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Hydrothermal syntheses and structural characterization of two sandwich-type arsenotungstates

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Two new organic–inorganic composite sandwich-type arsenotungstates $[\text{H}_2\text{dap}]_6\text{H}_8[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-AsW}_9\text{O}_{34})_2]_2 \cdot 33\text{H}_2\text{O}$ (**1**) and $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B}-\alpha\text{-AsW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$ (**2**) (dap = 1,2-diaminopropane) have been hydrothermally synthesized by reaction of $\text{Na}_8[\text{A}-\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 1,2-diaminopropane and characterized by elemental analysis, IR spectra, X-ray single-crystal diffraction, and thermogravimetric analysis. **1** crystallizes in the triclinic $P\bar{1}$ space group with $a = 16.351(6)$ Å, $b = 16.423(6)$ Å, $c = 19.894(7)$ Å, $\alpha = 110.630(6)^\circ$, $\beta = 92.684(7)^\circ$, $\gamma = 104.946(7)^\circ$, $V = 4774(3)$ Å³, $Z = 1$, $GOOF = 1.033$, $R_1 = 0.0517$, $wR_2 = 0.1086$. **2** also crystallizes in the triclinic $P\bar{1}$ space group with $a = 13.305(4)$ Å, $b = 13.882(4)$ Å, $c = 17.031(5)$ Å, $\alpha = 68.109(5)^\circ$, $\beta = 71.511(4)^\circ$, $\gamma = 88.407(5)^\circ$, $V = 2753.5(14)$ Å³, $Z = 1$, $GOOF = 1.051$, $R_1 = 0.0491$, $wR_2 = 0.1150$. Notably, **1** is a discrete structure, composed of two tetra- Ni^{II} substituted sandwich-type polyoxoanions $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ with different spatial orientation, whereas **2** displays a 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 means of $[\text{Ni}(\text{dap})_2]^{2+}$ bridges. Some previously reported transition-metal-substituted sandwich-type polyoxotungstates have been summarized.

Keywords: Polyoxometalate; Arsenotungstate; Trivacant Keggin structure; Nickel

1. Introduction

Polyoxometalates (POMs), as anionic early-transition-metal oxide clusters, have attracted interest due to molecular and electronic structural versatility and applications in magnetism, catalysis, biology, medicine, and materials science [1–5]. Investigations of lacunary derivatives of Keggin-type and Dawson-type polyoxoanions have been a significant focus in POM chemistry mainly because (a) these lacunary precursors can work as multidentate inorganic ligands and incorporate transition-metal (TM) complexes to their polyoxoanion matrixes generating transition-metal substituted polyoxometalates (TMSPs) and (b) the ability of lacunary polyoxoanions to

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incorporate magnetic TM's between nonmagnetic POM matrixes makes them especially valuable for quantification of magnetic interactions [6–9].

Arsenotungstates are an important subfamily in POM chemistry with diversity of structures and properties attracting interest. TM/Ln-substituted (Ln = Lanthanide) arsenotungstates containing the trivacant Keggin $[\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ unit are less developed [10–22]. For example, in 1986, Evans *et al.* [10] obtained the first $[\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ -containing analogue $\text{K}_{10}[\text{Zn}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 23\text{H}_2\text{O}$ from a mixture of $\text{HNO}_3/\text{Na}_2\text{HAsO}_4/\text{ZnSO}_4/\text{Na}_2\text{WO}_4$ with a molar ratio of 11:1:2:9 at 90–100°C. Later, Bi *et al.* [11] discovered the synthetic method of $\text{Na}_8[\alpha\text{-A-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ and reported high-yield and isomerically pure syntheses of $[\text{As}_2\text{W}_{18}\text{M}_4(\text{H}_2\text{O})_2\text{O}_{68}]^{10-}$ ($\text{M} = \text{Cd}^{\text{II}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}$) by reaction of $[\alpha\text{-A-AsW}_9\text{O}_{34}]^{9-}$ with M^{II} cations. In 2001, Wang *et al.* [12] provided an organic–inorganic composite polyoxotungstoarsenate $\text{K}_6[\{\text{Cu}(\beta\text{-Ala})_2(\text{H}_2\text{O})_2\}_2\{\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2\}] \cdot 17\text{H}_2\text{O}$ by the reaction of $\text{K}_{10}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20\text{H}_2\text{O}$ with β -alanine. In 2002, Rosu *et al.* [13] utilized a mixture of $\text{Na}_7\text{KAs}_4\text{W}_{40}\text{O}_{140} \cdot 56\text{H}_2\text{O}$, KMnO_4 and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ to prepare a tetra- Mn^{II} -sandwiched polyoxotungstate (POT) $[\text{Na}_9\text{K}[\text{Mn}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 35\text{H}_2\text{O}$. In 2003, two multi-nickel-substituted heteropolytungstates $[\text{Ni}_6\text{As}_3\text{W}_{24}\text{O}_{94}(\text{H}_2\text{O})_2]^{17-}$ and $[\text{Ni}_3\text{Na}(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{11-}$ were isolated by reaction of $\text{Na}_9[\text{AsW}_9\text{O}_{34}] \cdot 13\text{H}_2\text{O}$ with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1 mol L^{-1} NaCl solution [14]. In 2004, the first sandwich-type arsenotungstocerate $[\text{As}_2\text{W}_{18}\text{Ce}_3\text{O}_{71}(\text{H}_2\text{O})_3]^{12-}$ was obtained by Alizadeh *et al.* [15]. In 2005, Kortz *et al.* [16] group prepared a Cd^{II} -substituted tungstoarsenate $[\text{Cd}_4\text{Cl}_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{12-}$, in which the two external Cd^{II} s have a terminal Cl^- . Subsequently, they synthesized a giant dodecameric ball-shaped polytungstatoarsenate organotin derivative $[\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_{24}\{\text{Sn}(\text{CH}_3)_2\}_{12}(\text{A-AsW}_9\text{O}_{34})_{12}]^{36-}$ by reacting dimethylindichloride with the trilacunary Keggin precursor $[\text{A-AsW}_9\text{O}_{34}]^{9-}$ [17]. In 2007, Fukaya and Yamase [18] isolated three banana-shaped arsenotungstates $[\text{M}_6\text{As}_3\text{W}_{24}\text{O}_{94}(\text{H}_2\text{O})_2]^{17-}$ ($\text{M} = \text{Co}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Zn}^{\text{II}}$). In the same year, Khoshnavazi *et al.* [19] obtained a new bis(9-tungstoarsenato)tris(dioxouranate(VI)) polyoxoanion $[\text{As}_2\text{W}_{18}\text{U}_3\text{O}_{74}]^{12-}$, where three UO_2^{2+} ions are unsymmetrically sandwiched between two $[\text{A-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ groups leading to a structure of C_{3v} symmetry. In 2008, Niu *et al.* [20] communicated a novel Ln- and TM-substituted arsenotungstate $[\text{Fe}(\text{phen})_3]_2[\text{As}_2\text{W}_{18}\text{Fe}_2\{\text{Y}(\text{OH})_2\}_2\text{O}_{68}] \cdot 6.5\text{H}_2\text{O}$. Meanwhile, sandwich-type POMs $[(\text{A-}\alpha\text{-AsW}_9\text{O}_{34})_2(\text{MOH}_2)_3(\text{CO}_3)]^{11-}$ ($\text{M} = \text{Y}^{\text{III}}, \text{Yb}^{\text{III}}, \text{Sm}^{\text{III}}$) with a carbonate as a tridentate ligand were obtained [21]. In 2009, three sandwich-type tin derivatives $[\text{Sn}_3^{\text{II}}(\text{A-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{12-}$, $[(\text{PhSn}^{\text{IV}}\text{OH})_3(\text{A-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{12-}$, and $[(\text{HOSn}^{\text{IV}}\text{OH})_3(\text{AsW}_9\text{O}_{34})_2]^{12-}$ were reported by Khoshnavazi *et al.* [22]; other sandwich-type POTs $[\text{As}_2\text{W}_{18}(\text{UO}_2)_2\{(\text{H}_2\text{O})_3\text{M}\}_2\text{O}_{68}]^{10-}$ ($\text{M} = \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}$) simultaneously containing UO_2^{2+} and TM cations were separated by Khoshnavazi *et al.* [23]. As described above, most of the reported As-containing POTs are purely inorganic compounds with systems simultaneously containing organic and inorganic components less developed. We recently launched study on the reaction of $[\text{A-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ with TM or Ln cations in the presence of organic components. A $6^5 \cdot 8$ CdSO_4 -like 3-D framework $[\text{Cu}(\text{en})_2]_3[\alpha\text{-AsW}_{11}\text{NaO}_{39}] \cdot 2\text{H}_2\text{O}$ constructed by mono- Na^{I} -substituted Keggin arsenotungstates and $[\text{Cu}(\text{en})_2]^{2+}$ cations has been synthesized [24]. Very recently, an organic–inorganic composite multi- Ni^{II} -substituted arsenotungstate $[\text{Na}(\text{H}_2\text{O})_3]_2[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{Ni}(\text{H}_2\text{O})_5]\{[\text{Ni}_3(\text{dap})(\text{H}_2\text{O})_2]_2(\text{H}_2\text{W}_4\text{O}_{16})\}\{(\alpha\text{-H}_2\text{AsW}_6\text{O}_{26})[\text{Ni}_6(\text{OH})_2(\text{H}_2\text{O})(\text{dap})_2](\text{B-}\alpha\text{-HAsW}_9\text{O}_{34})_2\} \cdot 7\text{H}_2\text{O}$ consisting of three types of POT units has been communicated by us [25]. As a continuation, herein, we report two new

