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Hydrothermal synthesis and structure of a novel solid material with 3-D open-framework: $(NH_3CH_2CH_2NH_3)(NH_3CH_2CH_2NH_2)_3Na_3[Co_4Mo_{12}O_{24}(OH)_6(H_2O)_2(HPO_4)_2(PO_4)_6] \cdot 8H_2O$

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Abstract

A novel cobalt phosphomolybdate: $(NH_3CH_2CH_2NH_3)(NH_3CH_2CH_2NH_2)_3Na_3[Co_4Mo_{12}O_{24}(OH)_6(H_2O)_2(HPO_4)_2(PO_4)_6] \cdot 8H_2O$ **1**, has been hydrothermally synthesized (200°C, 5 days, autogenously pressure) and characterized by IR, ESR, XPS, elemental analyses and X-ray crystallography. The crystal data: monoclinic space group $C2/c$, $a = 12.3281(3)$ Å, $b = 21.5729(4)$ Å, $c = 26.0242(5)$ Å, $\beta = 99.5401°(3)$, $V = 6825(2)$ Å^3, $Z = 4$, $R_1 = 0.0346$, $wR_2 = 0.0650$. The structure of compound **1** is based on $Co[Mo_6P_4]_2$ units connected together via additional Co^{2+} ions to give a new three-dimensional framework. The interconnected void and channels in the cobalt molybdophosphate frameworks are filled with counter cations and water molecules. The magnetic property of **1** exhibits antiferromagnetic coupling interactions.

Keywords: Hydrothermal synthesis; Cluster compound; Transition metals; Magnetic properties

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1. Introduction

Since the discovery of the family of crystalline aluminophosphates (CAPOs) in 1982 [1], microporous zeolite-like materials have attracted much interest due to their potential applications in many fields such as ion-exchange, catalysis and adsorption, etc. [2–8], but only in recent years have other open-framework inorganic materials started to emerge. One of strategies adopted is to incorporate d-block elements into these materials as stoichimetric framework constituents through the combined effects of hydrothermal synthesis and amine templates. Through this strategy a lot of new solid-state materials have been successfully synthesized. Such examples include open-framework reduced molybdenum phosphates [9], iron molybdenum phosphates [10], cobalt molybdenum phosphate [11–12], vanadium phosphates [13–14], cobalt phosphate [15–16], vanadium oxides [17], and a number of layered molybdenum (VI) solids [18]. However, open-framework solids incorporating both octahedrally and tetrahedrally coordinated transition elements remain largely unexplored [19]. Here, we report the synthesis, crystal structural and characterization of a novel three-dimensional cobalt molybdophosphate with formula $(NH_3CH_2CH_2NH_3)(NH_3CH_2CH_2NH_2)_3Na_3[Co_4Mo_{12}O_{24}(OH)_6(H_2O)_2(HPO_4)_2(PO_4)_6] \cdot 8H_2O$. To the best of our knowledge, this is the first open-framework cobalt molybdenum phosphate constructed from $M[Mo_6P_4]_2$ as building blocks and containing both tetrahedrally and octahedrally coordinated transition metals.

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2. Experimental

2.1. Material and instrumentation

All chemicals were purchased from commercial sources and used without further purification. Infrared spectrum of the title compound was recorded with Perkin-Elmer SPECTRUM ONE FTIR spectrophotometer in the 225–4000 cm^{-1} regions using a powdered sample on a KBr plate. The elemental analysis was determined using a Perkin-Elmer 2400 series IICHNS/O elemental analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Perkin-Elmer Optima 3300 DV spectrometer. Determination of electron spin resonance (ESR) carried out on Bruker ER 200D-SRC spectrometer. The TG curve was obtained on a Perkin-Elmer TGA-7000 thermogravimetric analyzer in the flowing air with a temperature ramp rate of 20°C min^{-1}. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg-$K\alpha$ (1253.6 eV) achromatic X-ray source. Variable temperature magnetic susceptibility measurements for **1** were performed on a Quantum Design MPMS XL-5 SQUID magnetometor in 2–300 K.

