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# Synthesis, structure and magnetic properties of a two-dimensional polymer based on sandwich-type tetra-cobalt(II)-substituted polyoxotungstate anions and 1-D potassium-chains

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A 2-D coordination polymer,  $(C_7N_4H_{16})_2\{NH(CH_3)_3\}[\{K(H_2O)\}_4Na(H_2O)_5\{Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2\}] \cdot 2H_2O$  (**1**), was hydrothermally synthesized and structurally characterized by IR spectroscopy, elemental analysis, X-ray powder diffraction, and X-ray single-crystal crystallography. Crystal structure analysis shows a triclinic space group  $P\bar{1}$  with  $a = 12.4677(8) \text{ \AA}$ ,  $b = 12.5054(8) \text{ \AA}$ ,  $c = 18.5745(1) \text{ \AA}$ ,  $\alpha = 73.3220(1)^\circ$ ,  $\beta = 87.1890(1)^\circ$ ,  $\gamma = 62.2710(1)^\circ$ , and  $V = 2443.4(3) \text{ \AA}^3$ . Sandwich-type tetra-cobalt(II)-substituted  $[Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-}$  of **1** consists of two trivalent Keggin  $[B-\alpha-PW_9O_{34}]^{9-}$  moieties and a rhomb-like  $Co_4O_{16}$  unit. Each sandwich-type polyoxotungstate subunit connects 12 K(1) and K(2) centers from two adjacent 1-D K-chain units resulting in an interesting 2-D layer framework. Magnetic properties of **1** have been investigated.

*Keywords:* Polyoxotungstate; Sandwich type; Crystal structure; Magnetic properties

## 1. Introduction

Transition-metal-substituted polyoxometalates (TMSPs) as an important subfamily in polyoxometalates (POMs) chemistry have attracted interest in solid acid catalysis, medicine, magnetism, and materials science due to enormous structural variety and range of physical and chemical properties [1–7]. Since the first tetra- $Co^{II}$  substituted inorganic sandwich-type POM  $[Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-}$  was reported by Weakley *et al.* in 1973, sandwich-type polyoxotungstates (POTs) have developed as one of the most important domains in the field of TMSPs [8]. A number of sandwich-type POTs constructed from trivalent Keggin  $(B-\alpha-XW_9O_{34})^{n-}$  ( $X = P^V, As^V, Si^{IV}, Ge^{IV}$ ) or Dawson  $(\alpha-X_2W_{15}O_{56})^{12-}$  ( $X = P^V, As^V$ ) fragments and transition-metal clusters of two to eight nuclearity have been reported [9–14]. Sandwich-type tetra-metal-substituted POT-based complexes exhibit a variety of structures, such as 0-D, 1-D chain-like, and 2-D layer frameworks [12–17]. Among 2-D layer frameworks, most were obtained by coordination interactions between sandwich-type tetra-metal-substituted polyoxoanions and transition-metal coordination cations, such as  $[Cu(dien)$

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(H<sub>2</sub>O)<sub>2</sub>{[Cu(dien)(H<sub>2</sub>O)]<sub>2</sub>[Cu(dien)(H<sub>2</sub>O)]<sub>2</sub>[Cu<sub>4</sub>(SiW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]}·5H<sub>2</sub>O (dien = diethylenetriamine) [14], (NH<sub>4</sub>)<sub>2</sub>[Ni<sub>4</sub>(enMe)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>Ni<sub>4</sub>(enMe)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]·9H<sub>2</sub>O, and [DMAH]<sub>4</sub>{[Mn(DMF)<sub>4</sub>]<sub>2</sub>[Mn<sub>4</sub>(DMF)<sub>2</sub>(*α*-B-HPW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]} (DMA = dimethylamine, DMF = *N,N*-dimethylformamide) [15, 17]. Reports on 2-D structures in which sandwich-type tetra-metal-substituted polyoxoanions interlink through alkali metal complexes are rare [13, 16, 18, 19].

In 2007, Cronin *et al.* described the first 2-D hybrid network constructed from sandwich-type [Mn<sub>4</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> clusters and sodium [13]. In 2008, Dolbecq *et al.* reported a 2-D plane by connection of [Fe<sup>III</sup><sub>4</sub>(H<sub>2</sub>O)<sub>10</sub>(B-*α*-SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>6-</sup> polyoxoanions and sodium cations [16], and Wang *et al.* prepared four new POT-based 2-D frameworks consisting of sandwich-type tetra-metal-substituted polyoxoanions and potassium or sodium cations [18]. Peng *et al.* synthesized a 2-D layer structure through interconnection of sandwich-type [Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> polyoxoanions, [Co(en)<sub>2</sub>]<sup>2+</sup> and Na<sup>+</sup> ions [19]. As a part of our studies on POM-based compounds [20–22], herein, we report the hydrothermal synthesis and crystal structure of a 2-D coordination polymer, (C<sub>7</sub>N<sub>4</sub>H<sub>16</sub>)<sub>2</sub>{NH(CH<sub>3</sub>)<sub>3</sub>}{[K(H<sub>2</sub>O)]<sub>4</sub>Na(H<sub>2</sub>O)<sub>5</sub>{Co<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(*α*-B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>}}·2H<sub>2</sub>O (**1**), in which the sandwich-type tetra-Co<sup>II</sup>-substituted POTs are bridged by 1-D potassium chains to form a 2-D framework. The temperature-dependent magnetic susceptibility for **1** was investigated from 2 to 300 K.