organic–inorganic composite sandwich-type arsenotungstates $[\text{H}_2\text{dap}]_6\text{H}_8[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]_2 \cdot 33\text{H}_2\text{O}$ (**1**) and $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$ (**2**) (dap = 1,2-diaminopropane) from reaction of $\text{Na}_8[\text{A-}\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of 1,2-diaminopropane; **1** and **2** were characterized by elemental analysis, IR spectra, X-ray single-crystal diffraction and thermogravimetric (TG) analysis.

2. Experimental

$\text{Na}_8[\text{A-}\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ was prepared according to the literature [11] and confirmed by IR spectra. All other chemicals used for synthesis were reagent grade and used without purification.

2.1. Preparation of $[\text{H}_2\text{dap}]_6\text{H}_8[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]_2 \cdot 33\text{H}_2\text{O}$ (**1**)

$\text{Na}_8[\text{A-}\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ (0.181 g, 0.068 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.452 g, 1.902 mmol) were suspended in H_2O (5 mL), to which dap (0.05 mL, 0.740 mmol) and glacial acetic acid (0.05 mL, 0.874 mmol) were added under stirring. The resulting mixture was stirred for 3 h, sealed in a Teflon-lined stainless-steel autoclave (25 mL), kept at 160°C for 5 days and then cooled to room temperature. Yellow needle crystals were filtered, washed with distilled water, and dried in air at an ambient temperature. Yield: *ca* 38% (based on $\text{Na}_8[\text{A-}\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$). Anal. Calcd (%) for $\text{C}_{18}\text{H}_{154}\text{As}_4\text{N}_{12}\text{Ni}_8\text{O}_{173}\text{W}_{36}$: C, 2.02; H, 1.45; N, 1.57; Ni, 4.39; As, 2.80; W, 61.88. Found (%): C, 2.21; H, 1.60; N, 1.45; Ni, 4.28; As, 2.89; W, 61.75.

2.2. Preparation of $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$ (**2**)

A mixture of $\text{Na}_8[\text{A-}\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ (0.399 g, 0.150 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.119 g, 0.500 mmol), dap (0.20 mL, 2.356 mmol), glacial acetic acid (0.10 mL, 1.748 mmol), and H_2O (8 mL) was stirred for 2 h, sealed in a Teflon-lined stainless-steel autoclave (25 mL), kept at 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* 45% (based on $\text{Na}_8[\text{A-}\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$). Anal. Calcd (%) for $\text{C}_{30}\text{H}_{114}\text{As}_2\text{N}_{20}\text{Ni}_8\text{O}_{74}\text{W}_{18}$: C, 6.14; H, 1.96; N, 4.77; Ni, 8.00; As, 2.55; W, 56.39. Found (%): C, 6.25; H, 2.11; N, 4.68; Ni, 8.12; As, 2.51; W, 56.46.

2.3. Physical measurements

Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analyzer. Inductively coupled plasma (ICP) spectra were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. IR spectra were obtained from a sample powder palletized with KBr on a Nicolet170 SXFT-IR spectrophotometer from 4000 to 400 cm^{-1} . The TG analysis was conducted on a Mettler-Toledo TGA/SDTA 851° thermal analyzer in flowing air at a heating rate of 10 °C min^{-1} from 25°C to 800°C.

Table 1. Crystallographic data and structural refinements for **1** and **2**.

	1	2
Empirical formula	C ₁₈ H ₁₅₄ As ₄ N ₁₂ Ni ₈ O ₁₇₃ W ₃₆	C ₃₀ H ₁₁₄ As ₂ N ₂₀ Ni ₈ O ₇₄ W ₁₈
Formula weight	10695.49	5867.89
<i>T</i> (K)	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)		
<i>a</i>	16.351(6)	13.305(4)
<i>b</i>	16.423(6)	13.882(4)
<i>c</i>	19.894(7)	17.031(5)
α	110.630(6)	68.109(5)
β	92.684(7)	71.511(4)
γ	104.946(7)	88.407(5)
<i>V</i> (Å ³), <i>Z</i>	4774(3), 1	2753.5(14), 1
<i>D</i> _c (g cm ⁻³)	3.720	3.539
μ (mm ⁻¹)	23.151	20.738
<i>F</i> (000)	4750	2647
Crystal size (mm ³)	0.32 × 0.26 × 0.15	0.24 × 0.20 × 0.12
θ range for data collections (°)	1.83–25.00	1.62–25.00
Limiting indices	–19 ≤ <i>h</i> ≤ 19 –19 ≤ <i>k</i> ≤ 18 –14 ≤ <i>l</i> ≤ 23	–15 ≤ <i>h</i> ≤ 15 –16 ≤ <i>k</i> ≤ 16 –20 ≤ <i>l</i> ≤ 18
Reflections collected	24449	13654
Independent reflections	16585 (<i>R</i> _{int} = 0.0505)	9576 (<i>R</i> _{int} = 0.0360)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.033	1.051
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0517, 0.1086	0.0491, 0.1150
Largest difference peak and hole (e Å ⁻³)	2.950 and –3.415	2.955 and –3.392

2.4. X-ray crystallography

Intensity data of **1** and **2** were collected on a Bruker Apex-2 CCD detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 296 K. Both structures were solved by direct methods and refined using full-matrix least squares on *F*². The atoms were found from successive full-matrix least-squares refinements on *F*² and Fourier syntheses. All calculations were performed using the SHELXL-97 program package [26]. Intensity data were corrected for Lorentz and polarization effects as well as for multi-scan absorption. No hydrogens associated with water were located from the difference Fourier map. Positions of hydrogens attached to carbon and nitrogen were geometrically placed and refined isotropically as a riding mode using the default SHELXTL parameters. A summary of crystal data and structure refinements for **1** and **2** is listed in table 1. Selected bond lengths (Å) and angles (°) for **1** and **2** are displayed in table 2.