2.2. Preparations

Compound **1** was synthesized in 75% yield based on Mo. A mixture of $CoCl_2 \cdot 6H_2O$ (0.4 g), $Na_2MoO_4 \cdot 2H_2O$(1.2 g), en (0.11 mL), H_3PO_4 (0.20 mL, 85%) and distilled water (9 mL) in a mole ratio of 1:3:1:2:300 was neutralized to pH = 5 with en under stirring and sealed in a 30 mL Teflon-lined reactor, then heated at 200°C for 5 days. After cooling to room temperature, the brown-red block crystals were isolated, washed with water, and dried at ambient temperature. The IR spectrum of **1** exhibits an intense band at 952.99 cm^{-1}, characteristic of v (Mo–O) and features at 1016 and 1119 cm^{-1} associated with v (P–O), respectively. The features at 1603 and 1384 cm^{-1} are characteristic for the protonated ethylenediamine. Anal. Calc. For $C_8H_{65}Co_4Mo_{12}N_8Na_3O_{72}P_8$: C, 3.067%; H, 2.077%; N, 3.579%; Co, 7.54%; Mo, 36.81%; P, 7.92%; Na, 2.2%. Found: C, 3.06%; H, 2.075%; N, 3.58%; Co, 7.05%; Mo, 35.8%; P, 7.58%; Na, 2.05%.

2.3. Crystal structure determination

A suitable single crystal of **1** (0.377 × 0.354 × 0.173 mm^3) was carefully selected under a polarizing microscope and glued to the tip of a glass fiber. Single crystal structure determination by X-ray diffraction was performed on a Rigaku RAXIS-RAPID diffractometer with monochromoted Mo-$K\alpha$ radiation at 293 K in the range of $2.84 < \theta < 27.47$. A total of 31959 (6548 independent, $R_{\text{int}} = 0.0266$) reflections were measured. The structure was solved by direct method (SHELXL-97) and refined by the full-matrix least-squares methods on F^2. All of the non-hydrogen atoms were refined anisotropically. Structure solution and refinement were based on 526 parameters giving $R_1(wR_2) = 0.0266(0.0624)\{R_1 = \sum||F_o| - |F_c||/|F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$. CCDC reference number 212759.

3. Results and discussion

3.1. Description of the structure

The single crystal structure of compound **1** was determined by X-ray crystallography. Crystallographic and refinement details, and selected bond lengths are listed in Tables 1 and 2, respectively.

The single crystal X-ray analysis reveals that compound **1** consists of $[Co_4Mo_{12}O_{24}\ (OH)_6(H_2O)_2\ (HPO_4)_2(PO_4)_6]^{8-}$ cluster anions, sodium cations, protonated ethylenediamines and lattice water molecules. The IR result and elemental analysis data are in accordance to the chemical formula of compound **1**.

In $[Mo_6P_4]$ unit of compound **1**, the six oxo-bridged molybdenum atoms [Mo–O: 1.680(3)–2.342(3) Å] are approximately in the same plane and constitute a hexameric molybdenum ring with alternating Mo–Mo single bonds (av. 2.59 Å) and non-bonding Mo–Mo contacts (av. 3.47 Å). Among four phosphate groups [P–O: 1.506(3)–1.574(3) Å], a central one bridges the

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

Empirical formula	$C_8H_{65}Co_4Mo_{12}N_8Na_3O_{72}P_8$
Formula weight	3129.4 g mol^{-1}
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system space group	Monoclinic, $C2/c$
Unit cell dimensions	$a = 12.328(3)$ Å $\alpha = 90°$
	$b = 21.579(4)$ Å $\beta = 99.54(3)°$
	$c = 26.024(5)$ Å $\gamma = 90°$
Volume	6827(2) Å^3
Z, Calculated density	4, 3.044 g cm–^{3}
Absorption coefficient	3.415 mm^{-1}
$F(000)$	6040
Crystal size	0.377 × 0.354 × 0.173 mm^3
θ range for data collection	2.84–27.47°
Limiting indices	$0 \leqslant h \leqslant 150 \leqslant k \leqslant 27 - 33 \leqslant l \leqslant 33$
Reflections collected/unique	31959/6548 [R(int) = 0.0265]
Completeness to $\theta = 27.47$	83.7%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	6548/2/526
Goodness-of-fit on F^2	1.058
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0266$, w$R_2 = 0.0624$
R indices (all data)	$R_1 = 0.0346$, w$R_2 = 0.0650$
Largest diff peak and hole	2.085 and −0.674 eÅ^{-3}

