

# Hydrothermal synthesis and structural characterization of three inorganic–organic composite sandwich-type phosphotungstates

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## Abstract

Three inorganic–organic composite sandwich-type phosphotungstates  $[\text{Ni}(\text{tepa})(\text{H}_2\text{O})_4]\text{H}_2[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot 8\text{H}_2\text{O}$  (**1**),  $(\text{enH}_2)_3[\text{Ni}_2(\text{H}_2\text{O})_{10}][\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot \text{en} \cdot 8\text{H}_2\text{O}$  (**2**) and  $(\text{enH}_2)_{10}[\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]_2 \cdot 20\text{H}_2\text{O}$  (**3**) (tepa = tetraethylenepentamine and en = ethylenediamine) have been synthesized by the hydrothermal reaction of the trivacant Keggin polyoxoanion  $[\alpha\text{-A-PW}_9\text{O}_{34}]^{9-}$  with  $\text{Ni}^{2+}$  or  $\text{Mn}^{2+}$  ions in the presence of tepa or en and structurally characterized by IR spectra, elemental analysis, thermogravimetric analysis and variable temperature magnetic susceptibility. X-ray crystallographic analyses indicate that they all contain the classical tetra-*M* sandwiched polyoxoanions  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  ( $M = \text{Ni}^{2+}$  or  $\text{Mn}^{2+}$ ) and nickel-organamine cations or organamine cations work as the charge balance ions. The tetra-*M* clusters in **1**, **2** and **3** exhibit the familiar structural type of a  $\beta$ -junction at the sites of metal incorporation. The study of magnetic property of **1** is indicative of a typical ferromagnetic coupling between  $\text{Ni}^{2+}$  cations.

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**Keywords:** Polyoxometalates; Sandwich-type structure; Hydrothermal reaction; Trivacant Keggin derivatives

## 1. Introduction

Extensive interest in polyoxometalate (POMs) chemistry derives from potential applications in diverse fields including medicine, catalysis, analytical chemistry and magnetism [1–5]. Since the occurrence of the multitude of the lacunary POM precursors derived from the Keggin-type and Dawson-type polyoxoanions, the study and exploration on such lacunary polyoxotungstate (POT) derivatives have been an intensive focus in the chemistry of POMs [6–11]. Lacunary polyoxoanion precursors can act as multi-dentate inorganic ligands and allow the inclusion of the *d*-electron transition-metal (TM) cations, which lead to the rapidly growing class of the TM-substituted polyoxometalates (TMSPs) with a huge diversity of structures and properties.

The stable trivacant Keggin polyoxoanion  $[\alpha\text{-A-PW}_9\text{O}_{34}]^{9-}$  is one of the most extensively studied lacunary polyox-

oanions and often used as the reactant precursors in the preparation of novel and unique TMSPs [12–14]. In 1973, Weakley et al. [15] isolated the first sandwich-type phosphotungstate  $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  from the reaction of a 11:2:4:18 mixture of  $\text{HCl}/\text{Na}_2\text{HPO}_4/\text{Co}(\text{NO}_3)_2/\text{Na}_2\text{WO}_4$  at 90–100 °C and determined its structure by X-ray diffraction. Later, Finke et al. [16] synthesized the analogues  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  ( $M = \text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ) based on the  $[\beta\text{-PW}_9\text{O}_{34}]^{9-}$  starting material, which were structurally characterized by  $^{183}\text{W}$  NMR spectra. In 1986, Knoth and co-authors addressed a family of tri-*M* sandwiched phosphotungstates  $[\text{M}_3(\alpha\text{-A-PW}_9\text{O}_{34})_2]^{12-}$  ( $M = \text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$ ) and a tri- $\text{Ce}^{3+}$  sandwiched phosphotungstate  $[(\text{Ce}_3\text{O}_3 \cdot 2\text{H}_2\text{O})(\alpha\text{-A-PW}_9\text{O}_{34})_2]^{12-}$  by means of the  $[\alpha\text{-A-PW}_9\text{O}_{34}]^{9-}$  precursor [17]. Until 1993 and 1999, the  $[\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  and  $[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  phosphotungstates were still reported by Coronado et al. [18,19]. In 2004, Hill et al. [20] illustrated a novel double sandwich-type phosphotungstate  $[(\text{MnOH}_2)\text{Mn}_2\text{PW}_9\text{O}_{34}]_2(\text{PW}_6\text{O}_{26})^{17-}$ , which consists of

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two  $\alpha$ -B-[(Mn<sup>II</sup>OH<sub>2</sub>)Mn<sub>2</sub>PW<sub>9</sub>O<sub>34</sub>]<sup>3-</sup> units joined by a hexavacant [B-PW<sub>6</sub>O<sub>26</sub>]<sup>11-</sup> fragment to form a C-shaped TMSP. Recently, two inorganic–organic composite phosphotungstates [K = {Co(en)WO<sub>4</sub>}WO(H<sub>2</sub>O)( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>12-</sup> and [{Co(en)( $\mu$ -OH)<sub>2</sub>Co(en)}{PW<sub>10</sub>O<sub>37</sub>Co(en)}<sub>2</sub>]<sup>12-</sup> were separated by Pope et al. [21] by a one-pot reaction of [ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> with K[Co(en)(CO<sub>3</sub>)<sub>2</sub>] at 30–40 °C. All above-mentioned sandwich-type TMSPs were all prepared by the conventional aqueous solution method, however, the system containing trivacant Keggin [ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup>/TM ions in the participation of organic components remains less explored under hydrothermal conditions, which offers us great interest and opportunity. Recently, we have developed an effective synthetic strategy, i.e. using the lacunary sites of XW<sub>9</sub>O<sub>34</sub> (X = P/Si/Ge) fragments as the structure-directing agents to induce the formation of oligomers or large aggregates of TM clusters, as well as the multidentate amines as the structure-stabilizing agents to capture and stabilize TM oligomers formed *in situ*, further construct novel inorganic–organic composite POMs under hydrothermal conditions [22–26]. On the other hand, TM ions (Ni<sup>2+</sup> and Mn<sup>2+</sup>) were chosen ions here mainly because these TM ions have interesting magnetic properties and are easy to form unique magnetic clusters under the inducement of the lacunary sites of the XW<sub>9</sub>O<sub>34</sub>, as well as the rigidity of the non-magnetic polyoxoanion skeletons can impose their geometry to the magnetic TMSP, which provides an ideal model to study this kind of magnetic systems. Accordingly, we have successfully made a series of inorganic–organic composite TMSPs containing tetra-, hexa-, hepta-, octa- and even 13-nuclear TM clusters [22–26] and further studied the magnetic properties of some typical compounds [22,23,25]. As the continuance of our work, we report, here, three inorganic–organic composite sandwich-type phosphotungstates [Ni(tepa)(H<sub>2</sub>O)]<sub>4</sub>H<sub>2</sub>[Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] · 8H<sub>2</sub>O (**1**), (enH<sub>2</sub>)<sub>3</sub>[Ni<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>][Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] · en · 8H<sub>2</sub>O (**2**) and (enH<sub>2</sub>)<sub>10</sub>[Mn<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] · 20H<sub>2</sub>O (**3**) (tepa = tetraethylenepentamine and en = ethylenediamine).