3. Results and discussion

3.1. Synthesis

Trivalent Keggin POM precursor [A- α -AsW₉O₃₄]⁹⁻ can function as the polydentate inorganic ligand that coordinates to TM cations, forming lacunary POM derivatives. For example, purely inorganic sandwich-type POTs [As₂W₁₈M₄(H₂O)₂O₆₈]¹⁰⁻

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

1					
Ni1–O28	1.994(14)	Ni2–O6	2.030(14)	Ni3–O67	2.150(15)
Ni1–O1W	2.020(14)	Ni2–O16	2.068(14)	Ni3–O67 ^{#2}	2.152(12)
Ni1–O24	2.031(14)	Ni2–O33	2.132(14)	Ni4–O66 ^{#2}	1.995(14)
Ni1–O6	2.100(14)	Ni2–O33 ^{#1}	2.133(12)	Ni4–O2W	2.051(12)
Ni1–O33	2.102(13)	Ni3–O68	1.955(16)	Ni4–O63 ^{#2}	2.053(12)
Ni1–O16 ^{#1}	2.107(12)	Ni3–O60	1.974(12)	Ni4–O54	2.090(14)
Ni2–O14	1.998(15)	Ni3–O57	2.070(12)	Ni4–O57	2.103(13)
Ni2–O20	2.004(12)	Ni3–O54 ^{#2}	2.072(12)	Ni4–O67 ^{#2}	2.118(12)
2					
Ni1–N3	1.9998(4)	Ni2–N6	2.1074(4)	Ni4–O21 ^{#5}	2.0613(6)
Ni1–N1	2.0084(4)	Ni2–N6 ^{#3}	2.1074(5)	Ni4–N9	2.0861(6)
Ni1–N2	2.0175(4)	Ni3–N7	2.0830(4)	Ni4–O18 ^{#5}	2.1067(5)
Ni1–N4	2.0908(4)	Ni3–N7 ^{#4}	2.0830(4)	Ni4–O34	2.1626(6)
Ni1–O1W	2.1439(5)	Ni3–N8 ^{#4}	2.0831(5)	Ni5–O24 ^{#5}	1.9842(5)
Ni1–O1	2.1799(5)	Ni3–N8	2.0831(4)	Ni5–O33	1.9889(5)
Ni2–N5	2.0858(5)	Ni3–O32	2.1864(4)	Ni5–O21 ^{#5}	2.0508(6)
Ni2–N5 ^{#3}	2.0858(4)	Ni3–O32 ^{#4}	2.1864(5)	Ni5–O18	2.1014(6)
Ni2–O26 ^{#3}	2.0924(5)	Ni4–O27	2.0166(5)	Ni5–O34 ^{#5}	2.1173(6)
Ni2–O26	2.0924(5)	Ni4–O30	2.0349(5)	Ni5–O34	2.1184(5)

Symmetry codes: #1: $-x - 1, -y + 2, -z + 1$; #2: $-x, -y + 1, -z$; #3: $-x + 1, -y + 1, -z$; #4: $-x + 2, -y + 1, -z + 1$; #5: $-x + 1, -y + 1, -z + 1$.

(M = Cd^{II}, Co^{II}, Cu^{II}, Fe^{II}, Mn^{II}, Ni^{II}, Zn^{II}) were synthesized by Bi *et al.* in 2001 [11]. A banana-shaped POT [Ni₆As₃W₂₄O₉₄(H₂O)₂]¹⁷⁻ was also prepared by Mbomekalle *et al.* [14] by reaction of [A- α -AsW₉O₃₄]⁹⁻ with Ni²⁺ in 1 mol L⁻¹ NaCl solution. However, it is difficult to design a rational synthetic route to organic–inorganic composite TM-substituted arsen tungstates by conventional aqueous solution method at atmosphere pressure, because trivalent Keggin precursor [A- α -AsW₉O₃₄]⁹⁻, TM cations, and organic ligands poorly dissolve in aqueous solution. As a result, we employed the hydrothermal method to explore this system. The hydrothermal method has become very effective in preparing organic–inorganic composite solid materials because hydrothermal conditions are able to make the reaction shift from the thermodynamic to the kinetic so that the equilibrium phases are replaced by structurally more complicated metastable phases [27, 28].

Exploring the hydrothermal reaction of the trivalent Keggin precursor [A- α -AsW₉O₃₄]⁹⁻ (figure 1a) with TM cations, we firstly isolated a CdSO₄-like 3-D framework [Cu(en)₂]₃[α -AsW₁₁NaO₃₉]₂·2H₂O (**3**) (figure 1b) when the reaction was preformed with [α -AsW₉O₃₄]⁹⁻/Cu²⁺/en molar ratio of 0.050 : 0.252 : 1.480 at 160°C for 5 days [24]. The transformation of [A- α -AsW₉O₃₄]⁹⁻ → [α -AsW₁₁O₃₉]⁷⁻ was observed. When the [A- α -AsW₉O₃₄]⁹⁻/Cu²⁺/en molar ratio was changed to 0.100 : 1.000 : 2.220 and the reaction was kept at 160°C for 11 days, an unexpected saturated Dawson-type compound [H₂en]₃[α -As₂W₁₈O₆₂]₂·0.5en·9H₂O (**4**) (figure 1c) was afforded [29], where the structural transformation of the trivalent Keggin [A- α -AsW₉O₃₄]⁹⁻ polyoxoanion to the saturated Dawson [α -As₂W₁₈O₆₂]⁶⁻ polyoxoanion was prepared providing powerful experimental proof for the saturated Dawson polyoxoanion as fusion of two trivalent Keggin polyoxoanions by sharing six oxygens. Subsequently, when [A- α -AsW₉O₃₄]⁹⁻ reacted with Ni²⁺ in the presence of dap with [A- α -AsW₉O₃₄]⁹⁻/Ni²⁺/dap molar ratio of 0.050 : 0.500 : 0.589 at 160°C for 5 days, an organic–inorganic composite

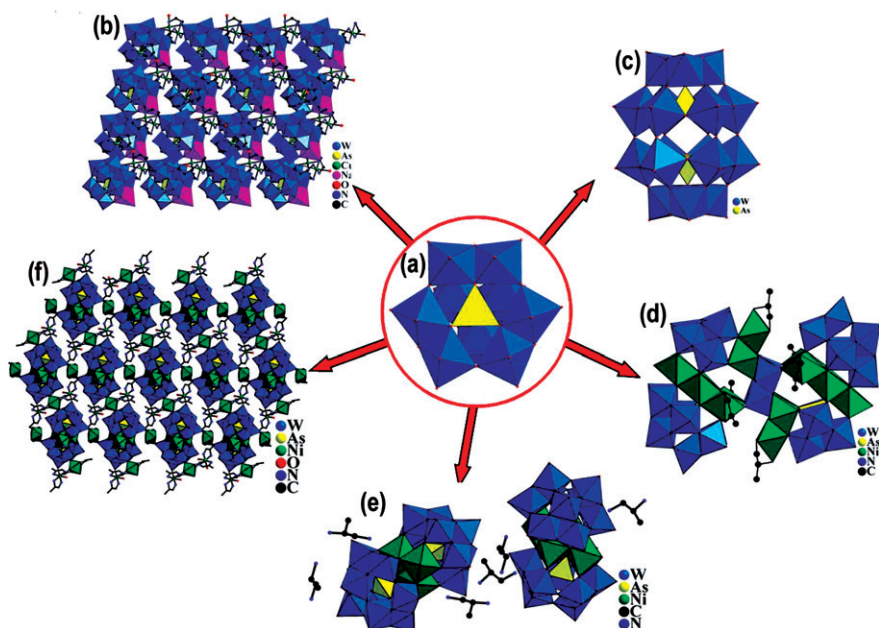


Figure 1. Summary of the trivalent Keggin precursor $[A-\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ and its derivatives.