## 2. Experimental

### 2.1. Materials and physical measurements

All chemicals were of reagent grade and used without purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer from 4000 to 400 cm<sup>-1</sup>. Variable-temperature magnetic susceptibility data were measured with a quantum design MPMS7 SQUID magnetometer; experimental data were corrected for diamagnetism of the constituent atoms estimated from Pascal's constants. X-ray powder diffraction (XRPD) patterns were recorded on a D/max- $\gamma$  rotating anode X-ray diffractometer with Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ).

### 2.2. Synthesis of polymer **1**

A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.177 g, 0.744 mmol), Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (0.822 g, 2.49 mmol), NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (0.078 g, 0.50 mmol), hexamethylenetetramine (0.525 g, 3.75 mmol), and distilled water (20 mL) was stirred for 30 min at room temperature, then sealed in a 30 mL Teflon-lined stainless autoclave and heated to 150 °C for four days. The resulting purple red block crystals of **1** were filtered off, washed with water, and dried at room temperature. Yield 28% (based on Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O). Anal. Calcd for C<sub>17</sub>H<sub>64</sub>Co<sub>4</sub>K<sub>4</sub>NaN<sub>9</sub>O<sub>81</sub>P<sub>2</sub>W<sub>18</sub> (%): C, 3.72; H, 1.18; N, 2.30. Found (%): C, 3.84; H, 1.09; N, 2.42. IR data (KBr pellet, cm<sup>-1</sup>): 3447(w), 1630(m), 1565(s), 1263(m), 1248(m), 1151(m), 1099(m), 1033(s), 937(vs), 881(s), 742(s), and 486(w).

### 2.3. X-ray crystallographic studies

A suitable crystal (0.24 × 0.20 × 0.18 mm<sup>3</sup>) was chosen for crystallographic study and then mounted on a Bruker SMART APEX CCD diffractometer with  $\omega$  and  $\phi$  scan mode in the

range of  $1.93 < \theta < 25.00^\circ$ . All diffraction measurements were performed at room temperature using graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). A total of 12,684 (8448 independent,  $R_{\text{int}} = 0.0577$ ) reflections were measured. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using SHELXL 97 [23]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques, and all hydrogens were geometrically fixed and allowed to ride on the parent atoms to which they were attached. A summary of the key crystallographic information is given in table 1. Selected bond lengths and angles for **1** are listed in tables 2 and 3.

### 3. Results and discussion

#### 3.1. The IR spectrum of **1**

The IR spectrum of **1** exhibits characteristic vibration patterns derived from the Keggin-type heteropolyanion from 1100 to  $700 \text{ cm}^{-1}$ . The band at  $1033 \text{ cm}^{-1}$  shows the characteristic of stretching frequency of  $\text{P-O}_a$ ; bands at 881, 742, and  $937 \text{ cm}^{-1}$  should be attributed to  $\nu(\text{W-O}_b)$ ,  $\nu(\text{W-O}_c)$  and  $\nu(\text{W-O}_t)$ , respectively. Comparing IR spectra of  $\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 9\text{H}_2\text{O}$  and **1**, the vibrational bands of the  $\text{W-O}_b$ ,  $\text{W-O}_c$ , and  $\text{W-O}_t$  bonds are red-shifted from 884, 778, and  $939 \text{ cm}^{-1}$  to 881, 742, and  $937 \text{ cm}^{-1}$ , respectively [24]. In addition, absorptions at 1630, 1565, 1263, 1248, and  $1151 \text{ cm}^{-1}$  are assigned to stretching vibrations characteristic of trimethylamine and *N*-methyl-hexamethylenetetramine molecules. Vibration at  $3446 \text{ cm}^{-1}$  suggests the presence of water. The IR spectrum is consistent with that of the single-crystal structural analysis.

Table 1. Crystallographic data and structure refinement for **1**.

