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A new 1-D chain-like organic–inorganic hybrid phosphotungstate constructed by sandwich-type clusters and $[\text{Ni}(\text{en})_2]^{2+}$ linkers

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A new 1-D chain-like organic–inorganic hybrid phosphotungstate based on tetra-Ni-sandwiched polyoxoanion, $[\text{Ni}(\text{en})_2]_2[\{\text{Ni}_3(\text{en})_6(\text{H}_2\text{O})_2\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2\}] \cdot 7\text{H}_2\text{O}$ (en = ethylenediamine) (**1**), has been synthesized under hydrothermal conditions and characterized by IR spectrum, UV spectrum, elemental analysis, thermogravimetric analysis, and single-crystal X-ray diffraction. **1** crystallizes in the triclinic *P*1 space group with cell parameters $a = 13.232(4)$ Å, $b = 15.591(5)$ Å, $c = 15.701(5)$ Å, $\alpha = 112.804(5)^\circ$, $\beta = 92.159(5)^\circ$, $\gamma = 109.012(5)^\circ$, $Z = 1$, $R_1 = 0.0588$, $wR_2 = 0.1387$. Compound **1** displays a 1-D chain-like architecture constructed by sandwich-type polyoxoanions and $[\text{Ni}(\text{en})_2]^{2+}$ linkers. Magnetic measurement reveals that intramolecular ferromagnetic interactions exist in the tetranuclear $\{\text{Ni}_4\text{O}_{16}\}$ cluster.

Keywords: Phosphotungstate; Hydrothermal; Crystal structure; Magnetic

1. Introduction

Designed synthesis and exploitation of transition-metal-substituted polyoxometalates (TMSPs) based on classical lacunary Keggin structures has attracted considerable attention not only due to their enormous structural diversities and electronic characteristics but also because of their potential technological applications in photochemistry, catalysis, and medicine [1–6]. Within numerous classes of TMSPs, sandwich-type polyoxometalates represent the largest subclass, arousing particular interest owing to their excellent catalysis and magnetism. Thus, sandwich-type TMSPs were frequently reported, since the first tetra-Co^{II}-substituted inorganic sandwich-type POM $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$ was reported by Weakley *et al.* in 1973 [7]. Organic–inorganic composite materials elicit increasing interest due to the possibility of combining different characteristics of organic and inorganic components to obtain unexpected structures and properties [8–12]. An emerging area focusing on connecting inorganic TMSP with transition-metal complexes (TMCs) or organic components offer

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the possibility to gain numerous organic–inorganic hybrid TMSP derivatives. Recently, sandwich-type TMSPs modified by TMC groups or organic components have been reported [13–16]. For example, in 2007, Yang *et al.* [13, 14] reported a series of 2-D hybrid networks constructed from tetra-TM-sandwiched POMs and TMCs bridges. Wang and co-workers addressed [15] two organoamine-modified phosphotungstates $[\text{Ni}_4(\text{enMe})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ and $\{\text{Ni}_4[\text{H}_4\text{N}_2(\text{CH}_2)_6]_2(\text{H}_2\text{PW}_9\text{O}_{34})_2\}^{10-}$. Subsequently, Dolbecq *et al.* [16] synthesized two hybrid tungstoantimonates functionalized by oxalato ligands $[\text{Fe}_4^{\text{III}}(\text{ox})_4(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2]^{14-}$ and $[\text{Fe}_4^{\text{III}}(\text{ox})_4(\text{SbW}_9\text{O}_{33})_2]^{14-}$ [16].