multi-Ni^{II}-substituted arsenotungstate $[\text{Na}(\text{H}_2\text{O})_3]_2[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{Ni}(\text{H}_2\text{O})_5]\{[\text{Ni}_3(\text{dap})(\text{H}_2\text{O})_2]_2(\text{H}_2\text{W}_4\text{O}_{16})\}\{(\alpha\text{-H}_2\text{AsW}_6\text{O}_{26})[\text{Ni}_6(\text{OH})_2(\text{H}_2\text{O})(\text{dap})_2](\text{B-}\alpha\text{-HAsW}_9\text{O}_{34})\}_2 \cdot 7\text{H}_2\text{O}$ (**5**) (figure 1d) consisting of three types of POT units was discovered [25]; the partial $[A-\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ precursors were isomerized to $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ and degraded to the $[\alpha\text{-AsW}_6\text{O}_{26}]^{11-}$ unit. When the $[A-\alpha\text{-AsW}_9\text{O}_{34}]^{9-}/\text{Ni}^{2+}/\text{dap}$ molar ratio was 0.068 : 1.902 : 0.740, the organic-inorganic composite sandwich-type arsenotungstate **1** was separated (figure 1e). When the $[A-\alpha\text{-AsW}_9\text{O}_{34}]^{9-}/\text{Ni}^{2+}/\text{dap}$ molar ratio was changed as 0.150 : 0.500 : 2.356, another organic-inorganic composite 2-D sandwich-type arsenotungstate **2** was synthesized (figure 1f). In the formation of **1** and **2**, the transformation of $[A-\alpha\text{-AsW}_9\text{O}_{34}]^{9-} \rightarrow [\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ was also observed. Similar configuration transformations were previously observed in the phosphotungstates and germanotungstates [30, 31]. It is interesting to explore the key factors in the configuration transformation of vacant POM units. In the formation of **1**, **2**, **3**, and **5** the pH of solution is the major factor controlling the configuration transformation. Because the pH values of **1**, **2**, and **5** are higher than that of **3**, the trivalent or polyvacant Keggin POM units can exist in **1**, **2**, and **5**, while the monovacant Keggin POM unit is formed in **3**. In the formation of **4**, the main factor in transforming the trivalent Keggin $[A-\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ polyoxoanion to the saturated Dawson $[\alpha\text{-As}_2\text{W}_{18}\text{O}_{62}]^{6-}$ polyoxoanion is the long time of reaction.

3.2. Crystal structures of **1** and **2**

The molecular structures of **1** and **2** are different although both crystallize in the triclinic $P\bar{1}$ space group. The common structural feature is that both contain the

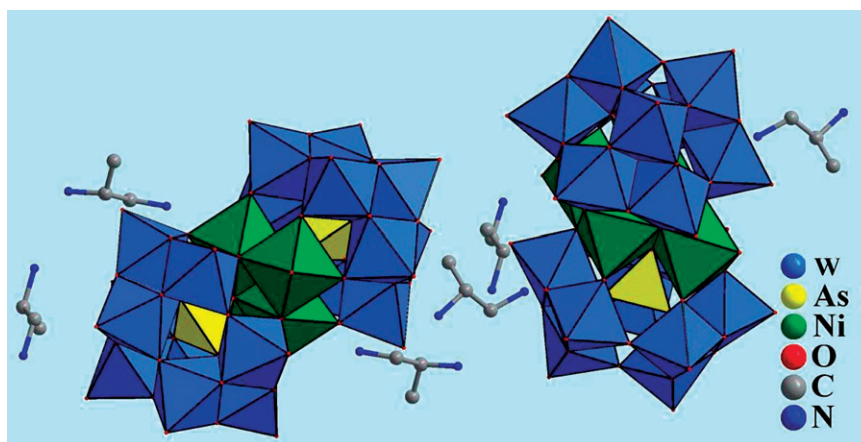


Figure 2. Combined ball-and-stick and polyhedral representation of the molecular structure of **1**. The hydrogen atoms attached to dap molecules, protons, and lattice water molecules are omitted for clarity.

classical tetra-Ni^{II} sandwiched polyoxoanions $[\text{Ni}_4(\text{L})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ ($\text{L} = \text{H}_2\text{O}$ for **1** and dap for **2**) as the fundamental building units. **1** is a discrete structure and is composed of two tetra-Ni^{II} sandwiched polyoxoanions $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ with different spatial orientation whereas **2** displays an organic–inorganic composite 2-D sheet architecture constructed by tetra-Ni sandwiched $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ units and $[\text{Ni}(\text{dap})_2]^{2+}$ bridges.

As shown in figure 2, the molecular structure of **1** consists of two tetra-Ni^{II}-sandwiched $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ polyoxoanions, six diprotonated $[\text{H}_2\text{dap}]^{2+}$ cations, eight protons, and 33 lattice waters. In **1**, there are four crystallographically independent Ni²⁺ cations, Ni1, Ni2, Ni3, and Ni4, which are all incorporated into the sandwich belts of two $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ polyoxoanions. Ni1 and Ni4 are six-coordinate octahedral constituted by two μ_2 -O from one $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ [Ni-O_{μ_2} : 1.994(14)–2.053(12) Å], two μ_3 -O from the other $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ [Ni-O_{μ_3} : 2.070(12)–2.107(12) Å], one μ_4 -O from the AsO_4 tetrahedron [Ni-O_{μ_4} : 2.102(13)–2.152(12) Å] and one oxygen from water [Ni-O_w : 2.020(14)–2.051(12) Å]. The Ni2 and Ni3 cations also adopt octahedral configurations, built by two μ_2 -O from two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ units [Ni-O_{μ_2} : 1.974(12)–2.004(12) Å], two μ_3 -O from two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ units [Ni-O_{μ_3} : 2.030(14)–2.072(12) Å] and two μ_4 -O from two AsO_4 tetrahedra [Ni-O_{μ_4} : 2.133(12)–2.152(12) Å]. Two $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ polyoxoanions in **1** have different spatial orientations, very similar to the previous reported phosphotungstate $(\text{enH}_2)_{10}[\text{Mn}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 20\text{H}_2\text{O}$ [32]. This type of a molecular unit containing double polyoxoanions is very rare [30, 32]. For example, Zhao *et al.* [30] reported a double-cluster POT $\{[\text{Ni}_7(\mu_3\text{-OH})_3\text{O}_2(\text{dap})_3(\text{H}_2\text{O})_6]\{\text{B-}\alpha\text{-PW}_9\text{O}_{34}\}\}[\{\text{Ni}_6(\mu_3\text{-OH})_3(\text{dap})_3(\text{H}_2\text{O})_6\}(\text{B-}\alpha\text{-PW}_9\text{O}_{34})][\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2] \cdot 4.5\text{H}_2\text{O}$ simultaneously containing hepta- and hexa -Ni^{II}-substituted trivacant Keggin units. In addition, molecules of **1** are aligned along the crystallographic *b* axis in the mode of –AAA– (figure 3). Diprotonated $[\text{H}_2\text{dap}]^{2+}$ and lattice water fill the gap of the polyoxoanions in **1**. Taking into account hydrogen-bonding interactions between nitrogens of $[\text{H}_2\text{dap}]^{2+}$ and oxygens of the polyoxoanions or lattice water ($\text{N} \cdots \text{O}$ distances of 2.80(2)–3.41(3) Å), 3-D supramolecular structures can be constructed. As a result, the interactions between

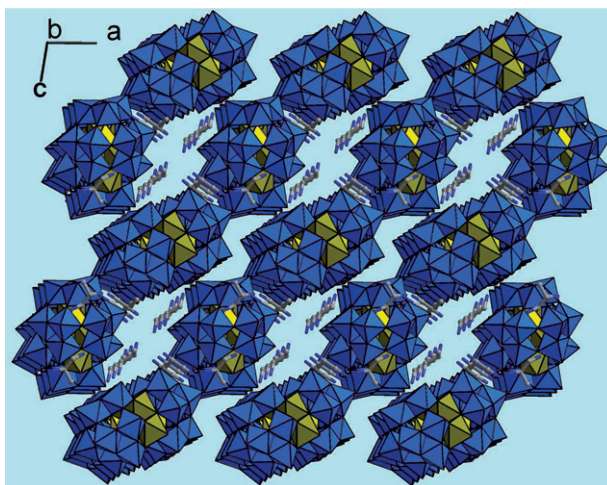


Figure 3. The 3-D supramolecular structure of **1** constructed via hydrogen bonds between nitrogens of $[\text{H}_2\text{dap}]^{2+}$ and oxygen of the polyoxoanions or lattice water.

the $[\text{H}_2\text{dap}]^{2+}$ cations and the polyoxoanions are mainly hydrogen bonds, van der Waals, and electrostatic forces.

