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Two 3d–4f heterometallic Keggin phosphotungstate derivatives

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Two 3d–4f heterometallic monovacant Keggin phosphotungstate derivatives [Cu(dap)(H₂O)₂]_{0.5}[Cu(dap)₂]₄H₂[Pr(α-PW₁₁O₃₉)₂]·3H₂O (**1**) and [Cu(en)₂(H₂O)]₂[Cu(en)₂]_{1.5}H₄[Pr(α-PW₁₁O₃₉)₂]·10H₂O (**2**) (dap = 1,2-diaminopropane, en = ethylenediamine) have been hydrothermally synthesized by reaction of the trivacant Keggin phosphotungstate precursor Na₉[A-α-PW₉O₃₄]·7H₂O with CuCl₂·2H₂O and PrCl₃ in the presence of dap or en and structurally characterized by elemental analyses, IR spectra, X-ray single-crystal diffraction, and thermogravimetric analyses. Compound **1** crystallizes in the triclinic space group *P* $\bar{1}$ with $a = 17.325(3)$, $b = 18.917(3)$, $c = 19.938(3)$ Å, $\alpha = 104.481(2)$, $\beta = 98.968(3)$, $\gamma = 91.306(3)^\circ$, $V = 6236.4(18)$ Å³, $Z = 2$, $GOOF = 1.000$, $R_1 = 0.0806$, $wR_2 = 0.2016$. Compound **2** also belongs to the triclinic space group *P* $\bar{1}$ with $a = 16.005(4)$, $b = 18.053(4)$, $c = 21.127(5)$ Å, $\alpha = 113.894(3)$, $\beta = 90.745(4)$, $\gamma = 94.255(4)^\circ$, $V = 5560(2)$ Å³, $Z = 2$, $GOOF = 0.999$, $R_1 = 0.0686$, $wR_2 = 0.1885$. Both **1** and **2** display organic–inorganic hybrid 2-D sheet architectures built by classic mono-Pr^{III} sandwiched dimeric moieties [Pr(α-PW₁₁O₃₉)₂]¹¹⁻ through [Cu(L)₂]²⁺ bridges (L = dap, en), which represent rare organic–inorganic hybrid 2-D 3d–4f heterometallic monovacant Keggin polyoxometalates.

Keywords: Polyoxometalate; Phosphotungstate; 3d–4f Heterometal; Lanthanide

1. Introduction

Polyoxometalates (POMs), as a unique class of anionic early-transition-metal oxide clusters, attract interest for molecular and electronic structural versatility and applications in magnetism, catalysis, analytical chemistry, biology, medicine, and materials science [1–5]. Lacunary polyoxotungstate (POT) precursors derived from Keggin- and Dawson-type polyoxoanions can function as polydentate ligands to incorporate 3d or 4f metal cations into multidimensional frameworks. A large number of 3d or 4f POTs with diverse metal nuclearities, beautiful structural topologies and