In the past several years, our group has focused on functionalization of sandwich-type TMSPs with TMC groups or organic components [17–21]. In 2006, we described the first hybrid 1-D chain-like sandwich-type germanotungstate $\{[\text{Cu}(\text{en})_2][\text{Cu}_4(\text{GeW}_9\text{O}_{34})_2]\}^{10-}$ [17]. We also reported a series of functionalized sandwich-type POMs, $[\text{Mn}_3(\mu\text{-OAc})_2(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})_2]^{14-}$ [18], $[\text{Cu}_6(\text{L})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{8-}$ (L = 2,2'-bpy or phen) [19], $\{[\text{M}(\text{L})_2\text{M}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]\}^{8-}$ (M = Co^{2+} , L = 2,2'-bpy; M = Mn^{2+} , L = phen) [20] and $\{[\text{Ni}(2,2'\text{-bpy})_2(\text{H}_2\text{O})_2]\}_2\{\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-XW}_9\text{O}_{34})_2\}^{4-}$ (X = P, As^V, Ge) [21]. As a part of our work, herein, we report a new organic–inorganic hybrid phosphotungstate modified by $[\text{Ni}(\text{en})_2]^{2+}$ groups $[\text{Ni}(\text{en})_2]_2\{[\text{Ni}_3(\text{en})_6(\text{H}_2\text{O})_2\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]\} \cdot 7\text{H}_2\text{O}$ (en = ethylenediamine) (**1**), which contains a tetra-Ni-sandwiched polyoxoanion $[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ decorated by two $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ pendants and linked by $[\text{Ni}(\text{en})_2]^{2+}$ bridges forming a 1-D chain-like architecture.

2. Experimental

2.1. Instruments and materials

$\text{Na}_7[\alpha\text{-PW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ and $\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot n\text{H}_2\text{O}$ were prepared as described in the literature and confirmed by IR spectra [22, 23]. Other chemical reagents were used as commercially purchased without purification. Elemental analyses (C, H, and N) were conducted on a Perkin-Elmer 2400-II CHNS/O Analyzer; IR spectrum was obtained in a KBr pellet with a Nicolet FT-IR 360 spectrometer from 4000 to 400 cm^{-1} ; thermogravimetric analyses (TGA) were performed under N_2 on a Mettler-Toledo TGA/SDTA851^o instrument with heating rate of 10 $^\circ\text{C min}^{-1}$ from 25 $^\circ\text{C}$ to 600 $^\circ\text{C}$. UV spectrum was recorded on a U-4100 spectrometer (distilled water as solvent) from 400 to 190 nm; magnetic susceptibility measurements were obtained by the use of a Quantum Design MPMS-XL7 SQUID magnetometer from 2 to 300 K.

2.2. Preparation of $[\text{Ni}(\text{en})_2]_2\{[\text{Ni}_3(\text{en})_6(\text{H}_2\text{O})_2\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]\} \cdot 7\text{H}_2\text{O}$ (**1**)

$\text{Na}_9[\alpha\text{-PW}_9\text{O}_{34}] \cdot 16\text{H}_2\text{O}$ (0.5 g, 0.1835 mmol), $\text{Na}_7[\alpha\text{-PW}_{11}\text{O}_{39}] \cdot n\text{H}_2\text{O}$ (0.5 g, 0.1738 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 g, 0.4207 mmol), and en (0.1 mL, 1.48 mmol) were dissolved into distilled water (10 mL). After stirring for 3 h, the resulting mixture was sealed in a 30 mL Teflon-lined reactor and kept at 170 $^\circ\text{C}$ for 5 days. After slowly cooling to room temperature, dark green crystals were collected by filtering, washing with distilled water, and drying in air. Yield: 46% (based on W). Elemental analyses

Table 1. Summary of crystal data and structure refinements for **1**.

	1
Empirical formula	C ₂₀ H ₁₀₂ N ₂₀ Ni ₉ O ₇₉ P ₂ W ₁₈
Weight	5786.42
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)	
<i>a</i>	13.232(4)
<i>b</i>	15.591(5)
<i>c</i>	15.701(5)
α	112.804(5)
β	92.159(5)
γ	109.012(5)
Volume (Å ³), <i>Z</i>	2772.6(15), 1
θ range for data collection (°)	1.98–25.00
Limiting indices	$-15 \leq h \leq 15$; $-18 \leq k \leq 10$; $-14 \leq l \leq 18$
Independent reflections	9635 [<i>R</i> (int) = 0.0521]
Completeness to $\theta = 25.00^\circ$ (%)	98.7
Data/restraints/parameters	9635/114/660
Goodness-of-fit on <i>F</i> ²	1.016
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0588, <i>wR</i> ₂ = 0.1387

Calcd (%) for **1**: C, 4.15; H, 1.78; N, 4.84. Found (%): C, 4.23; H, 1.89; N, 4.96. IR (KBr pellet): 3421, 3334, 1592 (m), 1457 (s), 1397 (m), 1038 (s), 944 (s), 887 (s), 774 (s), 730 (s), 668 (w), 513 (m).