The centric $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\}$ structural unit of **2** is composed of a tetra- Ni^{II} sandwiched $[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{8-}$ subunit, two pendent $[\text{Ni}1(\text{dap})_2(\text{H}_2\text{O})_3]^{2+}$ cations, and two crystallographic independent $[\text{Ni}(\text{dap})_2]^{2+}$ cations, $[\text{Ni}2(\text{dap})_2]^{2+}$ and $[\text{Ni}3(\text{dap})_2]^{2+}$ (figure 4). The $[\text{Ni}1(\text{dap})_2(\text{H}_2\text{O})_3]^{2+}$ is octahedral by four nitrogens from two dap ligands [Ni-N : 1.9998(4)–2.0908(4) Å], one water [Ni-O_w : 2.1439(5) Å], and one terminal oxygen from $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ [Ni-O_t : 2.1799(5) Å]. The $[\text{Ni}2(\text{dap})_2]^{2+}/[\text{Ni}3(\text{dap})_2]^{2+}$ on special sites with atomic coordinates of (1/2,1/2,0) and (1,1/2,1.2) lead to site occupancy of 50% for Ni2 and Ni3, respectively. The bridging $[\text{Ni}2(\text{dap})_2]^{2+}$ and $[\text{Ni}3(\text{dap})_2]^{2+}$ also are octahedral, in which four nitrogens from two dap's establish the equatorial plane [Ni-N : 2.0830(4)–2.1074(4) Å] and two terminal oxygens from adjacent $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ fragments occupy axial sites [Ni-O : 2.0924(5)–2.1864(4) Å]. Both Ni4 and Ni5 are incorporated in the sandwich belt of the $[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{8-}$ subunit with distorted octahedral geometries, however, the coordination environments of Ni4 and Ni5 are somewhat different. The octahedron of Ni4 is defined by two $\mu_2\text{-O}$ from one $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ unit [Ni-O_{μ_2} : 2.0166(5)–2.0349(5) Å], two $\mu_3\text{-O}$ from the other $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ unit [Ni-O_{μ_3} : 2.0613(6)–2.1067(5) Å], one $\mu_4\text{-O}$ from a AsO_4 tetrahedron [Ni-O_{μ_4} : 2.1626(6) Å] and one nitrogen from dap [Ni-N : 2.0861(6) Å], whereas the octahedron of Ni5 is built by two $\mu_2\text{-O}$ from two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ units [Ni-O_{μ_2} : 1.9842(5)–2.1014(6) Å], two $\mu_3\text{-O}$ from two $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ units [Ni-O_{μ_3} : 2.0508(6)–2.1014(6) Å], and two $\mu_4\text{-O}$ from two AsO_4 tetrahedra [Ni-O_{μ_4} : 2.1173(6)–2.1184(5) Å].

The organic-inorganic composite tetra- Ni^{II} sandwiched $[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{8-}$ subunit is constructed from two trivalent Keggin $[\text{B-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ fragments in a staggered fashion connected by a rhomb-like $\{\text{Ni}_4\text{O}_{14}\text{N}_2\}$ group. The tetra- Ni^{II} sandwiched $[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{8-}$ subunit in **2** is distinct from

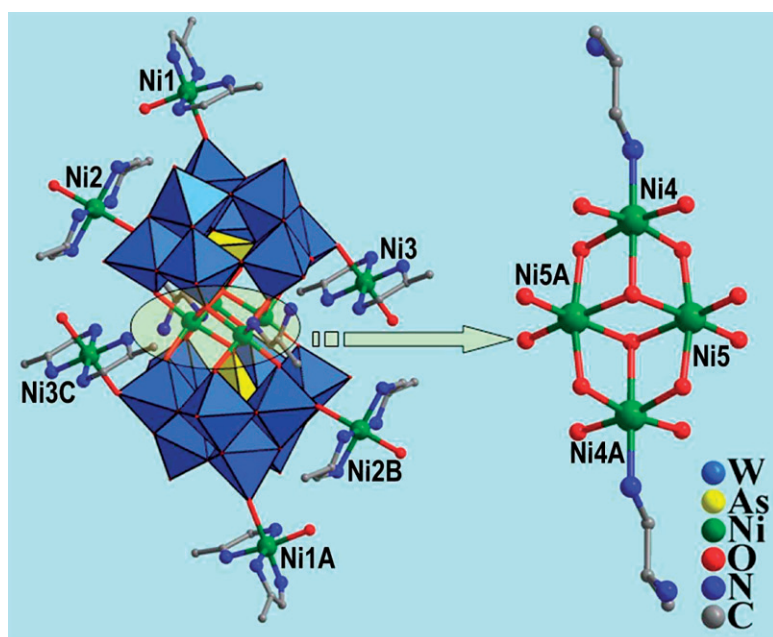


Figure 4. Polyhedral and ball-and-stick representation of **2**.

The atoms with the suffix A, B, and C are generated by the symmetry operation. A: $1-x, 1-y, 1-z$; B: $x, y, z+1$; C: $-1+x, y, z$. Lattice waters and hydrogens attached to carbon and nitrogen are omitted for clarity.

the reported inorganic $[M_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ polyoxoanions ($M = Zn^{II}, Cd^{II}, Co^{II}, Cu^{II}, Fe^{II}, Mn^{II}, Ni^{II}, Zn^{II}$) [10, 11]. Two monoprotonated dap ligands in **2** are substituted for two waters at two unshared MO_6 vertices from the rhomb-like M_4O_{16} group in $[M_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$ resulting in the $[Ni_4(Hdap)_2(B-\alpha-AsW_9O_{34})_2]^{8-}$ subunit. Organic N/O-ligands being substituted for two waters in sandwich-type POMs have been encountered in previous studies [33–36]. For instance, in 2008, Wang *et al.* [34] reported a sandwich-type POT $K_2Na_5[H_6N_2(CH_2)_6][Ni_4(H_2O)_2(H_2PW_9O_{34})_2] \cdot 4H_2O$, in which two hexanediamine ligands replaced two waters. Recently, we communicated a 2-D sandwich-type POT $[DMAH]_4\{[Mn(DMF)_4]_2[Mn_4(DMF)_2(\alpha-B-HPW_9O_{34})_2]\}$, where two DMF ligands replaced two waters (figure 5a) [35]. In 2009, Wang *et al.* [36] prepared two tetra-Co substituted germanotungstates $[enH_2][C_8N_4H_{22}]_3H_2[Co_4(enH)_2(GeW_9O_{34})_2] \cdot 6H_2O$ and $[Co(en)_3]_2H_6[Co_4(enH)_2(GeW_9O_{34})_2] \cdot 14H_2O$, in which two en ligands replaced two waters. Besides these organic–inorganic composite tetra-TM-substituted sandwich-type POM fragments, other organic–inorganic composite TM-substituted sandwich-type POM fragments have been reported [5, 37–39]. In 2005, Pope *et al.* [37] communicated a di- W^{VI} and mono- $[Co^{III}(en)]$ -sandwiched phosphotungstate $Na_{6.5}K_{5.5}[K\{Co(en)WO_4\}WO(H_2O)(PW_9O_{34})_2] \cdot 19H_2O$ (figure 5b) and a $[(en)Co^{III}(\mu-OH)_2Co^{III}(en)]^{4+}$ -sandwiched phosphotungstate $Na_{6.5}K_{5.5}[K\{Co(en)WO_4\}WO(H_2O)(PW_9O_{34})_2] \cdot 19H_2O$ (figure 5c). In 2008, Niu *et al.* [38] discovered a hexa-copper-2,2'-bipy cluster substituted sandwich-type germanotungstate $[Cu(2,2'-bipy)]_2[Cu(2,2'-bipy)_2]_2[Cu_6(2,2'-bipy)_2(GeW_9O_{34})_2] \cdot 3H_2O$ (figure 5d) with four supporting $[Cu(2,2'-bipy)]^{2+}$ complex cations.