Crystal data	<b>1</b>
Formula	$\text{C}_{17}\text{H}_{39}\text{Co}_4\text{K}_4\text{NaN}_9\text{O}_{81}\text{P}_2\text{W}_{18}$
Formula weight	5451.92
Crystal group	Triclinic
Space group	<i>P-1</i>
Unit cell dimensions ( $\text{\AA}$ , $^\circ$ )	
<i>a</i>	12.4677(8)
<i>b</i>	12.5054(8)
<i>c</i>	18.5745(1)
$\alpha$	73.3220(1)
$\beta$	87.1890(1)
$\gamma$	62.2710(1)
Volume ( $\text{\AA}^3$ ), <i>Z</i>	2443.4(3), 1
$D_c$ ( $\text{g cm}^{-3}$ )	3.705
$F(000)$	2409
Radiation ( $\text{\AA}$ )	0.71073
Theta min–max ( $^\circ$ )	1.93–25.00
Tot., Uniq. Data, $R(\text{int})$	12,684, 8448, 0.0577
Observed data [ $I > 2.0 \text{ sigma}(I)$ ]	7065
$R_{\text{ref}}$ , $N_{\text{par}}$	8448, 658
$R$ , $wR_2$ , $S$	0.0422, 0.1080, 1.020
Min. and max. resd. dens. [ $\text{e \AA}^{-3}$ ]	–1.094, 2.937

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

P(1)–O(34)	1.524(8)	K(1)–O(10E)	2.795(9)
P(1)–O(33)	1.546(8)	K(1)–O(2W)	2.819(12)
P(1)–O(31)	1.550(8)	K(1)–O(2WC)	2.865(13)
P(1)–O(32)	1.557(8)	K(1)–O(6F)	2.935(11)
Co(1)–O(10)	2.042(9)	K(1)–O(2E)	3.261(11)
Co(1)–O(30)	2.050(9)	K(2)–O(4)	2.703(9)
Co(1)–O(9W)	2.101(9)	K(2)–O(30A)	2.729(10)
Co(1)–O(13A)	2.109(9)	K(2)–O(1W)	2.791(14)
Co(1)–O(28A)	2.123(8)	K(2)–O(2J)	2.842(10)
Co(1)–O(34)	2.211(7)	K(2)–O(7D)	2.860(11)
Co(2)–O(23A)	2.008(9)	K(2)–O(1WB)	3.092(16)
Co(2)–O(12)	2.045(9)	K(2)–O(1B)	3.318(12)
Co(2)–O(28A)	2.059(8)	Na(1)–O(3W)	2.20(3)
Co(2)–O(13)	2.069(8)	Na(1)–O(5W)	2.34(3)
Co(2)–O(34A)	2.258(8)	Na(1)–O(7W)	2.375(16)
Co(2)–O(34)	2.282(8)	Na(1)–O(4W)	2.40(3)
K(1)–O(1)	2.690(10)	Na(1)–O(6W)	2.59(3)
K(1)–O(9D)	2.780(9)		

Note: Symmetry codes: A  $-x, -y+2, -z$ ; B  $-x, -y+3, -z$ ; C  $-x+1, -y+3, -z$ ; D  $x, y+1, z$ ; E  $-x+1, -y+2, -z$ ; F  $x+1, y, z$ ; J  $x-1, y+1, z$ .

### 3.2. Description of the crystal structure of **1**

Single-crystal structural analysis reveals that **1** crystallizes in the triclinic space group  $P\bar{1}$ . The molecular structure unit of **1** contains a sandwich-type tetra-metal-substituted POT  $[\{\text{K}(\text{H}_2\text{O})\}_4\text{Na}(\text{H}_2\text{O})_5\{\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2\}]^{5-}$ , one protonated trimethylamine, two protonated *N*-methyl-hexamethylenetetramine, and two lattice waters (figure 1). The trimethylamine and *N*-methyl-hexamethylenetetramine are generated from hexamethylenetetramine in the process of hydrothermal synthesis. The  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$  of **1** contains two trivalent Keggin  $[\text{B}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  moieties linked via a rhomb-like  $\text{Co}_4\text{O}_{16}$  unit resulting in a centrosymmetric arrangement ( $C_{2h}$  symmetry). As that found in  $\text{Co}_4\text{O}_{16}$  cluster structure in  $\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$ , O(34) of  $\text{PO}_4$  links to three Co ions on each side of the central  $\text{Co}_4$  plane, leading to a central unit of four edge-sharing  $\text{CoO}_6$  octahedra which form a regular rhomb-like cluster [25]. There are two crystallographically independent Co(II) centers and both with a six-coordinate environment. Co(1) is bonded to three oxygens O(10), O(30), and O(34) of  $[\text{B}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  on one side of the central  $\text{Co}_4$  plane, two oxygens O(13A) and O(28A) on the other side, and one oxygen O(9W) of water (symmetry code: A  $-x, 2-y, -z$ ). Co(2) is coordinated to six oxygens O(12), O(13), O(23A), O(28A), O(34), and O(34A) of two  $[\text{B}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  anions on two sides of the central  $\text{Co}_4$  plane. Co(1) and Co(2) are in a highly distorted octahedral coordination environment with Co(1)–O and Co(2)–O distances of 2.042(9)–2.211(7) Å and 2.008(9)–2.282(8) Å, respectively. The Co···Co separations in the rhomb-like  $\text{Co}_4\text{O}_{16}$  group are Co(1)···Co(1A), 5.53 Å; Co(2)···Co(2A), 3.36 Å, Co(1)···Co(2), 3.24 Å, and Co(1)···Co(2A), 3.23 Å (figure 2).