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electronic, optical, and magnetic properties have been reported [6–15]. However, 3d–4f heterometal containing POTs remain largely unexplored. Preparations of 3d–4f heterometallic POT species have developed as a focus. The 4f metal cations have high oxyphilic reactivity with POMs, leading to amorphous precipitate instead of crystallization [16, 17]. In contrast, the interaction between 3d metal cations and POMs is relatively weak, therefore, oxyphilic 4f metal cations and relatively less active 3d metal cations in the same reaction system creates competition for highly negative polyoxoanions [17]. Hence, it is comparatively difficult to find appropriate reaction conditions to prepare POT-based 3d–4f heterometallic derivatives. Only a few 3d–4f heterometallic POT species have been obtained [17–25]. For example, a class of 1-D 3d–4f heterometal containing monovacant Keggin POTs $\{[\text{Ln}(\text{PW}_{10}\text{O}_{39})_2]\{\text{Cu}_2(\text{bpy})_2(\mu\text{-ox})\}\}^{9-}$ (Ln = La^{III}, Pr^{III}, Eu^{III}, Gd^{III}, and Yb^{III}) were reported by Liu *et al.* [18]. In the same year, a POT-based 3d–4f heterometallic derivative $[\text{HMTA}-\text{CH}_3]_2\text{K}_{3.5}\text{Na}_{8.5}[\text{K} \subset \{\text{FeCe}(\text{AsW}_{10}\text{O}_{38})(\text{H}_2\text{O})_2\}_3] \cdot 36\text{H}_2\text{O}$ built by three $\{\alpha\text{-AsW}_{10}\text{O}_{38}\}$ units linked by three $\{\text{Fe}-(\mu_3\text{-O})_3\text{-Ce}\}$ heterometallic clusters and a 2-D inorganic aggregate $\text{K}_3\text{Na}_3[\text{Nd}_2(\text{H}_2\text{O})_{12}\text{Cu}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2] \cdot 21\text{H}_2\text{O}$ based on tetra-Cu^{II} substituted sandwich-type POM units and lanthanide linkers were isolated by Wang *et al.* [17, 19]. Soon after, Fang and Kögerler [20] communicated two antiferromagnetic POT-based manganese–cerium carboxylate clusters $[\{\alpha\text{-P}_2\text{W}_{16}\text{O}_{57}(\text{OH})_2\}\{\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}\text{O}_9(\text{O}_2\text{CCH}_3)_8\}]^{8-}$ containing a divacant Dawson POM $[\alpha\text{-P}_2\text{W}_{16}\text{O}_{57}(\text{OH})_2]^{10-}$ unit capped by a $[\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}\text{O}_9(\text{O}_2\text{CCH}_3)_8]^{2+}$ fragment and $[\{\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}\}\{\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}(\mu_3\text{-O})_4(\mu_2\text{-OH})_2\}_3(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)]^{47-}$ built by six trivacant Dawson POMs $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$, three $[\text{Ce}_3^{\text{IV}}\text{Mn}_2^{\text{IV}}\text{O}_6(\text{OH})_2]^{6+}$ fragments and a central PO_4^{3-} group [21]. In 2009, Mialane *et al.* [22] illustrated three 3d–4f heterometallic $\{\text{LnCu}_3(\text{OH})_3\text{O}\}$ cubane inserted silicotungstates $\{[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][(\text{Cu}(\text{en})(\text{OH}))_3\text{Ln}(\text{SiW}_{11}\text{O}_{39})(\text{H}_2\text{O})]_2\} \cdot 20\text{H}_2\text{O}$ (Ln = La^{III}, Gd^{III}, and Eu^{III}). In 2010, two $\{\text{P}_2\text{W}_{12}\}$ -based 3d–4f heterometallic aggregates $\text{K}_3\text{Na}_8[\text{K}_3 \subset \{\text{GdMn}(\text{H}_2\text{O})_{10}\}\{\text{HMnGd}_2(\text{Tart})\text{O}_2(\text{H}_2\text{O})_{15}\}\{\text{P}_6\text{W}_{42}\text{O}_{151}(\text{H}_2\text{O})_7\}] \cdot 44\text{H}_2\text{O}$ and $\text{K}_3\text{Na}_{10}[\text{K}_3 \subset \{\text{GdCo}(\text{H}_2\text{O})_{11}\}_2\{\text{P}_6\text{W}_{41}\text{O}_{148}(\text{H}_2\text{O})_7\}] \cdot 43\text{H}_2\text{O}$ were obtained by conventional aqueous solution method [23]. A Weakley-type 3d–4f heterometal substituted sandwich-type germanotungstate $[\{\text{Ce}(\text{H}_2\text{O})_2\}_2\text{Mn}_2(\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2]^{8-}$ was synthesized by incorporating 4f metal cations to preform Weakley-type POM backbone [24]. Subsequently, a 1-D 3d–4f double-chain silicotungstate $\text{Cs}_4[(\gamma\text{-SiW}_{10}\text{O}_{36})_2(\text{Cr}(\text{OH})(\text{H}_2\text{O}))_3(\text{La}(\text{H}_2\text{O})_7)_2] \cdot 20\text{H}_2\text{O}$ was separated [25]. Trivacant Keggin POM $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ is a versatile precursor in ambient aqueous solution and hydrothermal conditions to construct intriguing 3d or 4f substituted POMs [26–31]. However, studies on the reaction of $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ with 3d and 4f mixed metal cations are very limited [18]. Therefore, we recently launched a study on the reaction of $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ with 3d and 4f mixed metal cations in the presence of organic components. When $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ simultaneously reacted with Cu^{II} and Pr^{III} in the presence of 1,2-diaminopropane (dap) or ethylenediamine (en) under hydrothermal conditions, two hybrid 3d–4f heterometallic monovacant Keggin phosphotungstate derivatives $[\text{Cu}(\text{dap})(\text{H}_2\text{O})_2]_{0.5}[\text{Cu}(\text{dap})_2]_4\text{H}_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2[\text{Cu}(\text{en})_2]_{1.5}\text{H}_4[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 10\text{H}_2\text{O}$ (**2**) were synthesized and characterized by elemental analyses, IR spectra, X-ray single-crystal diffraction, and thermogravimetric (TG) analyses. The preparation of **1** and **2** indicates that assembly between lacunary POM precursors and 3d–4f heterometallic cations can be realized under hydrothermal conditions.

2. Experimental

$\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ was prepared according to the literature procedure [32] and confirmed by IR spectra. All other chemicals used for synthesis were reagent grade and used without purification.

2.1. Preparation of $[\text{Cu}(\text{dap})(\text{H}_2\text{O})_2]_{0.5}[\text{Cu}(\text{dap})_2]_4\text{H}_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 3\text{H}_2\text{O}$ (1)

$\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ (0.246 g, 0.094 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.062 g, 0.364 mmol), and PrCl_3 (0.042 g, 0.170 mmol) were suspended in H_2O (5 mL), to which dap (0.05 mL, 0.740 mmol) was 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. Purple prismatic crystals were filtered, washed with distilled water, and dried in air at ambient temperature. Yield: ca 42% (based on $\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$). Anal. Calcd (%) for $\text{C}_{25.50}\text{H}_{95}\text{Cu}_{4.50}\text{N}_{17}\text{O}_{82}\text{P}_2\text{PrW}_{22}$: C, 4.72; H, 1.48; and N, 3.67. Found (%): C, 4.59; H, 1.61; and N, 3.70.

2.2. Preparation of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2[\text{Cu}(\text{en})_2]_{1.5}\text{H}_4[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 10\text{H}_2\text{O}$ (2)

$\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ (0.255 g, 0.010 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.269 g, 1.578 mmol), and PrCl_3 (0.086 g, 0.348 mmol) were suspended in H_2O (5 mL), to which en (0.15 mL, 2.220 mmol) was added under stirring. The resulting mixture was stirred for 7 h, sealed in a Teflon-lined stainless steel autoclave (25 mL), kept at 160°C for 6 days, and then cooled to room temperature. Purple prismatic crystals were filtered, washed with distilled water, and dried in air at ambient temperature. Yield: ca 47% (based on $\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$). Anal. Calcd (%) for $\text{C}_{14}\text{H}_{84}\text{Cu}_{3.50}\text{N}_{14}\text{O}_{90}\text{P}_2\text{PrW}_{22}$: C, 2.64; H, 1.33; and N, 3.08. Found (%): C, 2.72; H, 1.45; and N, 2.99.

2.3. Physical measurements

Elemental analyses (C, H, and N) were carried out on a Perkin Elmer 240C analyzer. IR spectra were obtained from a KBr pellet on a Nicolet 170 SXFT-IR spectrophotometer from $4000\text{--}400\text{ cm}^{-1}$. TG analyses were conducted on a Mettler-Toledo TGA/SDTA 851^e thermal analyzer in flowing air with a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 800°C .