## 2. Experimental

### 2.1. Preparation of compounds

The starting material Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O was prepared according to the literature [14] and confirmed by IR spectroscopy. Other reagents were of analytical or guaranteed quality and were used as received without further purification.

#### 2.1.1. Preparation of [Ni(tepa)(H<sub>2</sub>O)]<sub>4</sub>H<sub>2</sub>[Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] · 8H<sub>2</sub>O (**1**)

Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O (0.246 g, 0.094 mmol) and NiCl<sub>2</sub> · 2H<sub>2</sub>O (0.119 g, 0.50 mmol) were suspended in H<sub>2</sub>O (5 mL), to which tetraethylenepentamine (0.05 mL, 0.264 mmol) and acetic acid (0.10 mL, 1.748 mmol) were added under stirring. The resulting mixture was stirred for

5 h, sealed in a Teflon-lined stainless steel autoclave (20 mL), kept 160 °C for 5 days and then cooled to room temperature. Green prismatic crystals were filtered, washed with distilled water and dried in air at ambient temperature. Yield: ca. 35% (based on Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O). Anal. calcd. (%) for: C, 6.48; H, 1.94; N, 4.72. Found (%): C, 6.37; H, 1.90; N, 4.55.

#### 2.1.2. Preparation of (enH<sub>2</sub>)<sub>3</sub>[Ni<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>][Ni<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] · en · 8H<sub>2</sub>O (**2**)

Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O (0.246 g, 0.094 mmol) and NiCl<sub>2</sub> · 2H<sub>2</sub>O (0.237 g, 0.10 mmol) were suspended in H<sub>2</sub>O (8 mL), to which ethylenediamine (0.05 mL, 0.740 mmol) and 2,3-pyridinedicarboxylic acid (0.084 g, 0.50 mmol) were added under stirring. The resulting mixture was stirred for 2.5 h, sealed in a Teflon-lined stainless steel autoclave (20 mL), kept 150 °C for 5 days and then cooled to room temperature. Olivine sheet crystals were filtered, washed with distilled water and dried in air at ambient temperature. Yield: ca. 22% (based on Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O). Anal. calcd. (%) for: C, 1.77; H, 1.45; N, 2.07. Found (%): C, 1.57; H, 1.64; N, 1.98.

#### 2.1.3. Preparation of (enH<sub>2</sub>)<sub>10</sub>[Mn<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>( $\alpha$ -B-PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] · 20H<sub>2</sub>O (**3**)

A mixture of Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O (0.123 g, 0.047 mmol) and MnCl<sub>2</sub> · 4H<sub>2</sub>O (0.099 g, 0.50 mmol) was suspended in H<sub>2</sub>O (10 mL) and ethylenediamine (0.10 mL, 1.480 mmol), and then was adjusted to pH = 5.0 using acetic acid, and stirred for 4.5 h, sealed in a Teflon-lined stainless steel autoclave (20 mL), kept 80 °C for 5 days and then cooled to room temperature. Yellow needle crystals were filtered, washed with distilled water and dried in air at ambient temperature. Yield: ca. 10% (based on Na<sub>9</sub>[ $\alpha$ -A-PW<sub>9</sub>O<sub>34</sub>] · 7H<sub>2</sub>O). Anal. calcd. (%) for: C, 2.31; H, 1.43; N, 2.69. Found (%): C, 2.43; H, 1.56; N, 2.80.

### 2.2. Physical measurements

The crystal structures of **1**, **2** and **3** were determined from X-ray single-crystal diffraction data. Intensity data were collected with a Rigaku Mercury 70 CCD diffractometer for **1** and **3** and a Rigaku Saturn 70 CCD diffractometer for **2** using graphite monochromatized MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293(2) K. Their structures were solved by direct methods and refined by the full-matrix least-squares method on  $F^2$  using SHELXL-97 [27]. Intensity data were corrected for Lorentz and polarization effects as well as for an empirical absorption. Their weighting schemes used were:  $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ,  $P = (F_o^2 + 2F_c^2)/3$ , where  $x = 0.0438$ ,  $y = 0$  for **1**,  $x = 0.0544$ ,  $y = 0$  for **2** and  $x = 0.0412$ ,  $y = 163.1420$  for **3**. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms, except those in water molecules, were placed in calculated positions. Crystal data collection parameters along with the values for the residuals after final refinement are summarized in Table 1.