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

Mo(1)–O(8)	1.682(3)	Mo(4)–O(31)	2.033(3)	Co(3)–O(12)	2.118(3)
Mo(1)–O(11)	1.938(3)	Mo(4)–O(23)	2.045(3)	Co(3)–O(19)	2.145(3)
Mo(1)–O(29)	1.961(3)	Mo(4)–O(22)	2.342(3)	P(1)–O(12)	1.511(2)
Mo(1)–O(7)	2.090(3)	Mo(4)–Mo(6)	2.5995(7)	P(1)–O(22)	1.543(3)
Mo(1)–O(26)	2.101(3)	Mo(4)–Mo(3)	3.436(12)	P(1)–O(15)	1.551(3)
Mo(1)–O(18)	2.247(3)	Mo(5)–O(16)	1.687(3)	P(1)–O(18)	1.556(3)
Mo(1)–Mo(2)	2.5850(6)	Mo(5)–O(14)	1.929(3)	P(2)–O(6)	1.515(3)
Mo(5)–Mo(1)	3.472(11)	Mo(5)–O(17)	1.985(3)	P(2)–O(32)	1.535(3)
Mo(2)–O(3)	1.680(3)	Mo(5)–O(4)	2.038(3)	P(2)–O(23)	1.541(3)
Mo(2)–O(11)	1.944(3)	Mo(5)–O(26)	2.095(3)	P(2)–O(25)	1.546(3)
Mo(2)–O(29)	1.968(3)	Mo(5)–O(18)	2.271(3)	P(3)–O(9)	1.506(3)
Mo(2)–O(20)	2.056(3)	Mo(6)–O(30)	1.683(3)	P(3)–O(20)	1.542(3)
Mo(2)–O(13)	2.100(3)	Mo(6)–O(10)	1.924(3)	P(3)–O(5)	1.544(3)
Mo(2)–O(15)	2.258(3)	Mo(6)–O(24)	1.984(3)	P(3)–O(27)	1.556(3)
Mo(3)–O(28)	1.692(3)	Mo(6)–O(27)	2.039(3)	P(4)–O(2)	1.507(3)
Mo(3)–O(14)	1.943(3)	Mo(6)–O(13)	2.106(3)	P(4)–O(4)	1.516(3)
Mo(3)–O(17)	1.974(3)	Mo(6)–O(15)	2.249(3)	P(4)–O(1)	1.518(4)
Mo(3)–O(31)	2.057(3)	Co(1)–O(24)	2.088(3)	P(4)–O(7)	1.574(3)
Mo(3)–O(25)	2.057(3)	Co(1)–O(17)	2.131(3)	C(1)–C(2)	1.454(16)
Mo(3)–O(22)	2.306(3)	Co(1)–O(29)	2.207(3)	C(1)–N(1)	1.826(11)
Mo(3)–Mo(5)	2.5760(6)	Co(2)–O(6)♯2	1.938(3)	C(2)–N(2)	1.722(16)
Mo(2)–Mo(6)	3.490(4)	Co(2)–O(5)	1.949(3)	C(4)–N(4)	1.444(11)
Mo(4)–O(21)	1.680(3)	Co(2)–O(2)♯3	1.962(3)	C(4)–C(3)	1.513(13)
Mo(4)–O(10)	1.948(3)	Co(2)–O(32)♯4	1.986(3)	N(3)–C(3)	1.425(14)
Mo(4)–O(24)	1.986(3)	Co(3)–O(9)	2.078(3)		

Symmetry transformations used to generate equivalent atoms: ♯1 $-x+9/2$, $-y+1/2$, $-z+1$; ♯2 $x-1$, y, z ♯3 $x-1/2$, $y-1/2$, z; ♯4 $-x+4$, y, $-z+1/2$.

hexamer internally and three peripheral ones each bridge long Mo–Mo contact externally. Structurally, all of molybdenum octahedra are edge-sharing each other [O–Mo–O: 72.9(10)–170.5(12)°] and all of phosphate tetrahedra are corner sharing with the corresponding molybdenum octahedron (av. O–P–O: 109.5°).