2.4. X-ray crystallography

Intensity data of **1** and **2** were collected on a Bruker Apex-2 CCD detector using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 296 K. Both structures were solved by direct methods and refined using full-matrix least-squares on F^2 . The remaining 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 [33]. 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. All hydrogens were refined isotropically as a riding mode using the default SHELXTL parameters. A summary of crystal data and structure refinement parameters for **1** and **2** is listed in table 1.

3. Results and discussion

3.1. Synthesis

Trivalent Keggin phosphotungstate $[A-\alpha-PW_9O_{34}]^{9-}$ can function as a polydentate ligand for 3d metal or 4f metal cations resulting in 3d or 4f metal substituted POT derivatives with diverse metal nuclearities and beautiful topologies under either conventional aqueous solution or hydrothermal conditions [7, 26, 29, 31, 34–37]. $[A-\alpha-PW_9O_{34}]^{9-}$ was first introduced to hydrothermal reactions by us in 2007 [26, 31]. When it was reacted with $NiCl_2 \cdot 6H_2O$, a family of hexa- Ni^{II} incorporated POTs $[\{Ni_6(\mu_3-OH)_3(en)_3(H_2O)_6\}(B-\alpha-PW_9O_{34})] \cdot 7H_2O$, $[\{Ni_6(\mu_3-OH)_3(en)_2(H_2O)_8\}(B-\alpha-PW_9O_{34})] \cdot 7H_2O$ and $[\{Ni_6(\mu_3-OH)_3(dap)_2(H_2O)_8\}(B-\alpha-PW_9O_{34})] \cdot 7H_2O$ and a double-cluster complex containing hexa-/hepta- Ni^{II} incorporated trivalent Keggin units $[\{Ni_7(\mu_3-OH)_3O_2(dap)_3(H_2O)_6\}(B-\alpha-PW_9O_{34})][\{Ni_6(\mu_3-OH)_3(dap)_3(H_2O)_6\}(B-\alpha-PW_9O_{34})][Ni(dap)_2(H_2O)_2] \cdot 4.5H_2O$ were separated [26]. The reactivity of $[A-\alpha-PW_9O_{34}]^{9-}$ with $FeSO_4 \cdot 7H_2O$ led to two tetrameric POTs $(enH_2)_3H_{15}[\{Fe_{1.5}^{II}Fe_{12}^{III}$

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

| | 1 | 2 |
|--|--|--|
| Empirical formula | $C_{25.50}H_{95}Cu_{4.50}Ni_{17}O_{82}P_2PrW_{22}$ | $C_{14}H_{34}Cu_{3.50}Ni_{14}O_{90}P_2PrW_{22}$ |
| Formula weight | 6485.67 | 6358.89 |
| Temperature (K) | 296(2) | 296(2) |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions (\AA , $^\circ$) | | |
| <i>a</i> | 17.325(3) | 16.005(4) |
| <i>b</i> | 18.917(3) | 18.053(4) |
| <i>c</i> | 19.938(3) | 21.127(5) |
| α | 104.481(2) | 113.894(3) |
| β | 98.968(3) | 90.745(4) |
| γ | 91.306(3) | 94.255(4) |
| Volume (\AA^3), <i>Z</i> | 6236.4(18), 2 | 5560(2), 2 |
| Calculated density (g cm^{-3}) | 3.454 | 3.798 |
| Absorption coefficient (mm^{-1}) | 21.441 | 23.867 |
| <i>F</i> (000) | 5741 | 5609 |
| Crystal size (mm^3) | $0.27 \times 0.24 \times 0.18$ | $0.35 \times 0.27 \times 0.21$ |
| θ range for data collections | $2.14\text{--}25.00^\circ$ | $1.85\text{--}25.00$ |
| Limiting indices | $-20 \leq h \leq 13$; $-21 \leq k \leq 22$; $-23 \leq l \leq 23$ | $-10 \leq h \leq 19$; $-21 \leq k \leq 21$; $-25 \leq l \leq 24$ |
| Reflections collected | 31,293 | 27,748 |
| Independent reflections | 21,644 [$R(\text{int}) = 0.0727$] | 19,322 [$R(\text{int}) = 0.0559$] |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Goodness-of-fit on F^2 | 1.000 | 0.999 |
| Final <i>R</i> indices [$I > 2\sigma(I)$] | $R_1 = 0.0806$, $wR_2 = 0.2016$ | $R_1 = 0.0686$, $wR_2 = 0.1885$ |