Table 1  
X-ray crystallographic data and refinements of compounds **1**, **2** and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>32</sub> H <sub>114</sub> N <sub>20</sub> Ni <sub>8</sub> O <sub>82</sub> P <sub>2</sub> W <sub>18</sub>	C <sub>8</sub> H <sub>78</sub> N <sub>8</sub> Ni <sub>6</sub> O <sub>88</sub> P <sub>2</sub> W <sub>18</sub>	C <sub>20</sub> H <sub>148</sub> N <sub>20</sub> Mn <sub>8</sub> O <sub>160</sub> P <sub>4</sub> W <sub>36</sub>
Formula weight	5932.01	5418.28	10411.58
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1
<i>a</i> (Å)	13.845	12.064(2)	12.160(3)
<i>b</i> (Å)	15.153	12.599(2)	16.891(4)
<i>c</i> (Å)	15.1725(2)	15.936(3)	20.278(5)
$\alpha$ (°)	70.108(5)	97.637(2)	88.823(4)
$\beta$ (°)	64.738(5)	108.0500(10)	88.121(5)
$\gamma$ (°)	78.229(5)	114.719(2)	83.482(4)
<i>V</i> (Å <sup>3</sup> )	2700.30(4)	1993.0(6)	4135.1(16)
<i>Z</i>	1	2	1
Limiting indices	−17 ≤ <i>h</i> ≤ 17 −14 ≤ <i>k</i> ≤ 19 −13 ≤ <i>l</i> ≤ 19	−14 ≤ <i>h</i> ≤ 14 −14 ≤ <i>k</i> ≤ 14 −18 ≤ <i>l</i> ≤ 17	−13 ≤ <i>h</i> ≤ 14 −16 ≤ <i>k</i> ≤ 20 −24 ≤ <i>l</i> ≤ 24
$\rho_{\text{calc}}$ (g cm <sup>−3</sup> )	3.648	9.029	4.181
$\mu$ (mm <sup>−1</sup> )	20.578	54.812	25.666
Reflections collected	21107	12653	26301
Unique reflections	12206	6854	14389
<i>R</i> <sub>int</sub>	0.0332	0.0466	0.0396
Refined parameters	729	566	1049
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
<i>R</i>	0.0374	0.0481	0.0598
<i>wR</i>	0.0837	0.1071	0.1172

C, H and N elements were determined on a Vario EL III elemental analyzer. Infrared spectra for solid samples were obtained as the KBr pellets on an ABB Bomem MB 102 FT-IR spectrometer in the range of 4000–400 cm<sup>−1</sup>. Thermogravimetric analyses (TGA) were performed on a Mettler TGA/SDTA851 thermal analyzer in the flowing air atmosphere with a heating rate of 10 °C min<sup>−1</sup> in the temperature region of 30–1000 °C. Variable temperature magnetic susceptibility measurements were carried out in the temperature range of 2–300 K on polycrystalline samples with a Quantum Design MPMS-5 magnetometer. The data were corrected for the contribution of the sample holder and diamagnetism estimated from Pascal's constants. For **1**, the diamagnetism contribution is −0.00137 emu mol<sup>−1</sup>.

### 3. Results and discussion

#### 3.1. Synthesis

Compounds **1**, **2** and **3** were synthesized by the hydrothermal reaction of the trivacant Keggin polyoxoanion [ $\alpha$ -*A*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> with Ni<sup>2+</sup> or Mn<sup>2+</sup> ions in the presence of *tepa* or *en* at the different temperature and not made using the conventional aqueous solution method. The inorganic–organic composite structure of **1** is interesting, however, the use of *en* instead of *tepa* in the synthesis resulted in a novel hexa-Ni<sup>2+</sup> incorporated phosphotungstate [ $\{[\text{Ni}_6(\mu_3\text{-OH})_3(\text{en})_2(\text{H}_2\text{O})_8\}(\alpha\text{-B-PW}_9\text{O}_{34})\} \cdot 7\text{H}_2\text{O}$ ] [25]. Since we have observed the successful synthesis of **1**,

we attempted to synthesize the isostructural compound containing Mn<sup>2+</sup> ions, however, we were unsuccessful in doing so, instead, we isolated **3** when *tepa* was replaced by *en*. In the subsequent exploitation with the aim of introducing carboxylic ligands into this system, compound **2** was unexpectedly obtained. It was worthily noted that the presence of 2,3-pyridinedicarboxylic acid was found to be necessary although it did not participate in the formation of **2** and its specific role was not clear. When 2,3-pyridinedicarboxylic acid was removed, the product was [ $\{[\text{Ni}_6(\mu_3\text{-OH})_3(\text{en})_2(\text{H}_2\text{O})_8\}(\alpha\text{-B-PW}_9\text{O}_{34})\} \cdot 7\text{H}_2\text{O}$ ] [25]. From the above analyses, the starting reactants and temperature have a significant influence on the products. It is of interest that the isomerization of [ $\alpha$ -*A*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> → [ $\alpha$ -*B*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> was observed in the formation of **1**, **2** and **3**. Actually, in 1986, Knoth et al. [17] demonstrated that [ $\alpha$ -*A*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> can be transformed to [ $\alpha$ -*B*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> in solution in the presence of the first-row TM upon heating. When Knoth et al. [17] reacted [ $\alpha$ -*A*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> with divalent first-row TM in a ratio of about 1:2 at room temperature, they obtained the dimeric heteropolyanions [ $M_3(\alpha\text{-A-PW}_9\text{O}_{34})_2$ ]<sup>12−</sup> (*M* = Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>). However, heating of these solutions above 60 °C resulted in a transformation to the well-known family of tetra-*M* sandwiched polyoxoanions, [ $M_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2$ ]<sup>10−</sup> [17]. In 1990, Domaille [14] showed that the same isomerization could be accomplished in the solid state. In 2002, Kortz et al. [28] also observed this isomerization when [ $\alpha$ -*A*-PW<sub>9</sub>O<sub>34</sub>]<sup>9−</sup> reacted with Ni<sup>2+</sup> ions to prepare [ $\text{Ni}_3\text{Na}(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2$ ]<sup>11−</sup>.

Furthermore, the isomerization of  $[\alpha\text{-}B\text{-PW}_9\text{O}_{34}]^{9-} \rightarrow [\alpha\text{-}A\text{-PW}_9\text{O}_{34}]^{9-}$  was also observed when grafting organometallic groups onto the polyoxoanion surface [29–32]. For example, the incorporation of  $R\text{PO}^{2+}$  ( $R = \text{Et}, \text{Bu}^n, \text{Bu}^t$  and  $\text{Ph}$ ) groups into the vacant sites induced the isomerization of  $[\alpha\text{-}B\text{-PW}_9\text{O}_{34}]^{9-} \rightarrow [\alpha\text{-}A\text{-PW}_9\text{O}_{34}]^{9-}$  [29], which was also observed for the preparation of organosilyl derivatives [30–32].