In compound **1**, the hexamer $[Mo_6P_4]$ units are bonded together with octahedral Co(1) (occupancy factor 50%) to form $Co[Mo_6P_4]_2$ clusters (Fig. 1). The cluster units then are linked via tetrahedral Co(2) and octahedral Co(3) (occupancy factor 50%) to construct three-dimensional structure (Figs. 2–4). There are three types of Co atoms being not crystallographically identical in **1**. Specifically, the octahedral Co(1) bridges two $[Mo_6P_4]$ units via three O atoms [O(17), O(24), O(29)], which link the metal–metal-bonded molybdenum atoms together with Co–O bond lengths of 2.131(3) Å × 2, 2.088(3) Å × 2 and 2.207(3) Å × 2, respectively, to produce centrosymmetric $Co[Mo_6P_4]_2$ dimers as shown in Fig. 3. The octahedral Co(3) and it's equivalent atoms each bridges two $Co[Mo_6P_4]_2$ units via oxygen atoms [O(9) and O(12)] from phosphate groups with Co–O bond lengths of 2.078(3) Å × 2 and 2.118(3) Å × 2 to produce chains along *c* direction. Meanwhile, Co(3) has terminal water molecule Ow(19), which completes its octahedral coordinated environment (Fig. 3). The tetrahedral Co(2) is coordinated by four oxygen atoms of phosphates from four $Co[Mo_6P_4]_2$ units with Co–O bond lengths of 1.938(3), 1.949(3), 1.962(3) and 1.986(3) Å, respectively, (Fig. 4). The chains formed through Co(3) octahedra linking $Co[Mo_6P_4]_2$ units are further connected via Co(2) tetrahedra and P–O tetrahedra to construct three-dimensional open-framework of compound **1**, in which there exist two types of channels along a axis (Fig. 5a). One kind of channels consists of mushroom type nine-membered rings formed from four P–O tetrahedra, two

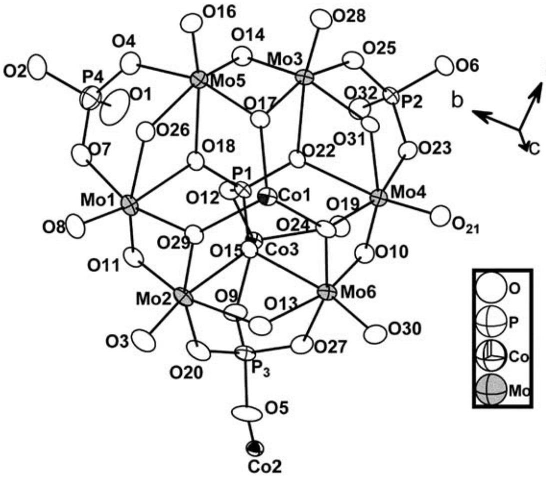

Fig. 1. Ball and stick representation of the anionic building unit $[Mo_6P_4]$ hexamer with atom labeling.

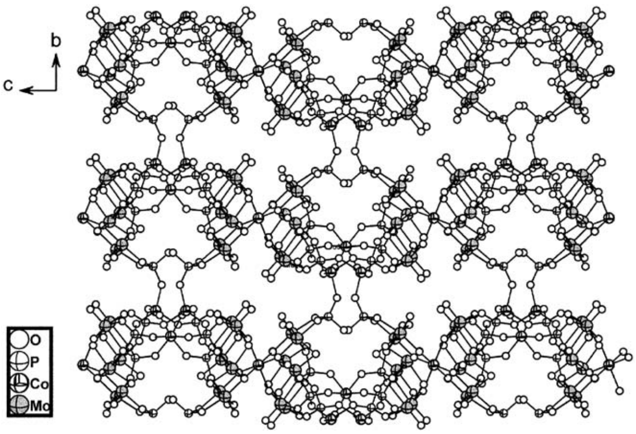

Fig. 2. View of the packing structure down *a*-axis. The coordinated water, protonated en and water are omitted for clarity.