The asymmetric unit of **1** contains two supporting potassiums. Each K is seven-coordinate (figure 3) with five coordination sites occupied by five oxygens [K(1): O(1), O(2), O(6), O(9), and O(10); K(2): O(1), O(2), O(4), O(7), and O(30)] which belong to three adjacent sandwich-type polyoxoanions, the other two coordinate two waters [K(1), O(2W), and O(2WC); K(2), O(1W), and O(1WB)] (symmetry codes: B,  $-x, 3-y, -z$ ; C,  $1-x, 3-y, -z$ ). Adjacent K(1) and K(2) are linked together through two oxygens O(1) and O(2) from

Table 3. Selected bond angles (°) for **1**.

O(34)–P(1)–O(33)	110.6(5)	O(9D)–K(1)–O(6F)	86.4(3)
O(34)–P(1)–O(31)	110.7(5)	O(10B)–K(1)–O(6F)	90.4(3)
O(33)–P(1)–O(31)	108.8(5)	O(2W)–K(1)–O(6F)	153.4(3)
O(34)–P(1)–O(32)	111.4(5)	O(2WE)–K(1)–O(6F)	84.7(3)
O(33)–P(1)–O(32)	107.2(5)	O(1)–K(1)–O(2B)	75.9(3)
O(31)–P(1)–O(32)	108.0(5)	O(9D)–K(1)–O(2B)	127.7(3)
O(10)–Co(1)–O(30)	92.8(4)	O(10B)–K(1)–O(2B)	53.3(2)
O(10)–Co(1)–O(9W)	89.5(4)	O(2W)–K(1)–O(2B)	68.1(3)
O(30)–Co(1)–O(9W)	89.1(4)	O(2WE)–K(1)–O(2B)	117.0(3)
O(10)–Co(1)–O(13A)	91.5(3)	O(6F)–K(1)–O(2B)	138.0(3)
O(9)–Co(1)–O(13A)	170.9(3)	O(4)–K(2)–O(30B)	172.9(3)
O(34)–Co(1)–O(13A)	99.0(4)	O(4)–K(2)–O(1W)	75.8(3)
O(10)–Co(1)–O(28A)	172.3(3)	O(30B)–K(2)–O(1W)	106.2(4)
O(30)–Co(1)–O(28A)	91.1(3)	O(4)–K(2)–O(2J)	90.9(3)
O(9W)–Co(1)–O(28A)	97.2(4)	O(30B)–K(2)–O(2J)	94.7(3)
O(13)–Co(1)–O(28A)	83.7(3)	O(1W)–K(2)–O(2J)	110.3(4)
O(10)–Co(1)–O(34)	90.4(3)	O(4)–K(2)–O(7D)	81.3(3)
O(30)–Co(1)–O(9W)	89.1(3)	O(30B)–K(2)–O(7D)	94.8(3)
O(9W)–Co(1)–O(34)	178.2(4)	O(1W)–K(2)–O(7D)	152.1(4)
O(13A)–Co(1)–O(34)	82.8(3)	O(2K)–K(2)–O(7D)	85.4(3)
O(28A)–Co(1)–O(34)	83.0(3)	O(4)–K(2)–O(1WB)	69.4(3)
O(23A)–Co(2)–O(12)	95.6(4)	O(30B)–K(2)–O(1WB)	104.8(3)
O(23A)–Co(2)–O(28A)	98.2(3)	O(1W)–K(2)–O(1WB)	68.1(4)
O(12)–Co(2)–O(28A)	91.2(4)	O(2K)–K(2)–O(1WB)	160.2(3)
O(23A)–Co(2)–O(13)	92.3(3)	O(7D)–K(2)–O(1WB)	89.2(3)
O(12)–Co(2)–O(13)	98.3(4)	O(4)–K(2)–O(1B)	133.5(3)
O(28A)–Co(2)–O(13)	165.1(3)	O(30B)–K(2)–O(1B)	52.8(3)
O(23A)–Co(2)–O(34A)	90.2(3)	O(1W)–K(2)–O(1B)	70.0(4)
O(12)–Co(2)–O(34A)	174.1(3)	O(2J)–K(2)–O(1B)	73.1(3)
O(28A)–Co(2)–O(34A)	86.8(3)	O(7D)–K(2)–O(1B)	137.8(3)
O(13)–Co(2)–O(34A)	82.6(3)	O(1WB)–K(2)–O(1B)	122.0(3)
O(23A)–Co(2)–O(34)	174.7(3)	O(3W)–Na(1)–O(5W)	171.1(10)
O(12)–Co(2)–O(34)	89.6(3)	O(3W)–Na(1)–O(7W)	87.1(7)
O(28A)–Co(2)–O(34)	82.7(3)	O(5W)–Na(1)–O(7W)	84.3(8)
O(13)–Co(2)–O(34)	85.9(3)	O(3W)–Na(1)–O(4W)	85.4(10)
O(34A)–Co(2)–O(34)	84.6(3)	O(5W)–Na(1)–O(4W)	97.1(11)
O(1)–K(1)–O(9D)	82.2(3)	O(7W)–Na(1)–O(4W)	91.0(8)
O(1)–K(1)–O(10B)	93.1(3)	O(3W)–Na(1)–O(3)	84.8(7)
O(9D)–K(1)–O(10B)	174.4(3)	O(5W)–Na(1)–O(3)	103.3(8)
O(1)–K(1)–O(2W)	108.3(4)	O(7W)–Na(1)–O(3)	167.3(7)
O(9D)–K(1)–O(2W)	75.0(3)	O(4W)–Na(1)–O(3)	98.0(8)
O(10B)–K(1)–O(2W)	109.5(3)	O(3W)–Na(1)–O(6W)	87.9(9)
O(1)–K(1)–O(2WC)	166.6(4)	O(5W)–Na(1)–O(6W)	90.0(10)
O(9D)–K(1)–O(2WC)	86.6(3)	O(7W)–Na(1)–O(6W)	91.3(6)
O(10B)–K(1)–O(2WC)	97.7(3)	O(4W)–Na(1)–O(6W)	172.7(10)
O(2W)–K(1)–O(2WC)	75.5(4)	O(3)–Na(1)–O(6W)	78.8(6)
O(1)–K(1)–O(6F)	87.3(3)		