### 3.2. Description of the crystal structures

Compounds **1**, **2** and **3** crystallize in the triclinic space group  $P\bar{1}$ , although their structures are different. Their common structural features are that they all contain the classical tetra- $M^{\text{II}}$  sandwiched polyoxoanions  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$  ( $M = \text{Ni}^{2+}$  or  $\text{Mn}^{2+}$ ) as the fundamental building blocks and nickel-organoamine cations or protonated organoamine cations work as the charge balance ions. As shown in Fig. 1, the molecular structure of **1** consists of a tetra- $\text{Ni}^{2+}$  sandwiched  $[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$  polyoxoanion, two kinds of crystallographic independent  $[\text{Ni}(\text{tepa})(\text{H}_2\text{O})]^{2+}$  (two  $[\text{Ni}3(\text{tepa})(\text{H}_2\text{O})]^{2+}$  and two  $[\text{Ni}4(\text{tepa})(\text{H}_2\text{O})]^{2+}$  ions), two protons and eight lattice water molecules. The

$[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$  polyoxoanion has the general structure of the series  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$  ( $M = \text{Co}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}$ ) [13,15,18,19] and contains two trivalent Keggin  $[\alpha\text{-}B\text{-PW}_9\text{O}_{34}]^{9-}$  fragments in an staggered fashion linked via a centrosymmetric tetrametallic unit  $\text{Ni}_4\text{O}_{16}$  leading to a sandwich-type structure. Specifically, the  $\text{Ni}_4\text{O}_{16}$  group is combined with two  $[\alpha\text{-}B\text{-PW}_9\text{O}_{34}]^{9-}$  fragments via exposed 14 bridging O atoms (two  $\mu_4\text{-O}$  from one  $\text{PO}_4$  groups and 12  $\mu_2\text{-O}$  from 12  $\text{WO}_6$  groups). Both Ni1 and Ni2 ions in the sandwich belt adopt a distorted octahedral coordination environment with the Ni–O distances of 1.989(6)–2.194(6) Å for the Ni1 ion and 2.015(6)–2.169(6) Å for the Ni2 ion. Both  $[\text{Ni}3(\text{tepa})(\text{H}_2\text{O})]^{2+}$  and  $[\text{Ni}4(\text{tepa})(\text{H}_2\text{O})]^{2+}$  cations adopt a six-coordinate octahedral coordination geometry with four nitrogen atoms from the chelating tepa ligand building the equatorial plane [Ni–N: 2.106(9)–2.178(9) Å for  $[\text{Ni}3(\text{tepa})(\text{H}_2\text{O})]^{2+}$  and 2.096(9)–2.119(9) Å for  $[\text{Ni}4(\text{tepa})(\text{H}_2\text{O})]^{2+}$ ], one water oxygen atom [Ni–O: 2.186(6) Å for  $[\text{Ni}3(\text{tepa})(\text{H}_2\text{O})]^{2+}$  and 2.200(9) Å for  $[\text{Ni}4(\text{tepa})(\text{H}_2\text{O})]^{2+}$ ] and one nitrogen atom from the same tepa ligand [Ni–N: 2.081(8) Å for  $[\text{Ni}3(\text{tepa})(\text{H}_2\text{O})]^{2+}$  and 2.080(10) Å for  $[\text{Ni}4(\text{tepa})(\text{H}_2\text{O})]^{2+}$ ] standing on the axial positions. Since the dimeric sandwich-type  $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$  was firstly found by Weakley in 1973 [15], to date, this Keggin-based architecture has been known for most first-row TM (including mixed metal) and it has also been possible to substitute the tetrahedral phosphorus(V) heteroatom by arsenic(V), silicon(IV), germanium(IV), iron(III) and copper(II) [15,16,18,19,33–45]. Therefore, this structural type represents one of the largest TMSP families. To the best of our knowledge, compound **1** is the first sandwich-type phosphotungstate with nickel–tepa complexes cations as the charge balance cations.

Compound **2** is constructed from one tetra- $\text{Ni}^{\text{II}}$  sandwiched polyoxoanion  $[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$ , one di-nuclear  $[\text{Ni}_2(\text{H}_2\text{O})_{10}]^{4+}$  cation, three protonated  $[\text{enH}_2]^{2+}$  ions, one en molecule and eight lattice water molecules (Fig. 2). Similar to **1**, Ni1 and Ni2 ions in the sandwich belt adopt an octahedral geometry with the Ni–O distances of 1.992(11)–2.187(9) Å for the Ni1 ion and 2.004(10)–2.137(10) Å for the Ni2 ion. The di-nuclear  $[\text{Ni}_2(\text{H}_2\text{O})_{10}]^{4+}$  cation contains two edge-sharing  $\text{NiO}_6$  octahedra with Ni–O distances of 1.916(16)–2.14(3) Å. Different from **1** and **2**, **3** is composed of two tetra-Mn sandwiched polyoxoanions  $[\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$ , 10 diprotonated en solvent molecules and 20 lattice water molecules (Fig. 3). Note that two  $[\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-}B\text{-PW}_9\text{O}_{34})_2]^{10-}$  polyoxoanions have the different spatial orientations. This type of a molecular unit containing double polyoxoanions is very rare [46].

The trivalent  $[\alpha\text{-}B\text{-PW}_9\text{O}_{34}]^{9-}$  fragment can formally be derived from the plenary Keggin  $[\alpha\text{-}PW_{12}O_{40}]^{3-}$  polyoxoanion by removal of three adjacent edge-sharing  $\text{WO}_6$  octahedra [47]. Two trivalent Keggin  $[\alpha\text{-}B\text{-PW}_9\text{O}_{34}]^{9-}$  fragments are linked via a rhombic  $\text{M}_4\text{O}_{16}$  unit leading