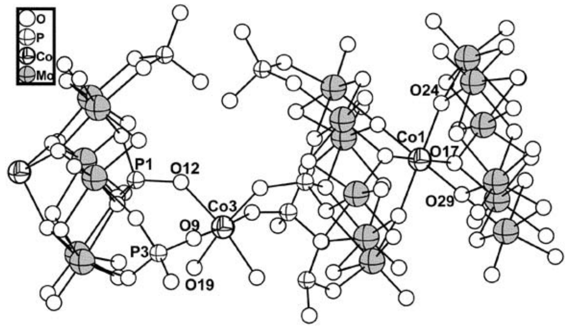

Fig. 3. The coordination environment of Co(1) and Co(3) atoms.

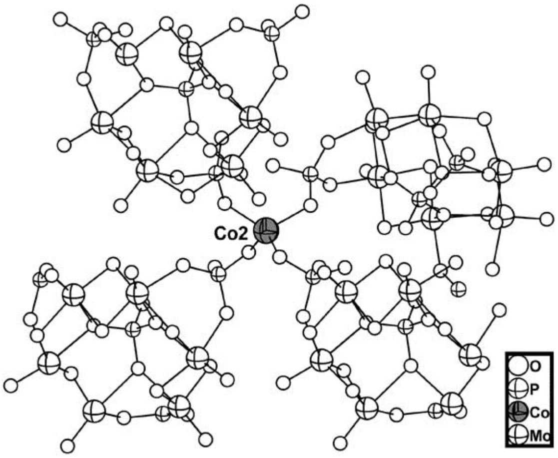

Fig. 4. The coordination environment of Co(2) atom.

Mo coordination octahedra, two Co coordination tetrahedra and one Co coordination octahedron. The other kind of channels is constructed of "╬" shape 12-membered rings produced from four Mo–O octahedra, two Co–O tetrahedra, two Co–O octahedral and four P–O tetrahedra. In addition, in the solid of compound **1** there also exist channels along *b*-axis (Fig. 5b) and *c*-axis (Fig. 5c). In fact, there are intercrossing three-dimensional channels in the open-framework of compound **1**. The channels are filled with water molecules, ethylenediamine ions and sodium ions.