Note: Symmetry codes: A  $-x, -y+2, -z$ ; B  $-x, -y+3, -z$ ; C  $-x+1, -y+3, -z$ ; D  $x, y+1, z$ ; E  $-x+1, -y+2, -z$ ; F  $x+1, y, z$ ; J  $x-1, y+1, z$ .

two sandwich-type polyoxoanion subunits with K(1)··K(2) separation of 4.46 Å, and adjacent K(1) ions are double-bridged by two oxygens of two symmetrical waters with K(1)··K(1) distance of 4.49 Å. Two adjacent K(2) ions are also joined by two symmetrical O(1W) with K(2)··K(2) distance of 4.87 Å. The K(1)–O and K(2)–O distances are 2.690(10)–3.261(11) Å and 2.703(9)–3.318(12) Å, respectively. Therefore, adjacent K ions are linked through three kinds of bridging interactions to form a 1-D chain (K-chain). Each sandwich-type  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$  subunit connects 12 K(1) and K(2) centers from two adjacent 1-D K-chains resulting in a 2-D layer framework (figure 4). Each





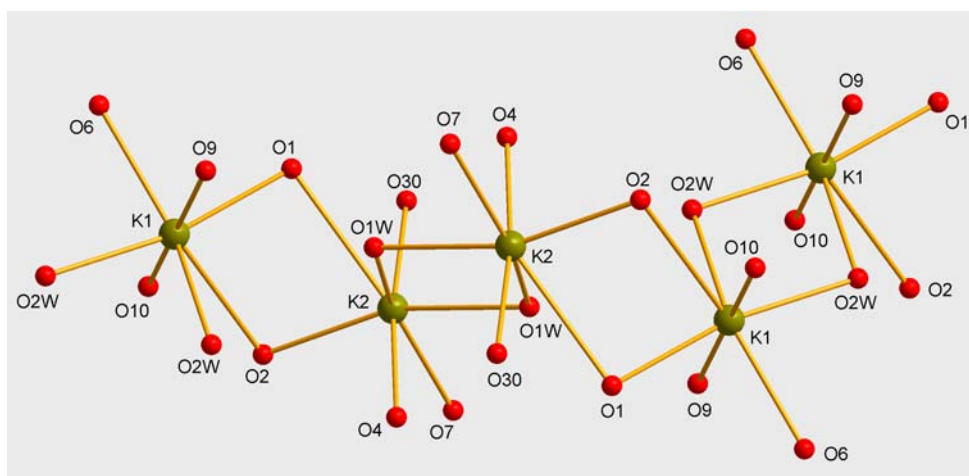


Figure 3. The presentation of 1-D K-chain in **1**.