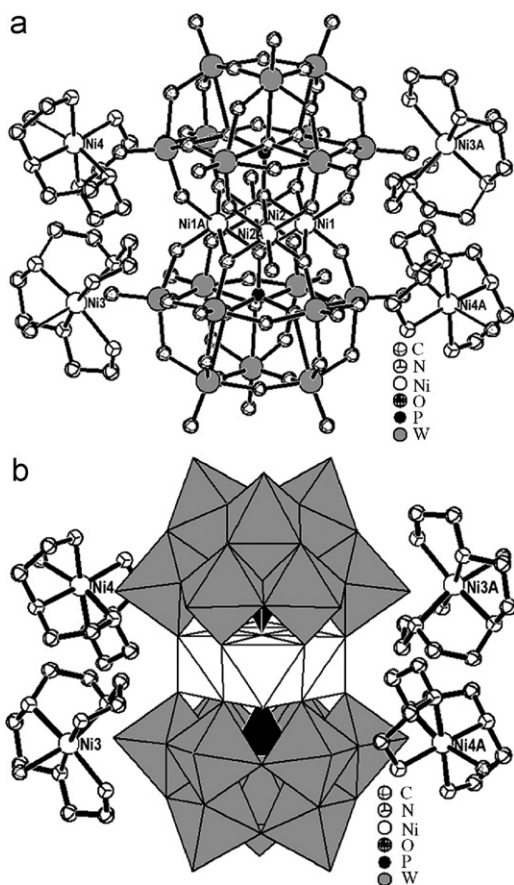


Fig. 1. (a) Ball-and-stick and (b) polyhedral/ball-and-stick representations of the molecular structure of **1**. The atoms with the suffix A are generated by the symmetry operation:  $1-x, 1-y, 1-z$ . The free protons and lattice water molecules are omitted for clarity.



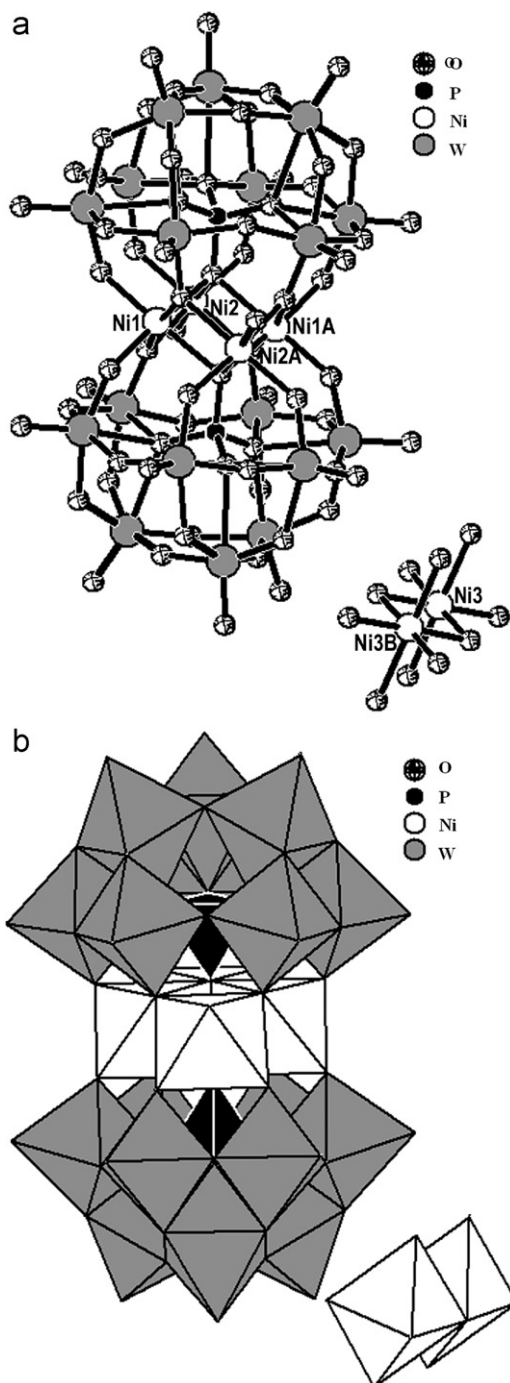


Fig. 2. (a) Ball-and-stick and (b) polyhedral representations of the molecular structure of **2**. The atoms with the suffixes A and B are generated by the symmetry operation:  $-x, 2-y, -z$  for A and  $-x, 3-y, 1-z$  for B. The protonated  $[\text{enH}_2]^{2+}$  ions, en and lattice water molecules are omitted for clarity.

to a sandwich-type structure. In the  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  polyoxoanions, four kinds of W–O distances are present (Table 2): W–O<sub>t</sub>, W–O<sub>W2</sub>, W–O<sub>W3P</sub> and W–O<sub>WM</sub> (the meanings of O<sub>t</sub>, O<sub>W2</sub>, O<sub>W3P</sub> and O<sub>WM</sub> atoms are the same as the footnote in Table 2), and their distances are 1.699(7)–1.720(6) Å, 1.869(6)–2.023(6) Å, 2.417(5)–2.532(6) Å and 1.801(6)–1.884(6) Å for **1**;

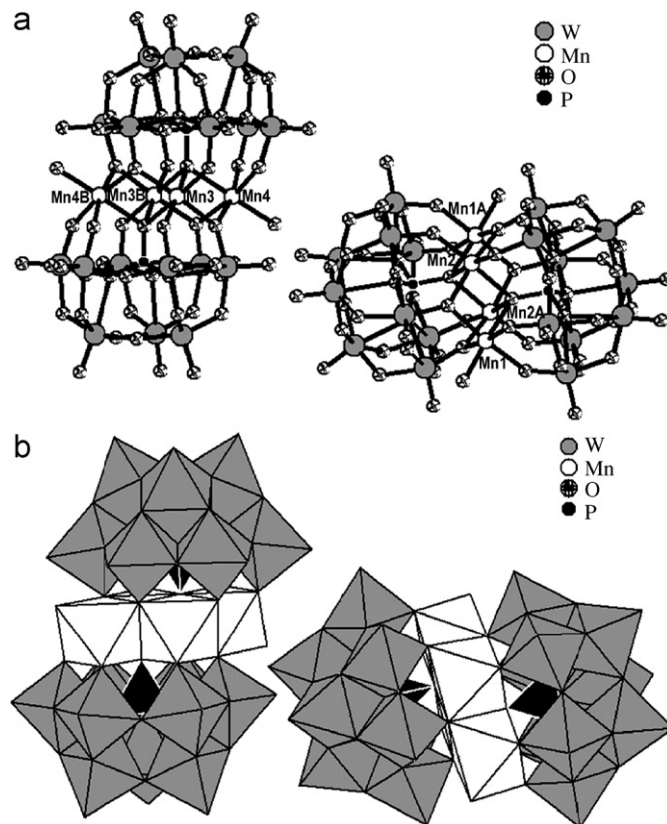


Fig. 3. (a) Ball-and-stick and (b) polyhedral representations of the molecular structure of **3**. The atoms with the suffixes A and B are generated by the symmetry operation:  $-x, 4-y, -z$  for A and  $-1-x, 5-y, 1-z$  for B. The protonated  $[\text{enH}_2]^{2+}$  ions and lattice water molecules are omitted for clarity.