$(\mu_3\text{-OH})_{12}(\mu_4\text{-PO}_4)_4\{\text{B-}\alpha\text{-PW}_9\text{O}_{34}\}_4 \cdot ca\ 130\text{H}_2\text{O}$ [26] and $(\text{enH}_2)_{3.5}\text{H}_{15}\{\{\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\mu_3\text{-OH})_{12}(\mu_4\text{-PO}_4)_4\}(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_4\} \cdot 83\text{H}_2\text{O}$ [31]. Subsequently, Dolbecq *et al.* also investigated the reaction behavior of $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ and $\text{Fe}_2(\text{SO}_4)_3$ in the presence of en, giving a tetrahedral POT $(\text{C}_2\text{N}_2\text{H}_{10})_{11}\{\{\text{B-}\alpha\text{-PW}_9\text{O}_{34}\}\text{Fe}_3(\text{OH})_3\}_4(\text{PO}_4)_4\text{Fe}\} \cdot 38\text{H}_2\text{O}$ and a square POT $\text{K}_4(\text{C}_2\text{N}_2\text{H}_{10})_{12}\{[\alpha\text{-PW}_{10}\text{Fe}_2\text{O}_{39}]_4\} \cdot 30\text{H}_2\text{O}$ [35]. At the beginning of our exploring the system containing $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and dap/en, an unprecedented 3-D POM $\{\{\text{Cu}_6(\mu_3\text{-OH})_3(\text{en})_3(\text{H}_2\text{O})_3\}(\text{B-}\alpha\text{-PW}_9\text{O}_{34})\} \cdot 7\text{H}_2\text{O}$ with an unusual six-connected $4^9 6^6$ topological framework built up of hexa- Cu^{II} clusters and trivacant Keggin $[\text{B-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ fragments was isolated [26]. Later, we obtained two mono- Cu^{II} substituted Keggin phosphotungstates $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2\{[\text{Cu}(\text{en})_2][\alpha\text{-PCuW}_{11}\text{O}_{39}\text{Cl}]\} \cdot 3\text{H}_2\text{O}$ and $[\text{Cu}(\text{dap})_2]_2\{[\text{Cu}(\text{dap})_2]_2[\text{Cu}(\text{dap})_2][\alpha\text{-PCuW}_{11}\text{O}_{39}]_2\} \cdot 3\text{H}_2\text{O}$ [37] and then five hybrid POTs $[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2[\text{Cu}(\text{H}_2\text{O})_2][\text{Cu}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cu}_6(\mu_3\text{-OH})_3(\text{en})_3(\text{H}_2\text{O})_5(\text{B-}\alpha\text{-PW}_9\text{O}_{34})] \cdot 6\text{H}_2\text{O}$, $\text{Na}_6\{[\text{Cu}_6(\mu_3\text{-OH})_3(\text{en})_3(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})]_2[\text{Cu}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2]\} \cdot 2\text{H}_2\text{en} \cdot 8\text{H}_2\text{O}$, $[\text{Cu}_6(\mu_3\text{-OH})_3(\text{en})_3(\text{H}_2\text{O})_3(\text{B-}\alpha\text{-PW}_9\text{O}_{34})] \cdot 4\text{H}_2\text{O}$ and $[\text{Cu}_6^{\text{II}}\text{Cu}_4^{\text{I}}(\mu_6\text{-O})(\text{OH})_{18}][\text{Cu}_6(\mu_3\text{-OH})_3(\text{enMe})_3(\text{H}_2\text{O})_3(\text{B-}\alpha\text{-PW}_9\text{O}_{34})]_4 \cdot 4\text{H}_3\text{O} \cdot 2\text{H}_2\text{O}$ were successively obtained by Li *et al.* [38]. With the design and preparation of 3d–4f, heterometallic POTs becoming a major focus in POM chemistry, reaction of $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ with 3d and 4f mixed cations in the presence of organic components was explored. When the system containing $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, PrCl_3 , and dap was introduced to hydrothermal conditions, the 3d–4f heterometallic monovacant Keggin phosphotungstate $[\text{Cu}(\text{dap})(\text{H}_2\text{O})_2]_{0.5}[\text{Cu}(\text{dap})_2]_4\text{H}_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 3\text{H}_2\text{O}$ (**1**) was synthesized. When a mixture of $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, PrCl_3 , and en was performed under hydrothermal conditions, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2[\text{Cu}(\text{en})_2]_{1.5}\text{H}_4[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2] \cdot 10\text{H}_2\text{O}$ (**2**) was also prepared. However, when $\alpha\text{-Na}_7\text{PW}_{11}\text{O}_{39} \cdot n\text{H}_2\text{O}$ replaced $\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ under similar conditions, **1** and **2** cannot be obtained. Currently, other 4f metal cations are being introduced to this system to obtain more 3d–4f heterometallic POTs. Under similar conditions to **2**, when $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was replaced by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, a hexa- Ni^{II} incorporated trivacant Keggin POT $\{\{\text{Ni}_6(\mu_3\text{-OH})_3(\text{en})_2(\text{H}_2\text{O})_8\}(\text{B-}\alpha\text{-PW}_9\text{O}_{34})\} \cdot 7\text{H}_2\text{O}$ was obtained [26]. Notably, the transformation of $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-} \rightarrow [\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ was observed in the preparation of **1** and **2**, which was encountered in the preparation of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2\{[\text{Cu}(\text{en})_2][\alpha\text{-PCuW}_{11}\text{O}_{39}\text{Cl}]\} \cdot 3\text{H}_2\text{O}$ and $[\text{Cu}(\text{dap})_2]_2\{[\text{Cu}(\text{dap})_2]_2[\text{Cu}(\text{dap})_2][\alpha\text{-PCuW}_{11}\text{O}_{39}]_2\} \cdot 3\text{H}_2\text{O}$ [37].

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

X-ray single-crystal diffraction analyses indicate **1** and **2** crystallize in the triclinic space group $P\bar{1}$. The construction of their 2-D sheet architectures are somewhat different, although **1** and **2** display 2-D sheet architectures built by classic mono- Pr^{III} sandwiched dimeric moieties $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ through $[\text{Cu}(\text{L})_2]^{2+}$ bridges (L = dap, en). In the crystal structures of **1** and **2**, Cu–O weak interactions will be considered because Jahn–Teller distortion of copper^{II} ions in the crystal field leads to elongation of the Cu–O distances [37, 39, 40].

As shown in figure 1, the asymmetrical structural unit of **1** is composed of a 1 : 2-type dimeric $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ (figure 1b), a half $[\text{Cu}(\text{dap})(\text{H}_2\text{O})_2]^{2+}$, four $[\text{Cu}(\text{dap})_2]^{2+}$, two protons and three lattice water molecules. In **1**, there are seven crystallographically independent Cu^{2+} cations, Cu1, Cu2, Cu3, Cu4, Cu5, Cu6, and Cu7, in which Cu1,