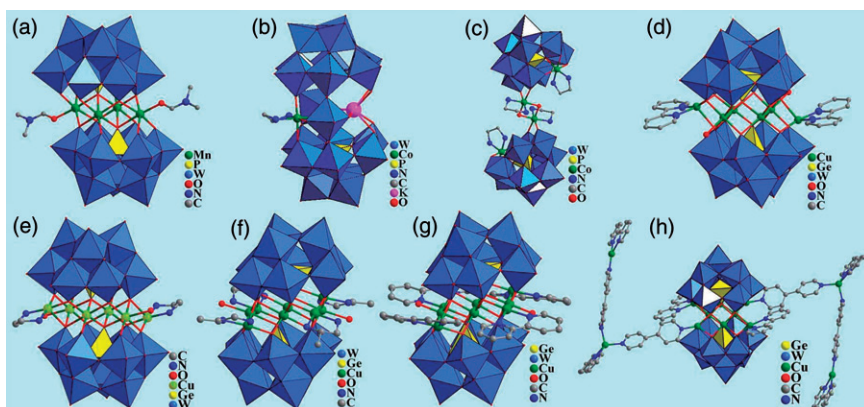


Figure 5. Other reported organic–inorganic composite sandwich-type fragments: (a) the $[\text{Mn}_4(\text{DMF})_2(\alpha\text{-B-HPW}_9\text{O}_{34})_2]^{8-}$ fragment in $[\text{DMAH}]_4\{[\text{Mn}(\text{DMF})_4]_2[\text{Mn}_4(\text{DMF})_2(\alpha\text{-B-HPW}_9\text{O}_{34})_2]\}$, (b) the $[\text{K}\{\text{Co}(\text{en})\text{WO}_4\}\{\text{WO}(\text{H}_2\text{O})\}\{\text{PW}_9\text{O}_{34}\}_2]^{12-}$ fragment in $\text{Na}_{6.5}\text{K}_{5.5}[\text{K}\{\text{Co}(\text{en})\text{WO}_4\}\text{WO}(\text{H}_2\text{O})\{\text{PW}_9\text{O}_{34}\}_2] \cdot 19 \text{H}_2\text{O}$, (c) the $\{[\text{Co}(\text{en})(\mu\text{-OH})_2\text{Co}(\text{en})]\{\text{PW}_{10}\text{O}_{37}\text{Co}(\text{en})\}_2\}^{8-}$ fragment in $\text{Na}_7\text{K}_5\{[\text{Co}(\text{en})(\mu\text{-OH})_2\text{Co}(\text{en})]\{\text{PW}_{10}\text{O}_{37}\text{Co}(\text{en})\}_2\} \cdot 20\text{H}_2\text{O}$, (d) the $[\text{Cu}_6(2,2'\text{-bipy})_2][\text{Cu}_6(2,2'\text{-bipy})_2(\text{GeW}_9\text{O}_{34})_2]^{8-}$ fragment in $[\text{Cu}(2,2'\text{-bipy})_2][\text{Cu}_6(2,2'\text{-bipy})_2][\text{Cu}_6(2,2'\text{-bipy})_2(\text{GeW}_9\text{O}_{34})_2] \cdot 3\text{H}_2\text{O}$, (e) the $[\text{Cu}_6(\text{en})_2(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{8-}$ fragment in $[\text{Cu}(\text{en})_2][\text{Cu}(\text{deta})(\text{H}_2\text{O})_2][\text{Cu}_6(\text{en})_2(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 6\text{H}_2\text{O}$, (f) the $[\text{Cu}_8(\text{dap})_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{4-}$ fragment in $\text{H}_4[\text{Cu}_8(\text{dap})_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 13\text{H}_2\text{O}$, (g) the $[\text{Cu}_8(2,2'\text{-bpy})_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{4-}$ fragment in $[\text{Cu}_2(\text{H}_2\text{O})_2(2,2'\text{-bpy})_2][\text{Cu}(\text{bdyl})_2][\text{Cu}_8(2,2'\text{-bpy})_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 4\text{H}_2\text{O}$, (h) the $[\text{Cu}_2(2,2'\text{-bpy})_2(4,4'\text{-bpy})_2][\text{Cu}_2\text{Cu}_6^{\text{II}}(2,2'\text{-bpy})_2(4,4'\text{-bpy})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{2-}$ fragment in $[\text{Cu}^{\text{I}}(2,2'\text{-bpy})(4,4'\text{-bpy})_2][\text{Cu}_2^{\text{I}}(2,2'\text{-bpy})_2(4,4'\text{-bpy})_2][\text{Cu}_2^{\text{II}}\text{Cu}_6^{\text{II}}(2,2'\text{-bpy})_2(4,4'\text{-bpy})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 2\text{H}_2\text{O}$.

Later, Zhao *et al.* [39] prepared a CdSO_4 -type 3-D framework $[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{deta})(\text{H}_2\text{O})_2][\text{Cu}_6(\text{en})_2(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 6\text{H}_2\text{O}$ constructed by hexa-copper-en cluster sandwich-type POT fragments (figure 5e). In 2008, Zhao *et al.* [5] also synthesized a family of unprecedented octa-copper-substituted sandwich-type germanotungstates, in which, the copper centers in the sandwich belt can be chelated by dap (figure 5f), en, 2,2'-bpy (figure 5g) or 4,4'-bpy (figure 5h), displaying novel structural motifs. As shown above, introducing the organic N/O-ligands to the sandwich belt of POMs can generate novel TMSPs, providing a meaningful route for designing and synthesizing more organic–inorganic composite high-nuclear TM-substituted sandwich-type POMs.

The most intriguing feature of **2** is that each $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\}$ unit connects to four others through four $[\text{Ni}(\text{dap})_2]^{2+}$ bridges giving rare 2-D sheet architecture in the *ac* plane (figure 6), almost isostructural to 2-D POTs $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\alpha\text{-B-HSiW}_9\text{O}_{34})_2]\} \cdot 7\text{H}_2\text{O}$, $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\alpha\text{-B-HGeW}_9\text{O}_{34})_2]\} \cdot 6\text{H}_2\text{O}$, and $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$ was reported by Zhao *et al.* [33]. Recently, several similar inorganic–organic composite 2-D layer structures constructed by tetra-M ($\text{M} = \text{Mn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$) substituted POM units $[\text{DMAH}]_4\{[\text{Mn}(\text{DMF})_4]_2[\text{Mn}_4(\text{DMF})_2(\alpha\text{-B-HPW}_9\text{O}_{34})_2]\}$ [35], $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{en})_2]_3[\text{Cu}_4(\text{GeW}_9\text{O}_{34})_2] \cdot 10\text{H}_2\text{O}$ [40], and $(\text{H}_2\text{en})\{[\text{Zn}(\text{en})_2]_4[\text{Zn}_4(\text{Hen})_2(\text{GeW}_9\text{O}_{34})_2]\} \cdot 10\text{H}_2\text{O}$ [40] have been reported. Furthermore, 1-D chain-like sandwich-type POTs $\text{K}_4\text{Na}_4[\text{Cu}_2(\text{H}_2\text{O})_8\text{Cu}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2] \cdot 14\text{H}_2\text{O}$ [41], $\text{K}_8[\text{Cu}_2(\text{H}_2\text{O})_8\text{Cu}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-SiW}_9\text{O}_{34})_2] \cdot 4\text{H}_2\text{O}$ [41], and $[\text{Cu}(\text{en})_2]_3[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}_4(\text{GeW}_9\text{O}_{34})_2][\text{Cu}(\text{en})_2] \cdot 9.5\text{H}_2\text{O}$ [42] have been reported. The inorganic–organic composite 2-D sheet structure constructed by octa- Cu^{II} substituted POM units

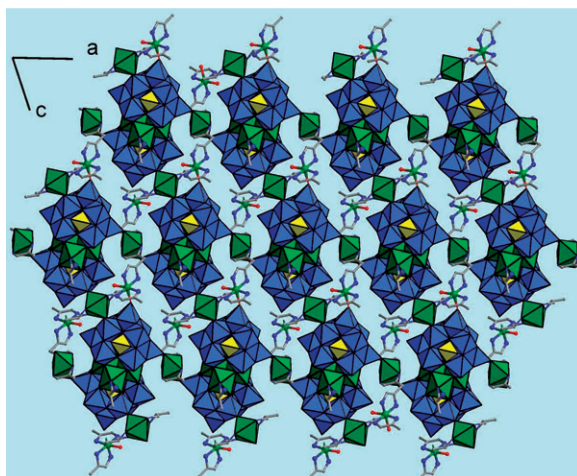


Figure 6. The inorganic–organic composite 2-D sheet architecture in the ac plane built by $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\}$ units through $[\text{Ni}(\text{dap})_2]^{2+}$ bridges.