$(B-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$  to form a 3-D supramolecular structure (figure 5). C(2), C(3), C(6), and C(7) of each *N*-methyl-hexamethylenetetramine form six C–H···O hydrogen bonds with six oxygens, O(17), O(21), O(24), O(8), O(20), and O(14), of three sandwich-type polyoxoanion subunits (table 4).

### 3.3. X-ray powder diffraction

The stability of this network was studied by XRPD. As shown in figure 6, the experimental XRPD pattern of the bulk product of **1** is in good agreement with the simulated XRPD pattern from single-crystal X-ray diffraction, indicating phase purity of the sample. The

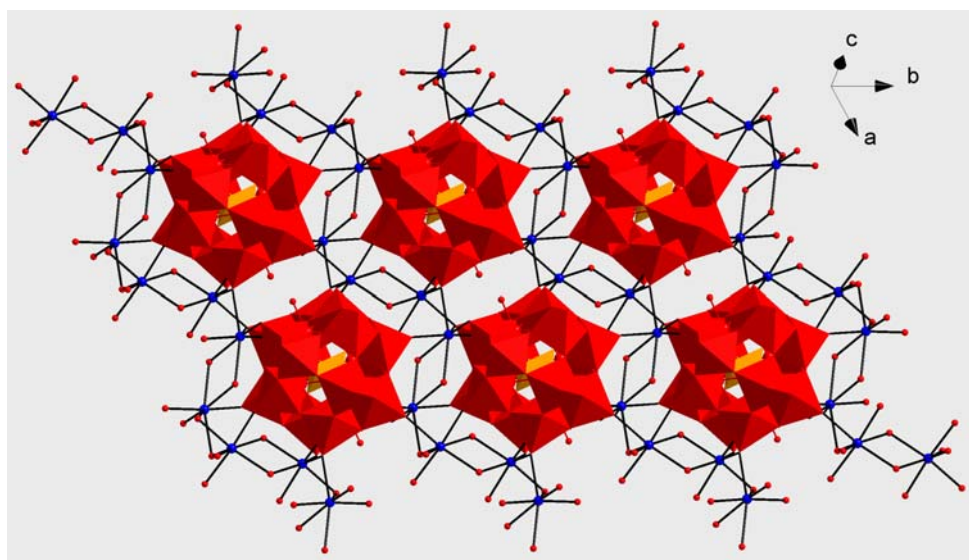


Figure 4. The 2-D framework of **1**. All the sodium cations, organic, and water molecules are omitted for clarity.

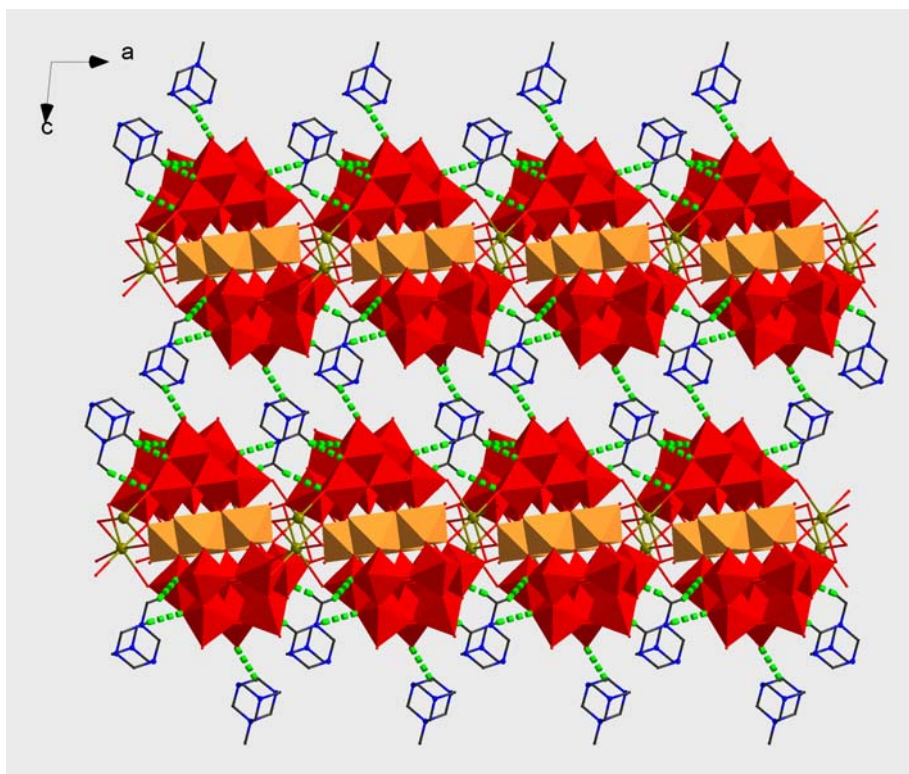


Figure 5. View of 3-D network in **1** with C–H···O hydrogen bonds as dashed lines. All sodium cations, trimethylamine, and water molecules are omitted for clarity.

intensity difference between experimental and simulated XRPD patterns is due to the variation in preferred orientation of the powder sample during collection of the experimental XRPD.