2.3. Crystal structure determination

A suitable single crystal with dimension $0.24 \times 0.14 \times 0.12$ mm³ for **1** was attached to the end of a glass fiber with cyanoacrylate adhesive. Intensity data were collected on a Bruker APEX-II CCD detector with Mo-K α radiation ($\lambda = 0.71073$ Å) at 296(2) K. Lorentz and polarization as well as multi-scan absorption corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares on *F*² using SHELXTL-97 software [24]. All of the non-hydrogen atoms were refined anisotropically. Positions of hydrogens attached to carbon and nitrogen were geometrically placed. The en hydrogens were refined isotropically as a riding mode using the default SHELXTL parameters. Those hydrogens attached to lattice water were not located. The crystal data and structural refinement of **1** are summarized in table 1. Selected bond lengths (Å) are listed in table 2.

3. Results and discussion

3.1. Crystal structure

Single-crystal X-ray diffraction reveals that **1** crystallizes in the triclinic *P* $\bar{1}$ space group and consists of a tetra-supporting sandwich-type polyoxoanion [$\{\text{Ni}_3(\text{en})_6(\text{H}_2\text{O})_2\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2\}$]⁴⁻, two $[\text{Ni}(\text{en})_2]^{2+}$ coordination cations, and seven lattice water molecules. Each polyoxoanion links to two adjacent ones through $[\text{Ni}(\text{en})_2]^{2+}$ bridges, forming a 1-D zigzag chain. Notably, the tetra-supporting sandwich-type

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

P(1)–O(34)	1.538(10)	Ni(2)–O(13)#1	2.086(10)	Ni(4)–O(7)	2.132(12)
P(1)–O(33)	1.553(9)	Ni(2)–O(11)#1	2.089(11)	Ni(4)–O(7)#3	2.132(12)
P(1)–O(31)	1.555(11)	Ni(2)–O(1W)	2.120(11)	Ni(3)–N(3)	2.057(17)
P(1)–O(32)	1.566(11)	Ni(2)–O(34)	2.185(11)	Ni(3)–N(4)	2.083(13)
Ni(1)–O(14)#1	1.983(10)	Ni(5)–N(7)#2	1.909(17)	Ni(3)–N(1)	2.091(13)
Ni(1)–O(10)	1.993(10)	Ni(5)–N(7)	1.909(17)	Ni(3)–N(2)	2.103(14)
Ni(1)–O(11)	2.052(11)	Ni(5)–N(8)	1.926(18)	Ni(3)–O(2 W)	2.156(11)
Ni(1)–O(13)#1	2.062(10)	Ni(5)–N(8)#2	1.926(18)	Ni(3)–O(8)	2.182(10)
Ni(1)–O(34)	2.189(10)	Ni(4)–N(6)	2.00(2)	Ni(6)–N(9)	1.893(16)
Ni(1)–O(34)#1	2.215(11)	Ni(4)–N(6)#3	2.00(2)	Ni(6)–N(9)#4	1.893(16)
Ni(2)–O(16)	2.019(10)	Ni(4)–N(5)	2.069(16)	Ni(6)–N(10)#4	1.911(16)
Ni(2)–O(12)	2.034(9)	Ni(4)–N(5)#3	2.069(16)	Ni(6)–N(10)	1.911(16)