Table 2  
Bond lengths (Å) and angles (°) of the polyoxoanions  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  in **1**, **2** and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
W–O <sub>t</sub> <sup>a</sup>	1.699(7)–1.720(6)	1.698(11)–1.741(9)	1.693(14)–1.745(15)
W–O <sub>W2</sub> <sup>b</sup>	1.869(6)–2.023(6)	1.861(9)–2.039(11)	1.837(14)–2.067(15)
W–O <sub>W3P</sub> <sup>c</sup>	2.417(5)–2.532(6)	2.386(8)–2.548(14)	2.408(12)–2.599(11)
W–O <sub>WM</sub> <sup>d</sup>	1.801(6)–1.884(6)	1.762(11)–1.858(12)	1.752(15)–1.839(12)
P–O	1.531(6)–1.563(6)	1.555(9)–1.568(10)	1.517(14)–1.569(13)
M–O <sub>H2</sub> <sup>e</sup>	2.051(6)	2.032(11)	2.154(15)–2.183(15)
O–W–O <sub>cis</sub>	71.7(2)–105.0(3)	72.2(4)–105.6(5)	71.7(5)–105.0(7)
O–W–O <sub>trans</sub>	154.2(3)–172.7(3)	154.2(5)–172.6(4)	153.6(6)–172.6(6)
O–P–O	108.1(3)–111.0(3)	108.4(5)–110.9(5)	107.9(8)–111.2(8)
O–M–O <sub>cis</sub>	82.9(2)–99.9(2)	82.6(4)–98.8(5)	81.8(5)–98.8(6)
O–M–O <sub>trans</sub>	168.2(2)–177.8(2)	168.1(4)–176.5(4)	166.5(5)–178.3(6)

<sup>a</sup>O<sub>t</sub> is double bonded with a tungsten atom.

<sup>b</sup>O<sub>W2</sub> is combined with two tungsten atoms.

<sup>c</sup>O<sub>W3P</sub> is linked to three tungsten and one phosphorous atoms.

<sup>d</sup>O<sub>WM</sub> is connected with one tungsten and one or two M atoms (M = Ni<sup>2+</sup> or Mn<sup>2+</sup>).

<sup>e</sup>O<sub>H2</sub> is the water ligand.

1.698(11)–1.741(9) Å, 1.861(9)–2.039(11) Å, 2.386(8)–2.548(14) Å and 1.762(11)–1.858(12) Å for **2**; 1.693(14)–1.745(15) Å, 1.837(14)–2.067(15) Å, 2.408(12)–2.599(11) Å and 1.752(15)–1.839(12) Å for **3**, respectively. The bond

distances and angles within the trivacant fragments are in excellent agreement with other closely related tetranuclear heteropolyanions [42]. The P atom in the central cavity resides in the  $\text{PO}_4$  tetrahedron with the P–O distances and O–P–O bond angles of 1.531(6)–1.563(6) Å and 108.1(3)–111.0(3) Å for **1**, 1.555(9)–1.568(10) Å, 108.4(5)–110.9(5) Å for **2**, and 1.517(14)–1.569(13) Å and 107.9(8)–111.2(8) Å for **3**, respectively, which are consistent with the results of the previous study [36,40]. Additionally, the tetra-*M* sandwiched  $[\text{M}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$  ( $M = \text{Ni}^{2+}$  or  $\text{Mn}^{2+}$ ) fragment in **1**, **2** and **3** is interesting in that it illustrates the familiar structural type of a  $\beta$ -junction at the sites of metal incorporation [13,18,19,48]. This type of junction was first reported by Weakley [15]. In contrast, the  $\alpha$ -junction has been seen at the sites of metal incorporation in several sandwich-type POMs [49–52]. This prevalence of the  $\beta$ -junction over the  $\alpha$ -junction in sandwich-type POMs is in direct contrast to the known relative thermodynamic stabilities exhibited by the  $\alpha$ - and  $\beta$ -isomers (for example, Baker–Figgis isomers) of the parent Keggin structure [52–55]. The most likely explanation for the prevalence of  $\beta$ -junctions in sandwich-type POMs is that the repulsion present between the coordinated water ligands of the external metal sites and the bridging oxygen atoms of the neighboring belt tungsten atoms in each of the  $[\alpha\text{-B-PW}_9\text{O}_{34}]^{9-}$  units dominates over the small energetic differences between the Baker–Figgis isomers [52].

It should be noted that the nickel-organoamine cations or organoamine cations fill the gap of the polyoxoanions in **1**, **2** and **3**. Their 3-D supramolecular structures can be constructed taking into account hydrogen-bonding interactions between the nitrogen atoms of the nickel-organoamine cations or organoamine cations and the oxygen atoms of the polyoxoanions or lattice water molecules that have  $\text{N}\cdots\text{O}$  distances from 2.916(10) to 3.522(11) Å for **1** (Fig. 4), from 2.73(2) to 3.354(16) Å for **2**, and from 2.78(3) to 3.38(4) Å for **3**, respectively. Therefore, the interactions between the nickel-organoamine cations or organoamine cations and the polyoxoanions are mainly hydrogen bonds, van der Waals and electrostatic forces.