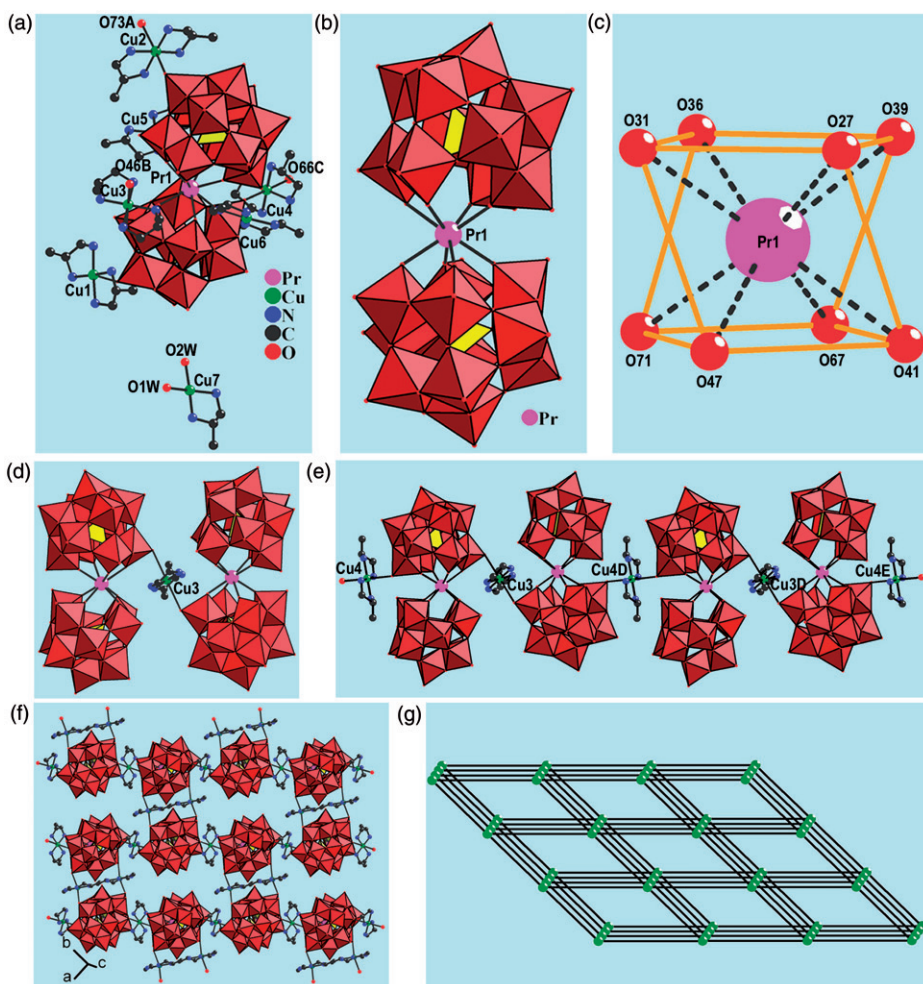


Figure 1. (a) The asymmetrical structural unit of **1** with the labeling scheme. Lattice water molecules, protons and hydrogens attached to carbon, nitrogen, and oxygen are omitted for clarity. (b) The 1:2-type dimeric $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ moiety. (c) The square antiprismatic geometry of Pr^{III} . (d) The centric $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ unit. Hydrogens attached to carbon and nitrogen are omitted for clarity. (e) The 1-D chain structure built by $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ and $[\text{Cu}4(\text{dap})_2]^{2+}$. Hydrogens attached to carbon and nitrogen are omitted for clarity. (f) The 2-D extended sheet architecture. Discrete $[\text{Cu}(\text{dap})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}(\text{dap})_2]^{2+}$ cations, pendent $[\text{Cu}(\text{dap})_2]^{2+}$, lattice water, protons, and hydrogens attached to carbon and nitrogen are omitted for clarity. (g) The 2-D (4,4)-topological network showing $-\text{AAA}-$ alignment. Atoms with suffix A, B, C, D, and E are generated by the symmetry operation. A: $-x, 3-y, -z$; B: $-x, 2-y, -z$; C: $1-x, 3-y, -z$; D: $-1+x, -1+y, z$; E: $-2+x, -2+y, z$.

Cu2, Cu6, and Cu7 are situated in the usual crystallographic sites with the site occupancy of 1, while Cu3, Cu4, and Cu5 occupy special crystallographic positions with site occupancy of 0.5 for each. The pendent $[\text{Cu}1(\text{dap})_2]^{2+}$ has a five-coordinate square pyramid constituted by four nitrogens from two dap $[\text{Cu}-\text{N}: 1.99(4)\text{-}2.05(3)\text{ \AA}]$ and one terminal oxygen from $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ $[\text{Cu}-\text{O}: 2.33(2)\text{ \AA}]$. The bridging $[\text{Cu}2(\text{dap})_2]^{2+}$ is a six-coordinate octahedral with four nitrogens from two dap ligands

in the basal plane [Cu–N: 1.93(3)–2.01(3) Å] and two terminal oxygens from adjacent 1:2-type $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ moieties occupying axial positions [Cu–O: 2.571(24)–2.617(25) Å]. The bridging $[\text{Cu}3(\text{dap})_2]^{2+}$ and $[\text{Cu}4(\text{dap})_2]^{2+}$ also display octahedral geometry defined by four nitrogens from two dap's [Cu–N: 1.94(3)–2.01(2) Å] and two terminal oxygens from two $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ [Cu–O: 2.504(20)–2.907(24) Å]. The discrete $[\text{Cu}5(\text{dap})_2]^{2+}$ and $[\text{Cu}6(\text{dap})_2]^{2+}$ cations exhibit a square planar geometry established from four nitrogens of two dap's [Cu–N: 1.92(4)–2.05(5) Å]. The discrete $[\text{Cu}7(\text{dap})(\text{H}_2\text{O})_2]^{2+}$ also has a square planar environment defined by two nitrogens from dap [Cu–N: 1.93(5)–2.097(12) Å] and two water molecules [Cu–O: 1.98(8)–2.18(7) Å]. The 1:2-type $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ is constructed from two monovacant Keggin $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ moieties in an asymmetrical fashion linked *via* a distorted square antiprismatic Pr^{III} cation resulting in a sandwich-type assembly. The Pr^{III} incorporates vacant sites of two $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ moieties with distorted square antiprismatic geometry (figure 1c), in which four oxygens from the vacant site of one $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ constitute the upper face of the square antiprism with Pr–O distances of 2.417(19)–2.51(2) Å and additional four oxygens from the vacant site of the other $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ give the bottom face of the square antiprism with Pr–O distances of 2.45(2)–2.497(19) Å. The Pr–O distances are within the usual range [41]. Two adjacent asymmetrical dimeric $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ moieties are combined by the $[\text{Cu}3(\text{dap})_2]^{2+}$ forming a centric $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ unit (figure 1d). Adjacent centric $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ units are further linked through $[\text{Cu}4(\text{dap})_2]^{2+}$ constructing a 1-D chain structure (figure 1e). Neighboring 1-D chains are interconnected *via* $[\text{Cu}2(\text{dap})_2]^{2+}$ giving a 2-D extended sheet architecture (figure 1f). In the 2-D extended sheet architecture, each centric $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ is connected to four others through two $[\text{Cu}4(\text{dap})_2]^{2+}$ bridges and four $[\text{Cu}2(\text{dap})_2]^{2+}$ bridges. From the topology, provided that the centric $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ units are looked on as four-connected nodes, the 2-D architecture is a (4,4)-topological network and adjacent sheets are aligned in the mode of –AAA– (figure 1g).