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

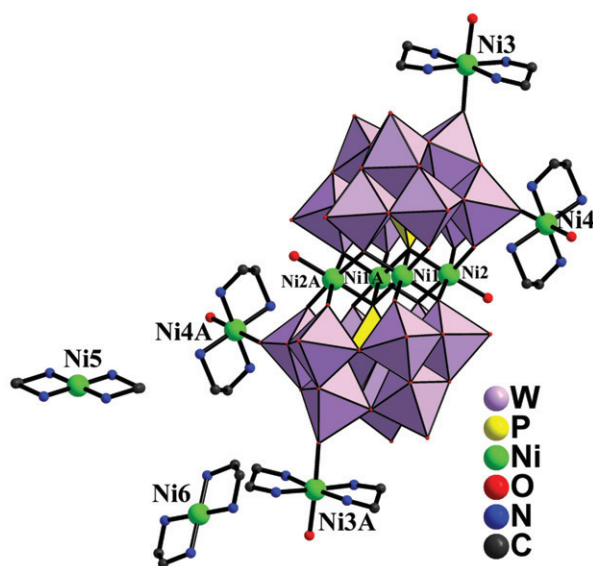


Figure 1. Molecular structure of **1** with partial atom-labeling scheme. All the hydrogens are omitted for clarity. The atoms with the suffix A are generated by the symmetry operation: A: $-x, -y, -z$.

polyoxoanion $[\{\text{Ni}_3(\text{en})_6(\text{H}_2\text{O})_2\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2\}]^{4-}$ in **1** (figure 1) contains a familiar Weakley's sandwich-type subunit $[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ decorated by two $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ coordination cations and two $[\text{Ni}(\text{en})_2]^{2+}$ bridges. Alternatively, this cluster can be viewed as a combination of two half-units $\{\text{Ni}_{1.5}(\text{en})_3(\text{H}_2\text{O})[\text{Ni}_2(\text{H}_2\text{O})(\alpha\text{-PW}_9\text{O}_{34})]\}$ related by an inversion center (0, 0, 0). The $[\text{Ni}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ subunit constructs from two trivacant $[\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ Keggin moieties linked by a rhomb-like Ni_4O_{16} group resulting in a sandwich-type assembly. In the skeleton of the sandwich-type polyoxoanion, each $[\text{Ni}(\text{en})(\text{H}_2\text{O})]^{2+}$ fragment coordinates to the "polar" position of the $\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ moiety through a terminal oxygen, while $[\text{Ni}(\text{en})]^{2+}$ grafts on the "belt" position of the two $\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ moieties *via* a terminal oxygen. The $[\text{Ni}(\text{en})]^{2+}$ on the "belt" position of $\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ links adjacent

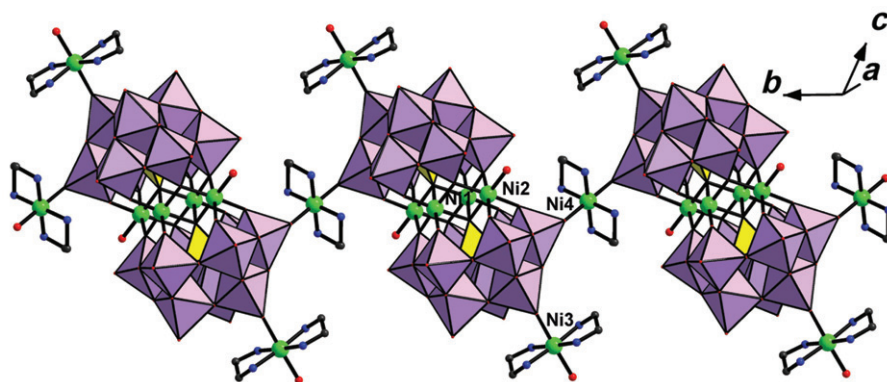


Figure 2. View of the 1-D chain-like alignment with four crystallographically unique nickels being marked. The discrete $[\text{Ni}(\text{en})_2]^{2+}$ and all hydrogens are omitted for clarity.

sandwich-type polyoxoanions generating a 1-D chain architecture (figure 2), which is obviously different from the analogous tetra-supporting sandwich-type anion $[\{\text{Ni}(2,2'\text{-bpy})_2(\text{H}_2\text{O})_2\}_2\{\text{Ni}(2,2'\text{-bpy})\}_2\{\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2\}]^{4-}$ [21]. Similar 1-D chain-like bridging of the $[\text{Ni}(\text{en})_2]^{2+}$ cation was observed in our previously reported sandwiched tungstogermanate $\{\text{Cu}_4(\text{GeW}_9\text{O}_{34})\}[\text{Cu}(\text{en})_2]^{10-}$ [17], where the $[\text{Ni}(\text{en})_2]^{2+}$ group links adjacent sandwiched polyoxoanions forming a 1-D chain.