### 3.3. IR spectra of 1–3

The IR spectra of **1–3** display the characteristic vibration patterns derived from the Keggin framework in the region 700–1100  $\text{cm}^{-1}$  (Fig. 5) [32,52,56]. Four characteristic bands attributable to  $\nu(\text{W-O}_i)$ ,  $\nu(\text{P-O}_a)$ ,  $\nu(\text{W-O}_b)$  and  $\nu(\text{W-O}_c)$ , appear at 967–943, 1040–1015, 899, 782–729  $\text{cm}^{-1}$  for **1**, 971–939, 1040–1019, 883 and 758–714  $\text{cm}^{-1}$  for **2**, and 951, 1042, 890 and 806–706  $\text{cm}^{-1}$  for **3**, respectively. In general, these feature bands can be easily assigned in comparison with the corresponding bands of the Keggin clusters. By a close examination of the IR spectra for **1**, **2** and **3**, the  $\nu(\text{P-O}_a)$  and  $\nu(\text{W-O}_c)$  stretching vibration bands splits into two or three bands as a consequence of the lower symmetry of the polyoxoanions in **1**, **2** and **3** than that of the plenary

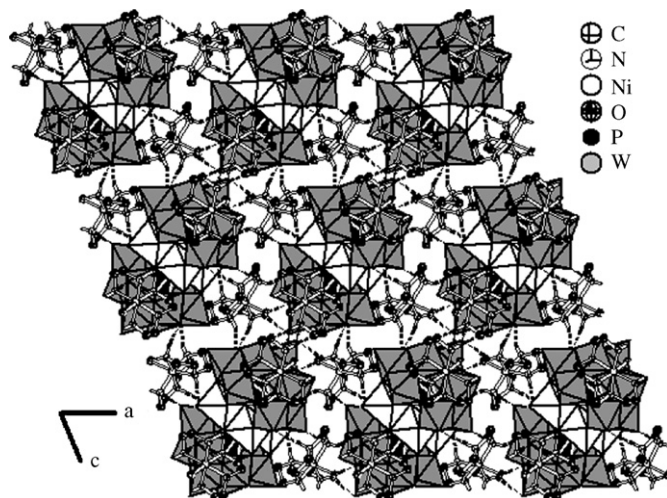


Fig. 4. The 3-D supramolecular structure of **1** constructed via hydrogen bonds between the nitrogen atoms of the nickel-tepa cations and the oxygen atoms of the polyoxoanions.

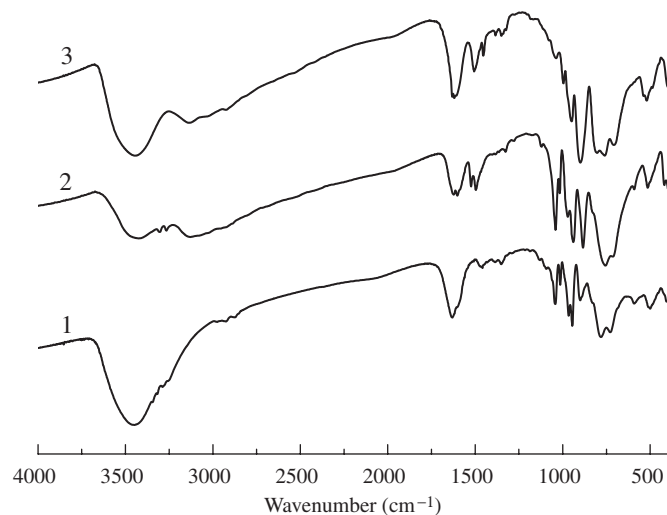


Fig. 5. Infrared spectra of compounds **1**, **2** and **3** displaying the characteristic vibration patterns derived from the Keggin framework in the region 700–1100  $\text{cm}^{-1}$ .

Keggin  $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$  cluster. In addition, the stretching bands of the  $-\text{OH}$  and  $-\text{NH}_2$  groups are observed at 3460–3430  $\text{cm}^{-1}$  and 3350–3250  $\text{cm}^{-1}$ , respectively. The bending vibration bands of  $-\text{NH}_2$  and  $-\text{CH}_2$  groups appear at 1631–1603 and 1490–1454  $\text{cm}^{-1}$ , respectively [57]. The occurrence of these resonance signals confirms the presence of organic amine groups, being in good agreement with the single-crystal structural analyses.

### 3.4. Thermogravimetric (TG) analysis of 1 and 2

The TG curves indicate that the weight loss of **1** and **2** can be divided into three steps in the range of 30–1000 °C (Fig. 6). In the case of **1**, the weight loss of 4.00% during the first step from 30 to 329 °C involves the loss of 8 lattice

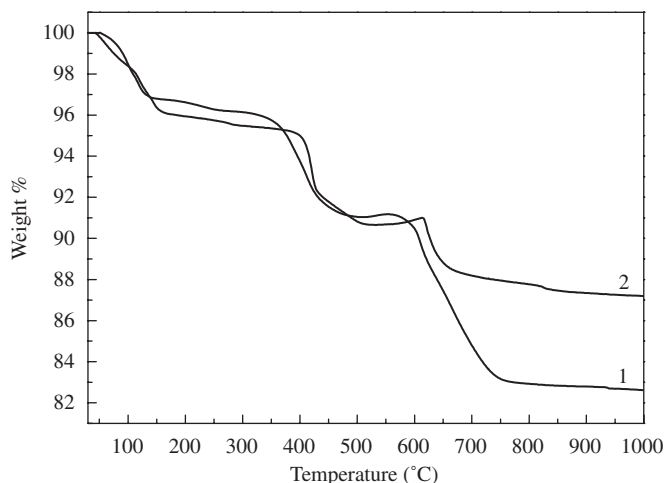


Fig. 6. Thermogravimetric curves of **1** and **2** measured in the flowing air atmosphere with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in the temperature region of 30–1000  $^{\circ}\text{C}$ .

water molecules and 5 coordinated water molecules (calc. 3.90%). On further heating, the material loses weight continuously during the second and third steps with combined weight loss of 13.36% between 329 and 1000  $^{\circ}\text{C}$ , corresponding to the removal of 1 coordinated water molecule, 4 teпа ligands and dehydration of 2 protons (calc. 13.56%). As for **2**, the first weight loss is 3.96% from 30 to 177  $^{\circ}\text{C}$ , corresponding to the release of 8 water lattice molecules and 1 free en molecule (calc. 3.75%). The combined weight loss of the second and third steps is 8.87% between 177 and 1000  $^{\circ}\text{C}$ , assigned to the removal of 12 coordinated water molecules, 3 free en molecules and dehydration of 6 protons (calc. 9.27%).