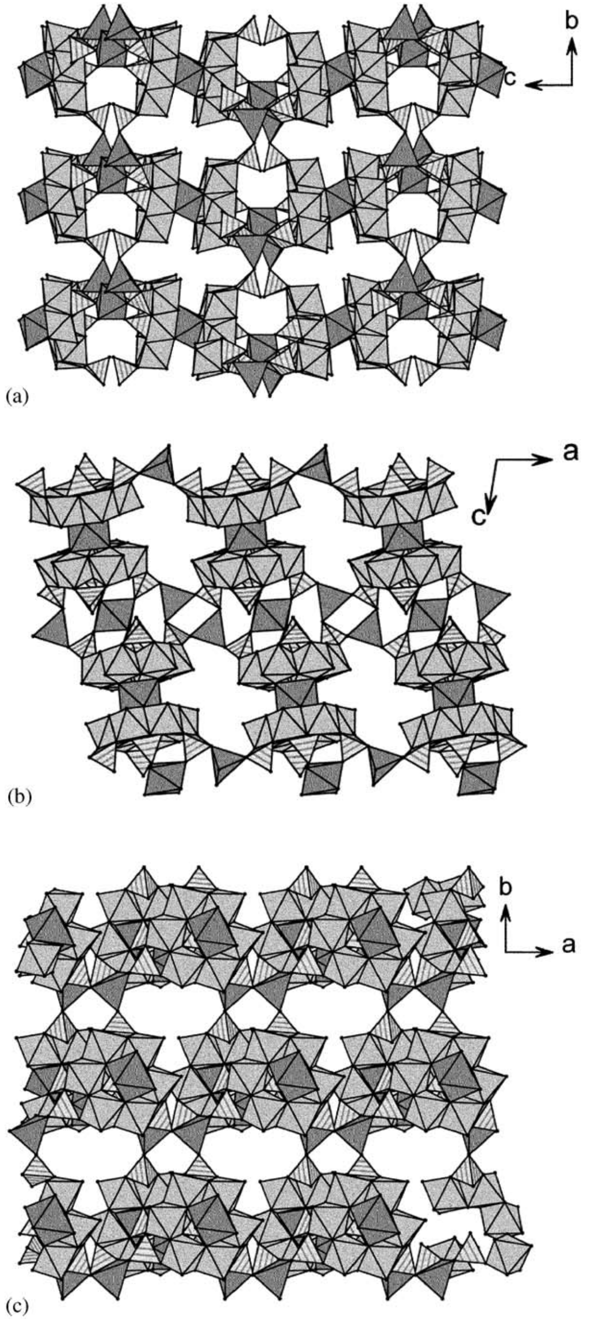

Fig. 5. Polyhedral views of compound **1** showing two types of channel are formed along *a*-axis (a), *b*-axis (b) and *c*-axis (c).

The title compound belongs to molybdenum phosphate containing two kinds of transition metals and with $M[Mo_6P_4]_2$ as structure units. Some of such compounds were reported previously [10,19–26]. The example include $(TMA)_2(H_3O)_3[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot$

11.5H_2O [19] in which two tetrahedral Zn connect the Zn[Mo_6P_4]$_2$ units into layer structure; [$(CH_3)_4N$](NH_4)$_2$[$Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2$]$\cdot n$$H_2O$ [10] in which one octahedral Fe connect the dimeric Fe[Mo_6P_4]$_2$ into three-dimensional structure and [$N(CH_3)_4$]$_2$[$Co_2Mo_6O_{12}(OH)_4(PO_4)(HPO_4)_2(H_2PO_4)$]$\cdot$ H_2O [23] in which three octahedral Co connect the dimeric Co[Mo_6P_4]$_2$ into one-dimensional chain. Compound **1** is a cobalt molybdenum phosphate containing both tetrahedrally and octahedrally coordinated transition metals, which possesses novel three-dimensional structure being different that of reported molybdenum phosphates containing M[Mo_6P_4]$_2$ as building blocks.

3.2. Characterization of the compound

Valence bond calculations for **1** (Table 3) confirm all Mo atoms being in reduced oxidation state (+5) and Co atoms being in +2 [26]. Bond-valence sums of 1.33, 1.03, 1.04 and 1.21 for O(1), O(13), O(26) and O(31), respectively, indicate them being hydroxy O atoms. While O(19) having bond-valence sum of 0.3 is shown to be water O atom [23].

XPS for compound **1** (Fig. 6) gives two peaks at 232.1 and 235.0 eV attributing to Mo^{5+} $3d_{5/2}$ and $3d_{3/2}$, respectively. The fit values are of 231.9 and 235.0 eV, respectively. The results further confirm the valence state of Mo atoms being +5.

The thermogravimetric analysis of **1** with a heating rate of 20°C min^{-1} shows that a total weight loss of 13.67% in the range of 35–603°C (calc. 13.42%), in which, the weight loss of 5.65% in 35–267°C corresponds to the loss of all crystal and most of coordination water (calc. 5.75%) and that of 8.02% in 265–603°C agrees with the loss of ethylenediamine (calc. 7.66%) and residual coordination water molecules.