Similar sandwich-type POM compounds have been continually reported. For example, in 2011, Wang *et al.* [25] reported two new methylimidazole-modified Hervé-sandwich-type polytungstoantimonates $\text{Na}_9[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{M}(\text{C}_4\text{H}_6\text{N}_2)\}_3(\text{SbW}_9\text{O}_{33})_2] \cdot 28\text{H}_2\text{O}$ ($\text{M} = \text{Co}$ or Mn), in which every M^{2+} ion coordinates to one methylimidazole. Recently, Khoshnavazi and Tayamon [26, 27] prepared a series of lanthanide-ion-substituted sandwich-type polyoxoanions $[(\text{A-PW}_9\text{O}_{34})_2(\text{H}_2\text{OM})_3\text{CO}_3]^{11-}$ ($\text{M} = \text{Eu}^{3+}$, Gd^{3+}) and $[(\text{A-}\beta\text{-GeW}_9\text{O}_{34})_2(\text{MOH}_2)_3\text{CO}_3]^{13-}$ ($\text{M} = \text{Y}^{3+}$, Sm^{3+} , and Yb^{3+}), in which the three lanthanides in the sandwich belt are stabilized by a $[\text{CO}_3]^{2-}$ template. In 2009, we reported two new organic-inorganic composite sandwich-type arsenotungstates, $[\text{H}_2\text{dap}]_6\text{H}_8[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]_2 \cdot 33\text{H}_2\text{O}$ and $\{\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2\}[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$, where the latter displays an organic-inorganic composite 2-D sheet architecture constructed by tetra- Ni^{II} sandwiched $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ units by $[\text{Ni}(\text{dap})_2]^{2+}$ bridges [28]. The same year, Chen *et al.* [29] addressed two inorganic-organic composite polyoxotungstates, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{en})_2]_3[\text{Cu}_4(\text{GeW}_9\text{O}_{34})_2] \cdot 10\text{H}_2\text{O}$ and $(\text{H}_2\text{en})[\text{Zn}(\text{en})_2]_4[\text{Zn}_4(\text{Hen})_2(\text{GeW}_9\text{O}_{34})_2] \cdot 10\text{H}_2\text{O}$, in which the sandwich polyoxoanions $[\text{Cu}_4(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{12-}$ or $[\text{Zn}_4(\text{Hen})_2(\text{GeW}_9\text{O}_{34})_2]^{10-}$ linked by $[\text{M}(\text{en})_2]^{2+}$ bridges forming a 2-D layer. Comparing with these above-mentioned sandwich-type TMSPs, **1** represents the rare example of 1-D chain-like organic-inorganic hybrid sandwich-type polyoxotungstates.

In the structural unit of **1**, there are six crystallographically unique nickels (figure 1). Both Ni1 and Ni2 fuse together and form a rhombic $\{\text{Ni}_4\text{O}_{16}\}$ cluster by edge-sharing; Ni3 and Ni4 complex cations graft on the polyoxoanion skeleton *via* a terminal oxygen, whereas Ni5 and Ni6 complex cations are discrete countercations. Ni1, Ni2, Ni3, and Ni4 all reside in distorted octahedral geometries, while Ni5 and Ni6 are tetrahedral in **1**. Both Ni1 and Ni2 ions are coordinated by six bridging oxygens or water molecules [Ni–O: 1.983(10)–2.215(11) Å]; Ni3 ion is defined by two oxygens from one terminal