Such 1:2 structural type of general formula $[\text{Ln}^{\text{III/IV}}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{n-}$ (Ln^{III} , $n = 11$; Ln^{IV} , $n = 10$) was first reported by Peacock and Weakley in 1971 [42, 43]. In this class of complexes, two $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ moieties sandwich one f metal cation, with four terminal oxygens associated with the monolacunary defect site coordinating to the central f-block metal cation. Such 1:2-type lanthanophosphomolydates $[\text{Ln}^{\text{III}}(\alpha\text{-PMO}_{11}\text{O}_{39})_2]^{11-}$ (where Ln = every trivalent lanthanide cation except promethium) have been structurally characterized by May *et al.* [44, 45]. Recently, two 1:2-type tetravalent metal monolacunary phosphomolybdates $[\text{M}^{\text{IV}}(\alpha\text{-PMO}_{11}\text{O}_{39})_2]^{10-}$ ($\text{M} = \text{Ce}^{\text{IV}}$ and Th^{IV}) have been isolated by May *et al.* [46]. We reported two 2:2 monolanthanide substituted phosphotungstates $[\{(\alpha\text{-PW}_{11}\text{O}_{39}\text{H})\text{Ln}(\text{H}_2\text{O})_3\}_2]^{6-}$ ($\text{Ln} = \text{Nd}^{\text{III}}$ and Gd^{III}) and $[\{(\alpha\text{-PW}_{11}\text{O}_{39})\text{Ln}(\text{H}_2\text{O})(\eta^2, \mu-1, 1)\text{-CH}_3\text{COO}\}_2]^{10-}$ ($\text{Ln} = \text{Sm}^{\text{III}}$, Eu^{III} , Gd^{III} , Tb^{III} , Ho^{III} , and Er^{III}) [47]. The former is built by two symmetrically related monolanthanide substituted α -Keggin units $[\alpha\text{-PW}_{11}\text{O}_{39}\text{Ln}(\text{H}_2\text{O})_3]^{4-}$ linked *via* two Ln–O–W bridges (figure 2a), while the latter is constructed from two monolanthanide substituted units $[(\alpha\text{-PW}_{11}\text{O}_{39})\text{Ln}(\text{H}_2\text{O})(\eta^2, \mu-1, 1)\text{-CH}_3\text{COO}]^{5-}$ bridged by two $(\eta^2, \mu-1, 1)$ -acetato ligands (figure 2b). Moreover, 1:2 $[\text{Ln}(\beta_2\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ ($\text{Ln}^{\text{III}} = \text{Tb}^{\text{III}}$, Dy^{III} , Ho^{III} , Er^{III} , Tm^{III} , and Yb^{III}) with monovacant β_2 -Keggin moieties (figure 2c) were discovered by Kortz *et al.* [48]. The banana-shaped lanthanophosphotungstate $[\text{Ce}_2(\text{PW}_{10}\text{O}_{38})(\text{PW}_{11}\text{O}_{39})_2]^{17-}$ including mixed monolacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and dilacunary $[\text{PW}_{10}\text{O}_{38}]^{11-}$ subunits (figure 2d) was also observed [49]. Transition metal substituted