3.3. Magnetic property

The variable temperature magnetic susceptibility of **1** was measured from 2 to 299 K at 5000 Oe. The thermal variations of $\chi_m T$ and $1/\chi_m$ are displayed in Fig. 7 (where χ_m is the magnetic susceptibility per molecular unit of **1**). The plot $\chi_m T$ versus T shows a $\chi_m T$ value of 13.5 emu K mol^{-1} at 299 K and exhibits a continuous decrease on cooling to a value of 5.97 emu K mol^{-1} at 2 K. This behavior for the $\chi_m T$ curve indicates that there exists antiferromagnetic exchange interaction in **1**. The room temperature value of $\chi_m T$ per formula unit (13.5 emu K mol^{-1}, $\mu_{\rm eff} = 10.4\,\mu_B$) is approximately

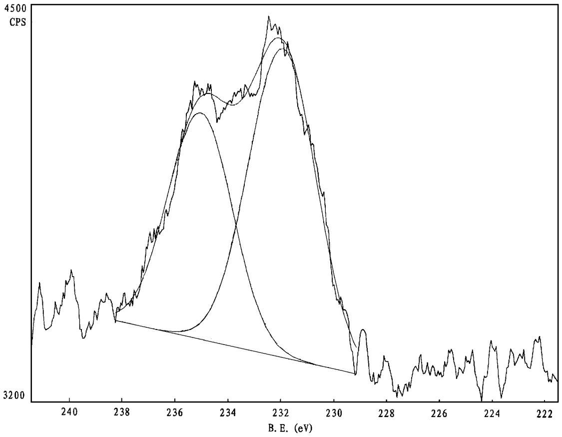

Fig. 6. XPS for Mo in compound **1**.

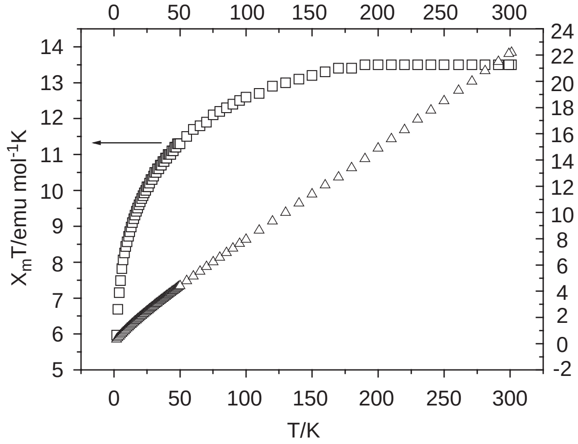

Fig. 7. The plot of χ_m^T and χ_m^{-1} *vs.* T for compound **1**.

Table 3
Bond valence sums (Σs) for **1**

Atom	Σs	Atom	Σs	Atom	Σs	Atom	Σs	Atom	Σs
Mo(1)	5.22	P(1)	4.92	O(6)	1.86	O(15)	1.88	O(24)	1.80
Mo(2)	5.25	P(2)	5.00	O(7)	1.67	O(16)	1.92	O(25)	1.81
Mo(3)	5.20	P(3)	4.97	O(8)	1.96	O(17)	1.78	O(26)	1.04
Mo(4)	5.26	P(4)	5.09	O(9)	1.73	O(18)	1.86	O(27)	1.81
Mo(5)	5.24	O(1)	1.33	O(10)	1.69	O(19)	0.30	O(28)	1.89
Mo(6)	5.28	O(2)	1.86	O(11)	1.66	O(20)	1.83	O(29)	1.80
Co(1)	1.79	O(3)	1.97	O(12)	1.67	O(21)	1.97	O(30)	1.96
Co(2)	1.95	O(4)	1.95	O(13)	1.03	O(22)	1.79	O(31)	1.21
Co(3)	1.92	O(5)	1.74	O(14)	2.06	O(23)	1.85	O(32)	1.72

equal to that expected for the total value of four uncoupled $S = 3/2$ spin for Co^{2+} atoms ($13.45\,\mathrm{emu\,K\,mol^{-1}}$, $\mu_{\mathrm{eff}} = 10.38\,\mu_{\mathrm{B}}$, assuming $g = 2.68$ for Co^{2+}) [27]. Although valence states of Mo atoms are $+5$, but owing to formation of Mo–Mo metal bonds thus they have no contribution to magnetism of compound **1**. The magnetic data of sample **1** obeys Curie–Weiss law [$\chi_{\mathrm{m}} = C/(T-\theta)$] and gives value of Curie constant $C = 14.04\,\mathrm{emu\,K\,mol^{-1}}$ and Curie–Weiss constant $\theta = -9.6\,\mathrm{K}$, showing characteristic of an antiferromagnetic interaction.