### 3.5. Magnetic property of **1**

The magnetic measurement of **1** was carried out on polycrystalline samples with a Quantum Design MPMS-5 magnetometer in an applied field of 5 kOe in the temperature range 2–300 K. The plots of  $\chi_{\text{M}}T$  and  $\chi_{\text{M}}^{-1}$  as a function of  $T$  are shown in Fig. 7. The  $\chi_{\text{M}}T$  value at 300 K is  $9.33\text{ emu mol}^{-1}\text{ K}$ , being in good agreement with the  $9.68\text{ emu mol}^{-1}\text{ K}$  value of eight non-interacting  $\text{Ni}^{2+}$  cations with  $g = 2.2$  [58]. The  $\chi_{\text{M}}T$  value gradually increases upon lowering of the temperature to reach a maximum ( $36.56\text{ emu mol}^{-1}\text{ K}$  at 13 K), indicating a typical ferromagnetic coupling between the  $\text{Ni}^{2+}$  cations. When the temperature is further lowered, a sudden decrease of the  $\chi_{\text{M}}T$  value occurs ( $24.30\text{ emu mol}^{-1}\text{ K}$  at 2 K), which could be mainly regarded as the contribution of the zero-field-splitting from the  $\text{Ni}^{2+}$  cations. Note that the observation that  $\chi_{\text{M}}T$  is less field-dependent precludes the presence of significant intermolecular interactions [59]. It is worth noting that more previous work has shown that the behavior of  $\chi_{\text{M}}T$  at very low temperature is related to an anisotropic coupling of the  $\text{Ni}^{2+}$  cations inside the cluster rather than a mean field correction [19,60]. The plot

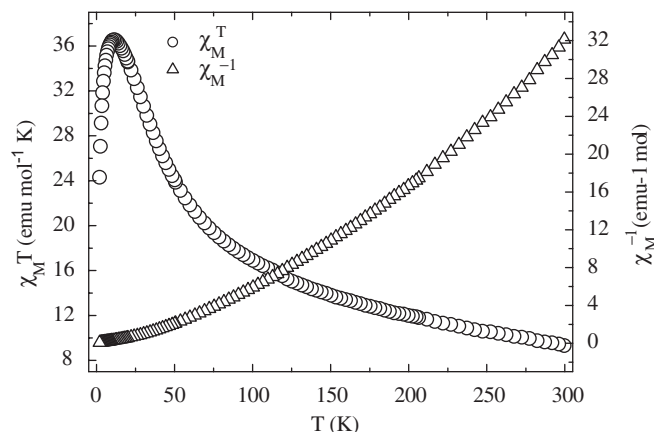


Fig. 7. The plots of  $\chi_{\text{M}}T$  and  $\chi_{\text{M}}^{-1}$  as a function of  $T$  for **1**. The data were recorded in an applied field of 5 kOe.

of  $\chi_{\text{M}}^{-1}$  vs.  $T$  in the range of 30–150 K is well described by the Curie–Weiss expression with Curie constant  $C = 7.15\text{ emu mol}^{-1}\text{ K}$  and Weiss constant  $\theta = 78.16\text{ K}$ , which further confirms the occurrence of strong ferromagnetic coupling between  $\text{Ni}^{2+}$  cations. Such ferromagnetic coupling in the rhombic  $\text{Ni}_4\text{O}_{16}$  cluster unit has been observed in  $\text{K}_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot 24\text{H}_2\text{O}$  reported by Coronado et al. [19]. Moreover, the ferromagnetic coupling in the cubane  $\text{Ni}_4\text{O}_4$  cluster unit in  $\text{Cs}_2[\text{H}_2\text{PW}_9\text{Ni}_4\text{O}_{34}(\text{OH})_3(\text{H}_2\text{O})_6] \cdot 5\text{H}_2\text{O}$  has been investigated by Kortz et al. [61]. In addition, the trimeric  $\text{Ni}^{2+}$  cluster units incorporated in the lacunary POM fragments, such as in  $[\text{Ni}_3\text{Na}(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{11-}$  [60] and  $[\text{Ni}_3(\text{H}_2\text{O})_3(\text{PW}_{10}\text{O}_{39})\text{H}_2\text{O}]^{7-}$  [19], also indicate the occurrence of the ferromagnetic exchange interaction. According to these investigators, the magnetic interaction is highly sensitive to the value of the Ni–O–Ni bridging angle: when the Ni–O–Ni angles are in the range of  $90 \pm 14^{\circ}$ , the Ni–Ni ferromagnetic coupling dominates [19,62]. In view of the geometry of the rhombic  $\text{Ni}_4\text{O}_{16}$  cluster in **1**, the Ni–O–Ni angles are comprised between  $92^{\circ}$  and  $101^{\circ}$ , which are close to the Ni–O–Ni angles ( $90\text{--}100^{\circ}$ ) in  $\text{K}_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot 24\text{H}_2\text{O}$  [19], therefore, the ferromagnetic exchange interaction is expected to occur in this system.

## 4. Conclusions

Three inorganic–organic composite sandwich-type phosphotungstates  $[\text{Ni}(\text{tepa})(\text{H}_2\text{O})_4\text{H}_2[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot 8\text{H}_2\text{O}$  (**1**),  $(\text{enH}_2)_3[\text{Ni}_2(\text{H}_2\text{O})_{10}][\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot \text{en} \cdot 8\text{H}_2\text{O}$  (**2**) and  $(\text{enH}_2)_{10}[\text{Mn}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2] \cdot 20\text{H}_2\text{O}$  (**3**) have been hydrothermally synthesized and structurally characterized by IR spectra, elemental analysis, TG analysis and single-crystal X-ray diffraction. The tetra- $M$  clusters in **1**, **2** and **3** exhibit the familiar structural type of a  $\beta$ -junction at the sites of metal incorporation. Magnetic property of **1** indicates a typical ferromagnetic coupling between  $\text{Ni}^{2+}$  cations.



## 5. Supplementary material

Crystallographic data for structural analysis reported in this paper have been deposited in the Cambridge Crystallographic Data Center with the deposited number CCDC Numbers 652448–652450 for **1**, **2** and **3**. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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