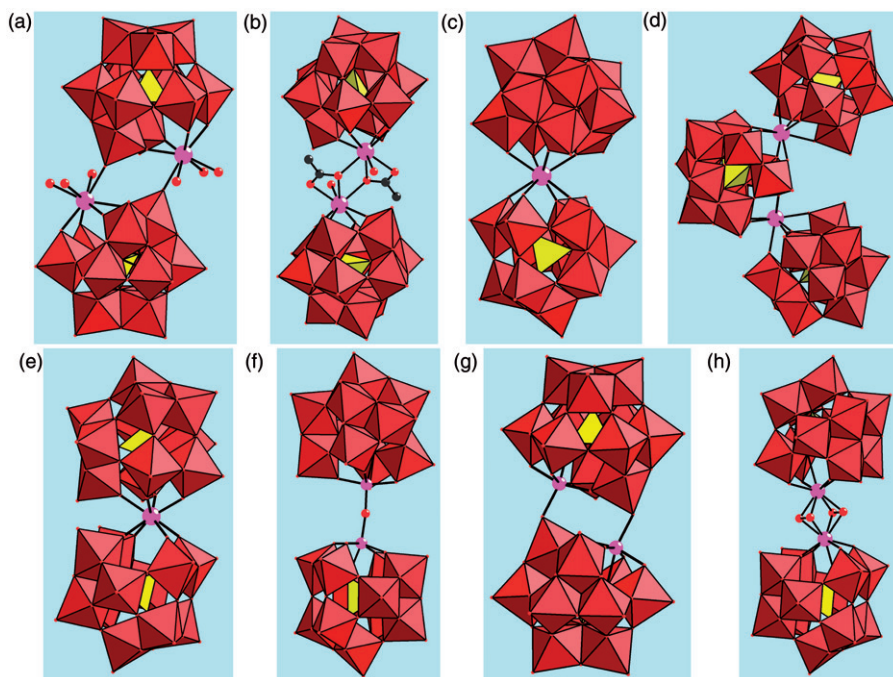


Figure 2. Combined ball-and-stick and polyhedral representations of: $\{[(\alpha\text{-PW}_{11}\text{O}_{39})\text{Ln}(\text{H}_2\text{O})_3]_2\}^{6-}$ (a), $\{[(\alpha\text{-PW}_{11}\text{O}_{39})\text{Ln}(\text{H}_2\text{O})(\eta^2, \mu-1, 1)\text{-CH}_3\text{COO}]_2\}^{10-}$ (b), $[\text{Ln}(\beta_2\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ (c), $[\text{Ce}_2(\text{PW}_{10}\text{O}_{38})(\text{PW}_{11}\text{O}_{39})_2]^{17-}$ (d), $[\text{Zr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ or $[\text{Hf}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ (e), $[(\alpha\text{-PTiW}_{11}\text{O}_{39})_2(\text{OH})]^{7-}$ (f), $[\alpha\text{-PCuW}_{11}\text{O}_{39}]_2^{10-}$ (g), and $[\text{M}_2(\text{O}_2)_2(\text{XW}_{11}\text{O}_{39})_2]^{12-}$ (h). The hydrogens attached to CH_3COO^- and coordinated water molecules are omitted for clarity.

phosphotungstates containing two $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ moieties for each molecular unit have been reported [37, 50–52]. Kato *et al.* prepared two 1:2-type $\text{Zr}^{\text{IV}}/\text{Hf}^{\text{IV}}$ sandwiched phosphotungstates $[\text{Zr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ and $[\text{Hf}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ (figure 2e), in which the $\text{Zr}^{\text{IV}}/\text{Hf}^{\text{IV}}$ cation has a square antiprism geometry [50]. Kholdeeva *et al.* [51] prepared one 2:2-type monotitanium substituted phosphotungstate $[(\alpha\text{-PTiW}_{11}\text{O}_{39})_2(\text{OH})]^{7-}$ (figure 2f), while Zhao *et al.* [37] isolated another 2:2-type monocopper substituted phosphotungstate $[\alpha\text{-PCuW}_{11}\text{O}_{39}]_2^{10-}$ (figure 2g). Very recently, Mal *et al.* [52] discovered 2:2-type peroxo-containing heteropolytungstates $[\text{M}_2(\text{O}_2)_2(\text{XW}_{11}\text{O}_{39})_2]^{12-}$ ($\text{M} = \text{Zr}^{\text{IV}}, \text{X} = \text{Si}^{\text{IV}}, \text{Ge}^{\text{IV}}; \text{M} = \text{Hf}^{\text{IV}}, \text{X} = \text{Si}^{\text{IV}}$) (figure 2h).

Different from **1**, the asymmetrical structural unit of **2** (figure 3a) consists of a 1:2-type $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$, two $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ cations, one and a half $[\text{Cu}(\text{en})_2]^{2+}$, four protons, and ten lattice water molecules. In **2**, there are five crystallographically unique Cu^{2+} , Cu1, Cu2, Cu3, Cu4, and Cu5, in which Cu2 and Cu5 stand on the usual crystallographic sites with site occupancy of 1 for each, whereas Cu1, Cu3, and Cu4 occupy special crystallographic positions with site occupancy of 0.5 for each. The bridging $[\text{Cu1}(\text{en})_2]^{2+}$, $[\text{Cu3}(\text{en})_2]^{2+}$, and $[\text{Cu4}(\text{en})_2]^{2+}$ have an octahedral geometry from four nitrogens of two en [$\text{Cu}\text{-N}$: 1.96(2)–2.05(2) Å] and two terminal oxygens [$\text{Cu}\text{-O}$: 2.523(16)–3.070(16) Å] from two $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ moieties. The $[\text{Cu2}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ also adopts octahedral configuration, in which two en's establish the equatorial plane [$\text{Cu}\text{-N}$: 1.96(2)–2.019(19) Å], one water and one terminal oxygen from

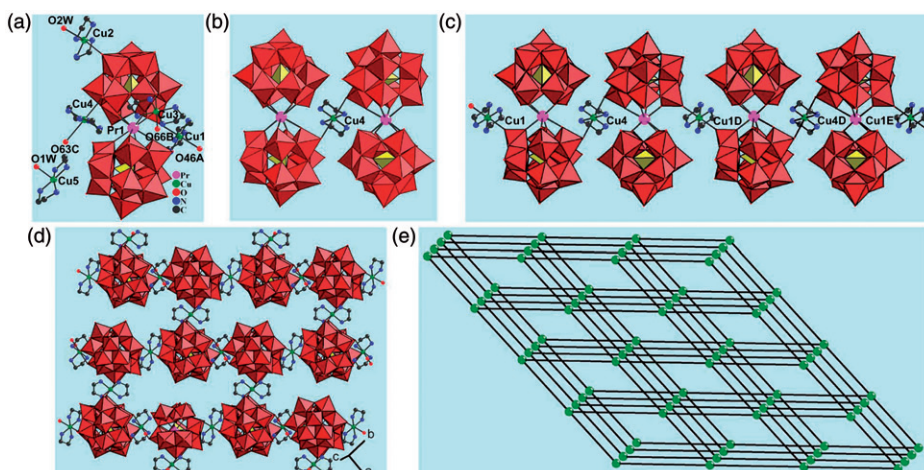


Figure 3. (a) The asymmetrical structural unit of **2** with labeling scheme. Lattice water molecules, protons, and hydrogens attached to carbon, nitrogen, and oxygen are omitted for clarity. (b) The centric $\{\text{Cu}(\text{en})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ unit. Hydrogens attached to carbon and nitrogen are omitted for clarity. (c) The 1-D chain structure built by $\{\text{Cu}(\text{en})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ and $[\text{Cu1}(\text{en})_2]^{2+}$. Hydrogens attached to carbon and nitrogen are omitted for clarity. (d) The 2-D extended sheet architecture. Discrete $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$, pendent $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$, lattice water, protons, and hydrogens attached to carbon and nitrogen are omitted for clarity. (e) The 2-D (4,4)-topological network showing -AAA- alignment. Atoms with suffix A, B, C, D, and E are generated by the symmetry operation. A: $-x, 1-y, 1-z$; B: $-x, 2-y, 1-z$; C: $1-x, 2-y, 1-z$; D: $1+x, 1+y, z$; E: $2+x, 2+y, z$.