### 3.4. Magnetic properties

The temperature-dependent magnetic susceptibility for **1** was performed on polycrystalline sample from 2 to 300 K under an external magnetic field of 1 T. The temperature dependences of  $\chi_m$  and  $\chi_m T$  are shown in figure 7. The  $\chi_m$  value slowly increases from

Table 4. Hydrogen bonding interactions (Å, °) in **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)	Symmetry transformation for A
C(2)–H(2B)···O(17)	0.97	2.37	3.33(2)	174	$1+x, -1+y, z$
C(3)–H(3B)···O(21)	0.97	2.36	3.31(2)	166	
C(3)–H(3B)···O(24)	0.97	2.53	3.06(2)	114	
C(6)–H(6B)···O(8)	0.97	2.49	3.10(2)	120	$1-x, 1-y, 1-z$
C(7)···H(7B)···O(20)	0.96	2.58	3.42(2)	145	
C(7)···H(7C)···O(14)	0.96	2.30	3.19(2)	153	$1+x, -1+y, z$

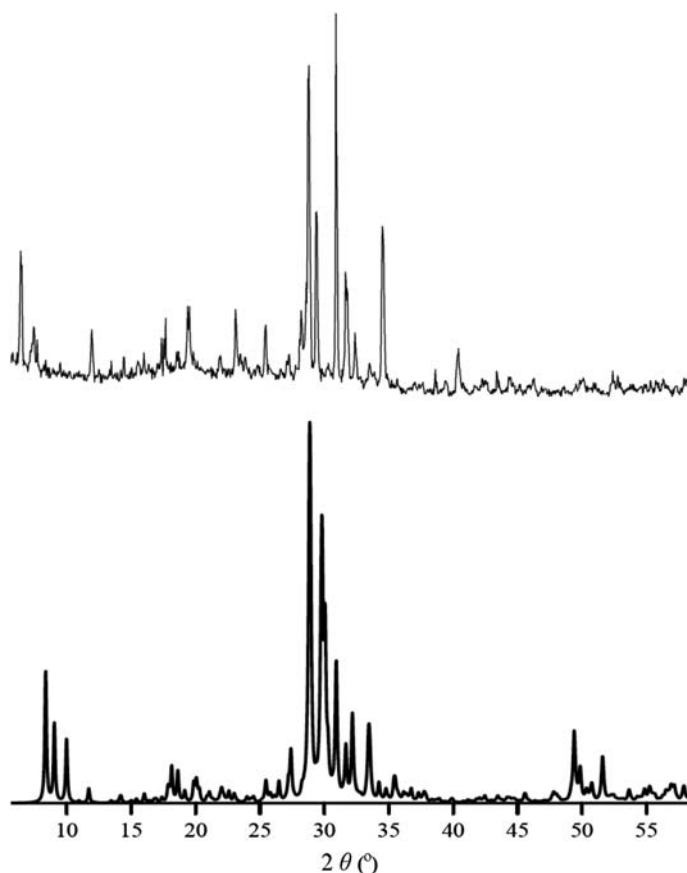


Figure 6. The XRPD pattern of **1** (top) and its calculated pattern based on single-crystal data.

0.027 emu mol<sup>-1</sup> at 300 K to 0.225 emu mol<sup>-1</sup> at 28 K and then rapidly reaches 3.711 emu mol<sup>-1</sup> at 2 K. The  $\chi_m T$  product is 7.96 emu K mol<sup>-1</sup> at 300 K, which is slightly larger than the spin-only value (7.50 emu K mol<sup>-1</sup>) expected for four non-interacting high-spin Co<sup>II</sup> ions ( $S_i = 3/2$ ) considering  $g = 2.0$ . The magnetic behavior indicates the presence of orbital contribution arising from the ground state triplet  $^4T_1$  of each Co<sup>II</sup>, which is known to be significant in an octahedral field [26, 27]. Upon cooling,  $\chi_m T$  gradually decreases to a minimum of 6.564 emu K mol<sup>-1</sup> at 34 K and then increases to 8.02 emu K mol<sup>-1</sup> at 6.3 K before dropping sharply to 7.40 emu K mol<sup>-1</sup> at 2 K. The decrease at higher temperatures is due to the spin-orbit coupling of Co<sup>II</sup> ions and/or anti-ferromagnetic interactions, which is further confirmed by a negative Weiss constant  $\theta = -6.19$  K derived from fitting the Curie–Weiss law to the magnetic data between 52 and 300 K (figure 8). The maximum at lower temperatures implies that ferromagnetic interactions occur within the rhomb-like Co<sub>4</sub>O<sub>16</sub> cluster [28]. A sudden decrease of the  $\chi_m T$  value below 6.3 K may be ascribed to large anisotropy coupling of the Co<sup>II</sup> ions inside the Co<sub>4</sub>O<sub>16</sub> cluster and the presence of the zero-field splitting effects within the ground state [27, 29].