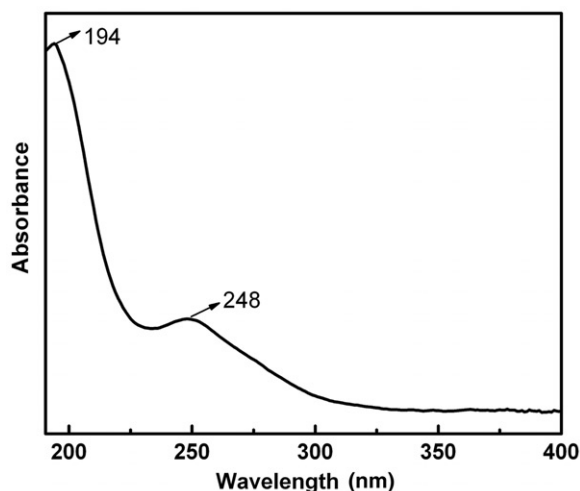


Figure 3. The UV spectrum of **1**.

oxygen of α -[PW₉O₃₄]⁹⁻ moiety and one water molecule and four nitrogens from two en ligands [Ni–O: 2.156(11)–2.182(10) Å and Ni–N: 2.057(17)–2.103(14) Å]; the octahedral geometry of the Ni4 is from two oxygens of two adjacent α -[PW₉O₃₄]⁹⁻ moieties and four nitrogens from two en [Ni–O: 2.132(12) Å and Ni–N: 2.000(20)–2.069(16) Å]; both tetrahedral Ni5 and Ni6 are combined with four nitrogen donors from two en ligands [Ni–N: 1.893(16)–1.926(18) Å]. Separations of adjacent nickels on the sides of the rhomb-like {Ni₄O₁₆} cluster are 3.154(4) to 3.186(3) Å and the distances of two nickels in the diagonals are between 3.232(3) and 5.455(3) Å.

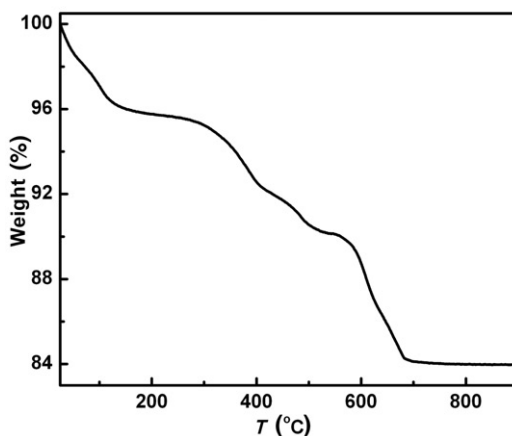
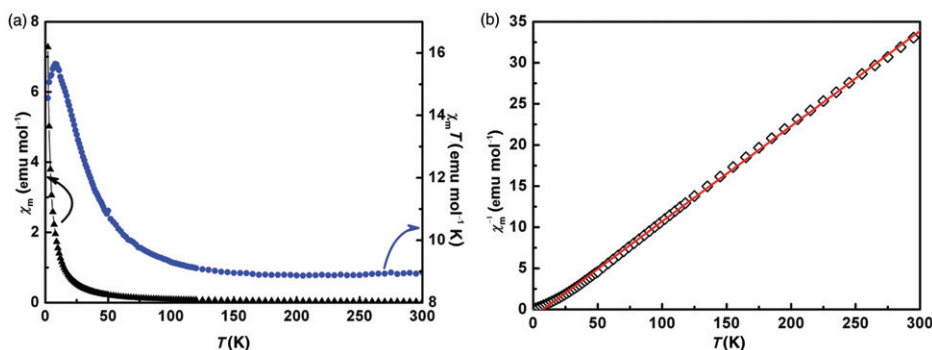
3.2. IR and UV spectra

IR spectrum shows that **1** displays characteristic vibrations of the Keggin-type polyoxoanion frameworks [30]. In the low-wavenumber region, ν (P–O_a) are observed at 1043 and 1007 cm⁻¹, while other obvious characteristic bands centered at 945, 883, 774, and 723 cm⁻¹ are ascribed to ν (W–O_t), ν (W–O_b), and ν (W–O_c), respectively. In addition, the stretching vibrational bands of –OH and –NH₂ appear at 3437 and 3335–3277 cm⁻¹, respectively, suggesting the presence of crystal water and en.