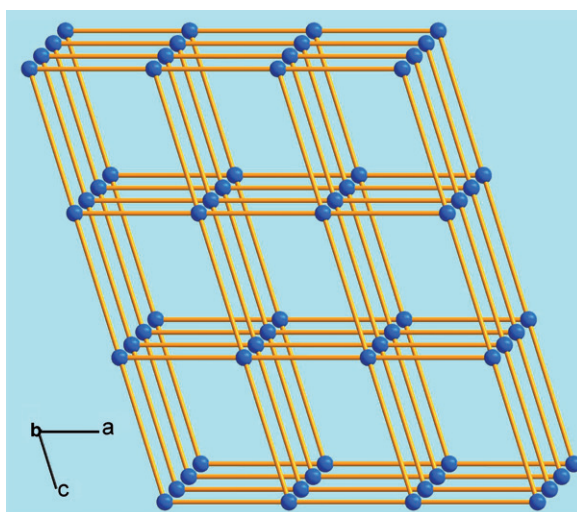


Figure 7. The packing alignment of the 2-D (4,4)-topology along the b -axis.

$[\text{Cu}_2(\text{H}_2\text{O})_2(2,2'\text{-bpy})_2]\{[\text{Cu}(\text{bdyl})]_2[\text{Cu}_8(2,2'\text{-bpy})_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$ has been addressed by Zhao *et al.* [5]. From the topological point of view, considering $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\}$ as a four-connected node, the structure belongs to a 2-D (4,4)-topology network (figure 7). Adjacent sheets are aligned along the crystallographic b axis in the mode of $-\text{AAA}-$ (figure 7). Additionally, taking into account strong hydrogen bonding interactions between $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})_2]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\}$ units and water, the 3-D supramolecular structures are formed through $\text{N-H} \cdots \text{O}$ hydrogen bonds with $\text{N} \cdots \text{O}$ distances of 2.9197(6)–3.3923(8) Å.

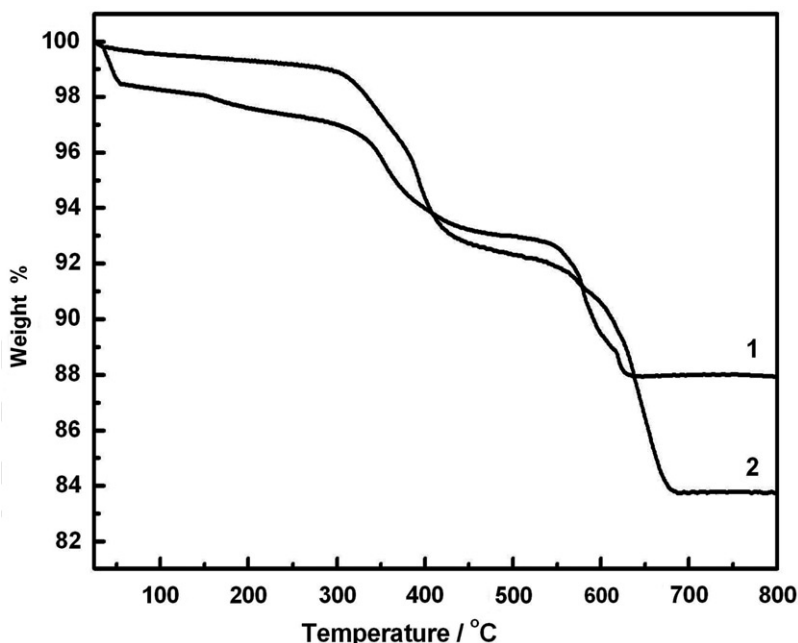


Figure 8. The TG curves of **1** and **2** measured in flowing air with a heating rate of $10^{\circ}\text{C min}^{-1}$ from 25°C to 800°C .

3.3. IR spectra

As expected, IR spectra of **1** and **2** display the characteristic vibrations of the Keggin-type structure in the low-wavenumber region. Four characteristic vibrations resulting from the Keggin-type polyoxoanion, $\nu(\text{W}-\text{O}_t)$, $\nu(\text{As}-\text{O}_a)$, $\nu(\text{W}-\text{O}_b)$, and $\nu(\text{W}-\text{O}_c)$, are observed at 946 , 882 , 761 , and 690 cm^{-1} for **1**, and 946 , 881 , 769 , and 713 cm^{-1} for **2**, respectively. These characteristic bands can be easily assigned by comparing with the corresponding bands of trivacant or plenary Keggin polyoxoanions. In comparison with those of $\text{Na}_8[\text{A}-\alpha\text{-HAsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ [953 , 841 , 785 , and 704 cm^{-1} for $\nu(\text{W}-\text{O}_t)$, $\nu(\text{As}-\text{O}_a)$, $\nu(\text{W}-\text{O}_b)$, and $\nu(\text{W}-\text{O}_c)$], the characteristic $\nu(\text{W}-\text{O}_t)$, $\nu(\text{As}-\text{O}_a)$, $\nu(\text{W}-\text{O}_b)$, and $\nu(\text{W}-\text{O}_c)$ vibration frequencies in **1** and **2** have shifts which may be related to the structural transformation of $[\text{A}-\alpha\text{-AsW}_9\text{O}_{34}]^{9-} \rightarrow [\text{B}-\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ and the stronger interactions between organic/metal-organic cations and polyoxoanions. Additionally, stretching bands of $-\text{NH}_2$ and $-\text{CH}_2$ are observed at 3126 and 2933 cm^{-1} for **1**, and 3246 and 2965 cm^{-1} for **2**, and the bending vibration bands of the $-\text{NH}_2$ and $-\text{CH}_2$ groups also appear at 1613 and 1437 cm^{-1} for **1** and 1589 and 1460 cm^{-1} for **2**. The appearance of these characteristic signals confirms the presence of dap in **1** and **2** and are consistent with the reported data [5]. The occurrence of a band at 3416 cm^{-1} for **1** and 3451 cm^{-1} for **2** suggests the presence of the lattice water.

3.4. TG analysis

Thermal stabilities of **1** and **2** were investigated on crystalline samples under air from 25°C to 800°C (figure 8). The TG curve of **1** shows three weight-loss steps. One (3.27%)

between 25°C and 310°C corresponds to the loss of 18 lattice waters (Calcd 3.03%). The combined weight loss of the second and third steps is 8.75% between 310°C and 800°C, assigned to the removal of the remaining 15 lattice waters, two coordinated waters, six diprotonated dap molecules, and dehydration of eight protons (Calcd 8.71%). The TG curve of **2** also exhibits three stages of weight loss. The first of 1.10% from 25°C–301°C corresponds to the release of four lattice waters (Calcd 1.23%). The second weight loss of 7.48% from 301°C to 572°C is attributed to the removal of two coordinated waters and five dap molecules (Calcd 6.93%). After 572°C, a weight loss of 7.29% until 800°C is observed and assigned to the decomposition of three dap ligands and two monoprotinated dap ligands (Calcd 6.62%).