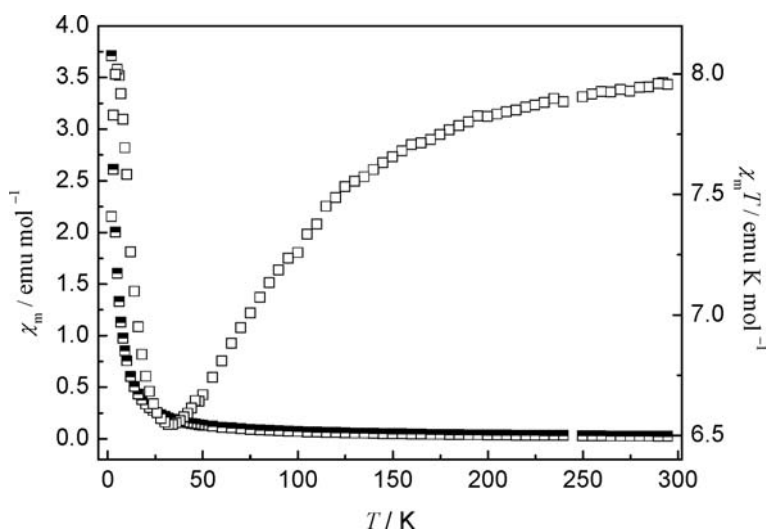


Figure 7. Temperature variation of the magnetic susceptibility of **1** as  $\chi_m$  and  $\chi_m T$  vs.  $T$  between 2 and 300 K.

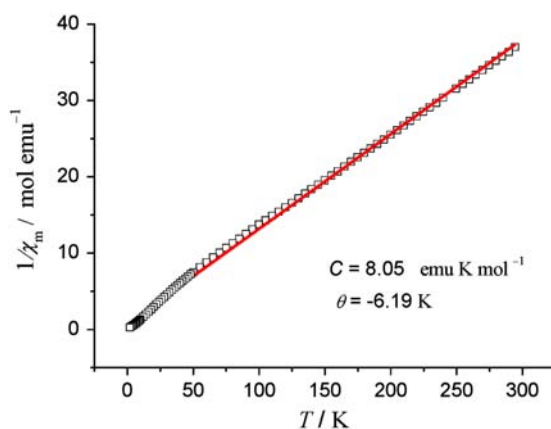


Figure 8. Temperature dependence of the inverse magnetic susceptibility for **1** between 52 and 300 K. Solid line is generated from the best fit by the Curie–Weiss expression.

#### 4. Conclusion

We have synthesized a new 2-D POT-based coordination polymer  $(C_7N_4H_{16})_2\{NH(CH_3)_3\}[\{K(H_2O)\}_4Na(H_2O)_5\{Co_4(H_2O)_2(\alpha-B-PW_9O_{34})_2\}]\cdot 2H_2O$  (**1**) under hydrothermal condition.  $[Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-}$  contains two trivacant Keggin  $[B-\alpha-PW_9O_{34}]^{9-}$  moieties and a rhomb-like  $Co_4O_{16}$  cluster, which is a classical structure exhibited in other tetrametal-substituted sandwich-type phosphotungstate compounds. The structure is different from that of reported 2-D sandwich-type tetra-metal-substituted polyoxoanion complexes interlinked through alkali metals, which are rare among compounds containing  $[B-\alpha-PW_9O_{34}]^{9-}$  [12–14], [19], [30–32]. Compounds in the literature [13, 16, 18, 19] form links resulting in 2-D structure of POT-alkali meta-POT. But in **1**, each  $[Co_4(H_2O)_2$

( $B\text{-}\alpha\text{-PW}_9\text{O}_{34}$ )<sub>2</sub>]<sup>10-</sup> unit is linked by two adjacent 1-D K-chains and generates an interesting 2-D layer structure. Temperature-dependent magnetic susceptibility was investigated from 2 to 300 K.

### Supplementary material

CCDC-862834 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +441223336033; or E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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