UV spectrum in aqueous solution from 400 to 190 nm (figure 3) displays two characteristic peaks: strong absorption centered at 194 nm and weak at 248 nm. The former higher energy absorption band can be assigned to the $p\pi$ – $d\pi$ charge-transfer transitions of the O_t → W bond, whereas the latter lower energy absorption is attributed to $p\pi$ – $d\pi$ charge-transfer transitions of the O_{b,c} → W bonds [31].

3.3. Thermogravimetric analysis

TGA were examined on pure samples of **1** under flowing nitrogen. The TG curve of **1** exhibits two weight losses from 25°C to 900°C (figure 4). The first of 4.00% at 25–150°C corresponds to release of seven crystal water molecules and four-coordinated

Figure 4. TG curve of **1**.Figure 5. (a) The plots of χ_m and $\chi_m T$ vs. T in the temperature 2–300 K for **1**; and (b) temperature dependence of $\chi_m T$ for **1** in the temperature range 2–300 K.

water molecules (Calcd 3.42%). The second weight loss of 11.23% from 281°C to 690°C is attributed to removal of 10 en ligands (Calcd 10.39%).

3.4. Magnetic behavior

The magnetic behavior of **1** is shown in figure 5 as thermal variation of $\chi_m T$ versus T plot, where χ_m is the corrected molar magnetic susceptibility. The χ_m value slowly increases from 0.030 emu mol⁻¹ at 300 K to 0.456 emu mol⁻¹ at 26 K (figure 5a), then exponentially reaches maximum of 7.277 emu mol⁻¹ at 2 K. The observed value of $\chi_m T$ is 8.97 emu mol⁻¹ K at room temperature, which is slightly smaller than the spin-only value (9.90 emu mol⁻¹ K) for nine non-interacting Ni(II) ions ($S = 1$, $g = 2.20$). Upon cooling, the value of $\chi_m T$ rises slowly until 100 K, subsequently rapidly increases, and finally reaches the maximum value 15.65 emu mol⁻¹ K at 8 K. This feature is related to the ferromagnetic interactions within the rhomb-like Ni₄O₁₆ cluster. Below 8 K, the $\chi_m T$ value sharply drops to 14.55 emu mol⁻¹ K at 2 K, which corresponds to the

presence of the zero-field-splitting (ZFS) effects between the ground state Ni^{II} cations [13]. Additionally, the behavior of $\chi_M T$ at very low temperature may result from an anisotropic coupling of Ni^{II} cations inside the Ni₄O₁₆ cluster rather than to a mean field correction [32]. The curve of χ_m^{-1} versus T over the temperature range 2–300 K follows the Curie–Weiss law with $C = 7.58 \text{ emu K mol}^{-1}$ and $\theta = 8.63 \text{ K}$ (figure 5b), further confirming the presence of predominant ferromagnetic interactions between adjacent Ni^{II} centers mediated by the oxygen bridge.

4. Conclusion

A new organic–inorganic composite sandwich-type phosphotungstate [Ni(en)₂]₂{[Ni₃(en)₆(H₂O)₂Ni₄(H₂O)₂(α -PW₉O₃₄)₂]} · 7H₂O based on sandwich-type polyoxoanions and nickel coordination cations has been synthesized hydrothermally and characterized structurally by IR and UV spectra, thermal behavior, and magnetic properties. This phosphotungstate compound contains the classical tetra-Ni^{II} sandwiched polyoxoanion [Ni₄(H₂O)₂(B- α -PW₉O₃₄)₂]⁹⁻ as the fundamental building unit, which alternately links with [Ni(en)]²⁺ bridges forming an organic–inorganic composite 1-D chain-like architecture. Magnetic measurements reveal that intramolecular ferromagnetic Ni–Ni interactions exist in the tetranuclear {Ni₄O₁₆} cluster.

Supplementary material

Crystallographic data for the structural analyses reported in this article have been deposited with the Cambridge Crystallographic Data Centre with CCDC number 774688 for **1**. Copies 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).

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