4. Conclusions

Two new organic–inorganic composite sandwich-type arsenotungstates $[\text{H}_2\text{dap}]_6\text{H}_8[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]_2 \cdot 33\text{H}_2\text{O}$ (**1**) and $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]\} \cdot 4\text{H}_2\text{O}$ (**2**) have been hydrothermally synthesized and structurally characterized. The common structural feature is that both contain the classical tetra-Ni^{II}-sandwiched polyoxoanions $[\text{Ni}_4(\text{L})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ (L = H₂O for **1** and dap for **2**) as the fundamental building units. **1** is composed of two tetra-Ni^{II}-sandwiched polyoxoanions $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ with different spatial orientation, while **2** displays an organic–inorganic composite 2-D sheet architecture constructed by tetra-Ni sandwiched $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-AsW}_9\text{O}_{34})_2]^{10-}$ units and $[\text{Ni}(\text{dap})_2]^{2+}$ bridges. The system containing the trivalent Keggin precursor $[\text{A-}\alpha\text{-AsW}_9\text{O}_{34}]^{9-}$ with TM cations has been extensively explored. Herein, some previously reported organic–inorganic composite TM-substituted sandwich-type POTs have been summarized.

Supplementary material

CCDC 761876 and 761877 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

- [1] M.T. Pope. *Heteropoly and Isopoly Oxometalates*, p. 31, Springer, New York (1983).
- [2] A. Müller, H. Reuter, S. Dillinger. *Angew. Chem. Int. Ed. Engl.*, **34**, 2328 (1995).
- [3] J.M. Clemente-Juan, E. Coronado. *Coord. Chem. Rev.*, **193–195**, 361 (1999).
- [4] J.P. Wang, J.W. Zhao, P.T. Ma, J.C. Ma, L.P. Yang, Y. Bai, M.X. Li, J.Y. Niu. *Chem. Commun.*, 2362 (2009).
- [5] J.W. Zhao, C.M. Wang, J. Zhang, S.T. Zheng, G.Y. Wang. *Chem. Eur. J.*, **14**, 9223 (2008).
- [6] K. Wassermann, M.H. Dickman, M.T. Pope. *Angew. Chem. Int. Ed. Engl.*, **36**, 1445 (1997).
- [7] P. Mialane, A. Dolbecq, J. Marrot, E. Rivière, F. Sécheresse. *Angew. Chem. Int. Ed.*, **42**, 3523 (2003).
- [8] C. Dablemont, C.G. Hamaker, R. Thouvenot, Z. Sojka, M. Che, E.A. Maatta, A. Proust. *Chem. Eur. J.*, **12**, 9150 (2006).
- [9] N. Zamstein, A. Tarantul, B. Tsukerblat. *Inorg. Chem.*, **46**, 8851 (2007).
- [10] H.J. Evans Jr, C.M. Tourné, G.F. Tourné, T.J.R. Weakley. *J. Chem. Soc., Dalton Trans.*, 2699 (1986).
- [11] L.-H. Bi, R.-D. Huang, J. Peng, E.-B. Wang, Y.-H. Wang, C.-W. Hu. *J. Chem. Soc., Dalton Trans.*, 121 (2001).
- [12] Y. Wang, C. Hu, J. Peng, E. Wang, Y. Xu. *J. Mol. Struct.*, **598**, 161 (2001).
- [13] C. Rosu, D.C. Crans, T.J.R. Weakley. *Polyhedron*, **21**, 959 (2002).
- [14] I.M. Mbomekalle, B. Keita, M. Nierlich, U. Kortz, P. Berthet, L. Nadjó. *Inorg. Chem.*, **42**, 5143 (2003).
- [15] M.H. Alizadeh, H. Eshtiagh-Hosseini, R. Khoshnavazi. *J. Mol. Struct.*, **688**, 33 (2004).
- [16] F. Hussain, L.-H. Bi, U. Rauwald, M. Reicke, U. Kortz. *Polyhedron*, **24**, 847 (2005).
- [17] U. Kortz, F. Hussain, M. Reicke. *Angew. Chem. Int. Ed.*, **44**, 3773 (2005).
- [18] K. Fukaya, T. Yamase. *Bull. Chem. Soc. Jpn.*, **80**, 178 (2007).
- [19] R. Khoshnavazi, H. Eshtiagh-hosseini, M.H. Alizadeh, M.T. Pope. *Inorg. Chim. Acta*, **360**, 686 (2007).
- [20] J. Wang, W. Wang, J. Niu. *J. Mol. Struct.*, **873**, 29 (2008).
- [21] R. Khoshnavazi, A. Salimi, A.G. Moaser. *Polyhedron*, **27**, 1303 (2008).
- [22] R. Khoshnavazi, L. Bahrami. *J. Coord. Chem.*, **62**, 2067 (2009).
- [23] R. Khoshnavazi, L. Kaviani, F.M. Zonoz. *Inorg. Chim. Acta*, **362**, 1223 (2009).
- [24] J.W. Zhao, Q.X. Han, P.T. Ma, L.J. Chen, J.P. Wang, J.Y. Niu. *Inorg. Chem. Commun.*, **12**, 707 (2009).
- [25] L.J. Chen, J.W. Zhao, P.T. Ma, Q.X. Han, J.P. Wang, J.Y. Niu. *Inorg. Chem. Commun.*, **13**, 50 (2010).
- [26] G.M. Sheldrick. *SHEXTL-97, Programs for Crystal Structure Refinements*, University of Göttingen, Germany (1997).
- [27] J. Gopalakrishnan. *Chem. Mater.*, **7**, 1265 (1995).
- [28] D. Hargman, C. Sangregorio, C.J. O'Connor, J. Zubieta. *J. Chem. Soc., Dalton Trans.*, 3707 (1998).
- [29] L.J. Chen, Y. Liu, P.T. Ma, J.W. Zhao. *Chem. Res.*, **20**, 38 (2009).
- [30] J.W. Zhao, H.P. Jia, J. Zhang, S.T. Zheng, G.Y. Yang. *Chem. Eur. J.*, **13**, 10030 (2007).
- [31] J.W. Zhao, C.M. Wang, J. Zhang, S.T. Zheng, G.Y. Yang. *Chem. Eur. J.*, **14**, 9223 (2008).
- [32] J.W. Zhao, S.T. Zheng, G.Y. Yang. *J. Solid State Chem.*, **180**, 3317 (2007).
- [33] J.W. Zhao, B. Li, S.T. Zheng, G.Y. Yang. *Cryst. Growth Des.*, **7**, 2658 (2007).
- [34] Z. Zhang, J. Liu, E. Wang, C. Qin, Y. Li, Y. Qi, X. Wang. *Dalton Trans.*, 463 (2008).
- [35] J.W. Zhao, J.L. Li, P.T. Ma, J.P. Wang, J.Y. Niu. *Inorg. Chem. Commun.*, **12**, 450 (2009).
- [36] J.P. Wang, J.P. Liu, J.Y. Niu. *J. Coord. Chem.*, **62**, 3599 (2009).
- [37] N. Belai, M.T. Pope. *Chem. Commun.*, 5760 (2005).
- [38] J.P. Wang, J. Du, J.Y. Niu. *CrystEngComm*, **10**, 972 (2008).
- [39] J.W. Zhao, S.T. Zheng, Z.H. Li, G.Y. Yang. *Dalton Trans.*, 1300 (2009).
- [40] L. Chen, L. Zhang, Y. Gao, L. Pang, G. Xue, F. Fu, J. Wang. *J. Coord. Chem.*, **62**, 2832 (2009).
- [41] Z.M. Zhang, S. Yao, Y.G. Li, E.B. Wang. *J. Coord. Chem.*, **62**, 1415 (2009).
- [42] J.P. Wang, X.D. Du, J.Y. Niu. *Chem. Lett.*, **35**, 1408 (2006).