to the existence of moderate hydrogen bonds involving some of the O atoms of the MoO_6 units. It is noteworthy in the structure of **1**, that the partially protonated ethylenediamine moieties that serves as the cation. The ethylenediamine ions interact with the framework through contacts between the N atoms of the ethylenediamine ions and the O atoms of the framework with $N-H \cdots O$ 2.88–3.38 Å. However, uncertainty is encountered in locating H atoms attached to the N atoms due to the severe disordering of the ethylenediammonium ions in the crystal packing of **1**.

Hybrid materials provide new opportunities in the realm of molecules for studying magnetically condensed systems. The temperature dependent magnetic susceptibilities of **1** has been measured in the range 300–2 K. The magnetism may be attributed solely to the presence of Co^{2+} ions ($3d^7$, $S = 3/2$) which reside in the $\{Co_3Mo_4P_4O_{28}\}$ framework in the structure. Since Mo^{6+} ($4d^0$, $S = 0$) ions do not possess an effective magnetic moment, they do not contribute to the bulk properties. The effective magnetic moment of **1** at room temperature (300 K), determined by the equation $\mu_{eff} = 2.83(\chi_M T)^{1/2}$ where χ_M being mole magnetic susceptibility per formula unit, is $8.40\mu_B$ being larger than that expected for the total spin-only value $6.71\mu_B$ of three Co(II) with $S = 3/2$. The coupled interaction between the magnetic orbitals probably results in this situation. Fig. 3 shows that the effective magnetic moments of **1** decrease as temperature decreasing from 300 to 16 K, which is in agreement with Weiss constant $\theta < 0$, indicating presence of antiferromagnetic exchange interaction in compound **1**. While in 16–2 K, the

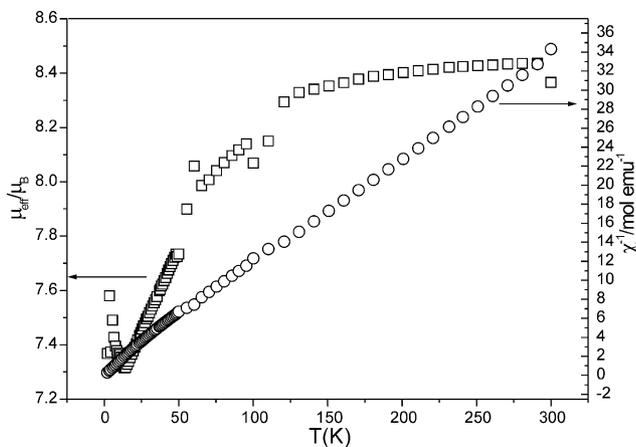


Fig. 3. The effective magnetic moment μ_{eff} and inverse molar susceptibility vs temperature for compound **1**.

effective magnetic moments increase with temperature decreasing, showing there is ferromagnetic coupled interaction in **1** in this temperature range. Because no suitable theoretical model is available in the literature for such a complex system, detailed magnetic analyses were not performed for the present compound.

The EPR spectrum of **1** at room temperature shows the Co^{2+} signal with $g = 1.9266$, in accordance with the valence sum calculations. In the XPS spectra for compound **1**, XPS gives one peak at 781.5 eV, attributed to Co^{2+} , and XPS also shows peak at 232.65 eV, ascribed to Mo^{6+} . The results further confirm the structure analysis. The TG gives a total weight loss of 21.5% in the range of 360–700 °C, which agrees well the calculated value of 21.25%.

In conclusion, we have successfully combined cobalt–molybdenum phosphate compound. The connectivity leads to the formation of intersecting channels in all the crystallographic directions resembling the aluminosilicate zeolite, and the channels are filled with charge-compensating ethylenediamine ions. Compound **1** can also be considered as one example of the hybrids of phosphate, which may possess new and unique properties in contrast to single cobalt or molybdenum phosphates, and provided a new strategy for design of solid-state materials. This work also shows that hydrothermal synthesis is a powerful method to obtain novel structural materials.

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