4. Conclusion

A new cobalt phosphomolybdate: $(NH_3CH_2CH_2NH_3)(NH_3CH_2CH_2NH_2)_3Na_3[Co_4Mo_{12}O_{24}(OH)_6(H_2O)_2(HPO_4)_2(PO_4)_6] \cdot 8H_2O$ **1** has been hydrothermally synthesized. It possesses novel three-dimensional framework constructed of building block $[Mo_6P_4]$ units connected via both tetrahedrally and octahedrally coordinated Co atoms, in which intercrossing channels having different pore sizes are included. Compound **1** exhibits antiferromagnetic coupling interactions. It is likely that many other double transition metal phosphates with same structure as **1** can also be hydrothermally synthesized.

Acknowledgments

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References

[1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Canon, E.M. Flanigen, J. Am. Chem. Soc. 104 (1982) 1146.

[2] J.M. Thomas, Angew. Chem. Int. Ed. Engl. 33 (1994) 913.

[3] M.E. Davis, Microporous Mesoporous Mater. 21 (1998) 173.

[4] F.S. Xiao, S. Qiu, Q.W. Pang, R. Xu, Adv. Mater. 11 (1999) 1091.

[5] C.N.R. Rao, S. Natarajan, A. Choudhury, S. Neeraj, A.A. Ayi, Acc. Chem. Res. 34 (2001) 80.

[6] B. Zhang, A. Clearfield, J. Am. Chem. Soc. 119 (1997) 2751.

[7] A.K. Cheetham, G. Ferey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268.

[8] J.Y. Ying, M.S. Wong, Angew. Chem. Int. Ed. 38 (1999) 56.

[9] R. Haushalter, L. Mundi, Chem. Mater. 4 (1992) 31.

[10] L.A. Muhdi, R.C. Haushalter, Inorg. Chem. 32 (1993) 1579.

[11] J.J. Lu, Y. Xu, N.K. Goh, L.S. Chia, Chem. Commun. (1998) 1709.

[12] C.L. Pan, J.Q. Xu, Y. Sun, D.Q. Chu, L. Ye, Z.L. Lü, T.G. Wang, Inorg. Chem. Commun. 6 (2003) 233.

[13] Y. Lu, R. Haushalter, J. Zubieta, Inorg. Chim. Acta 268 (1998) 257.

[14] V. Soghomonian, Q. Chen, R. Haushalter, J. Zubieta, Chem. Mater. 5 (1993) 1595.

[15] J. Chen, R. Jones, S. Natarajan, M. Hursthouse, J. Thomas, Angew. Chem., Int. Ed. Engl. 33 (1994) 639.

[16] P. Feng, X. Bu, S. Tolbert, G. Stucky, J. Am. Chem. Soc. 119 (1997) 2497.

[17] Y. Zhang, R. Haushalter, A. Clearfield, Inorg. Chem. 35 (1996) 4950.

[18] W. Harrison, L. Dussack, A. Jacobson, Inorg. Chem. 33 (1994) 6043.

[19] L.A. Muhdi, R.C. Haushalter, Inorg. Chem. 31 (1992) 3050.

[20] L. Xu, Y.Q. Sun, E.B. Wang, J. Solid State Chem. 146 (1999) 533.

[21] M. Yuan, E.B. Wang, Inorg. Chem. Commun. 5 (2002) 505.

[22] Y. Xu, B. Zhang, N.K. Goh, L.S. Chia, Inorg. Chim. Acta 282 (1998) 10.

[23] P. Lightfoot, D. Masson, Acta Crystallogr C 52 (1996) 1077.

[24] P. Lightfoot, D. Masson, Mater. Res. Bull. 30 (1995) 1005.

[25] Y.S. Zhou, L.J. Zhang, X.Z. You, S. Natarajan, Solid State Chem. 159 (2001) 209.

[26] L.D. Brown, D. Altermatt, Acta. Crystallogr. B 41 (1985) 244.

[27] C.M. Liu, D.Q. Zhang, M. Xiong, D.-B. Zhu, Chem. Commun. (2002) 1416.