$[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ occupy axial sites [Cu–O: 2.651(22)–2.758(17) Å]. The discrete $[\text{Cu5}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ has a square pyramidal geometry defined by nitrogens from two en [Cu–N: 1.96(3)–2.15(5) Å] and one water [Cu–O: 2.43(3) Å]. Similar to **1**, Pr1^{III} in $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ of **2** also displays distorted square antiprismatic geometry built by eight oxygens from two $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ with Pr–O distances of 2.423(14)–2.499(14) Å. Similar to **1**, two adjacent asymmetrical $[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{11-}$ moieties are linked through $[\text{Cu4}(\text{en})_2]^{2+}$ generating a centric $\{\text{Cu}(\text{en})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ unit (figure 3b). Adjacent $\{\text{Cu}(\text{en})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ units are further connected *via* $[\text{Cu1}(\text{en})_2]^{2+}$ constructing a 1-D chain architecture (figure 3c). Neighboring 1-D chains are interconnected through $[\text{Cu3}(\text{en})_2]^{2+}$ constructing a 2-D extended sheet (figure 3d). Compounds **1** and **2** represent rare 3d–4f heterometallic monovacant Keggin phosphotungstate species although two 2-D 3d–4f heterometallic silicotungstates $[\text{Cu}(\text{en})_2][(\text{Cu}(\text{en})(\text{OH}))_3\text{La}(\text{SiW}_{11}\text{O}_{39})] \cdot 20\text{H}_2\text{O}$ [22] and $\text{K}_3\text{Na}_3\{\text{Nd}_2(\text{H}_2\text{O})_{12}\text{Cu}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2\} \cdot 21\text{H}_2\text{O}$ [19] have been reported. Obviously different from **1**, each $\{\text{Cu}(\text{en})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ unit in the 2-D extended sheet architecture is connected to four others through two $[\text{Cu1}(\text{en})_2]^{2+}$ bridges and two $[\text{Cu3}(\text{en})_2]^{2+}$ bridges. If the $\{\text{Cu}(\text{dap})_2[\text{Pr}(\alpha\text{-PW}_{11}\text{O}_{39})_2]_2\}^{20-}$ units are viewed as four-connected nodes, the 2-D structure of **2** also exhibits a 2-D (4,4)-topological network with the -AAA- arrangement (figure 3e). In POM chemistry, similar 2-D (4,4)-topological networks have been encountered [3, 15, 53, 54]. In 2007–2010, five 2-D (4,4)-topological POTs constructed from tetra-transition-metal substituted Keggin POM units $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\alpha\text{-B-HSiW}_9\text{O}_{34})_2]\} \cdot 7\text{H}_2\text{O}$ [53], $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2[\text{Ni}(\text{dap})_2]_2[\text{Ni}_4(\text{Hdap})_2(\alpha\text{-B-HGeW}_9\text{O}_{34})_2]\} \cdot 6\text{H}_2\text{O}$ [53], $\{[\text{Ni}(\text{dap})_2(\text{H}_2\text{O})]_2$

[Ni(dap)₂]₂[Ni₄(Hdap)₂(α-B-PW₉O₃₄)₂]} · 4H₂O [53], [DMAH]₄{[Mn(DMF)₄]₂[Mn₄(DMF)₂(α-B-HPW₉O₃₄)₂]} [54], and {[Ni(dap)₂(H₂O)₂]₂[Ni₄(Hdap)₂(B-α-AsW₉O₃₄)₂]} · 4H₂O [15] were reported by Zhao *et al.*, which show the –AAA– arrangement mode. In 2008, a 2-D (4,4)-topological germanotungstate built by octa-Cu substituted Keggin POM units [Cu₂^{II}(H₂O)₂(2,2'-bpy)₂]{[Cu^{II}(bdyl)]₂[Cu₈^{II}(2,2'-bpy)₄(H₂O)₂(B-α-GeW₉O₃₄)₂]} · 4H₂O was discovered by Zhao *et al.* showing the –ABAB– arrangement [3].

Comparing **1** and **2** with reported organic–inorganic hybrid 3d–4f heterometal phosphotungstates {[Ln(PW₁₁O₃₉)₂]{Cu₂(bpy)₂(μ-ox)}}^{9–} (Ln = La^{III}, Pr^{III}, Eu^{III}, Gd^{III}, and Yb^{III}) [18], the common feature is that they are organic–inorganic hybrid 3d–4f heterometal phosphotungstates constructed by 1:2-type [Ln^{III}(α-PW₁₁O₃₉)₂]^{11–} units and copper complexes. Three obvious discrepancies are observed between them: (1) the former are synthesized by reaction of Na₉[A-α-PW₉O₃₄] · 7H₂O with CuCl₂ · 2H₂O, and Ln^{III} cations in the presence of organoamines at 160°C in hydrothermal conditions, while the latter are prepared by reacting H₃PW₁₂O₄₀ · xH₂O with CuCl₂ · 2H₂O, and Ln^{III} cations in the presence of oxalic acid and 2,2'-bipyridine at room temperature in a stepwise synthetic method; (2) the former display organic–inorganic hybrid 2-D sheet architectures, in contrast, the latter show organic–inorganic hybrid 1-D chains with two types of organic ligands; (3) the 2-D sheet architectures of the former are established by 1:2-type [Ln^{III}(α-PW₁₁O₃₉)₂]^{11–} units and the mononuclear [Cu(dap)₂]²⁺ or [Cu(en)₂]²⁺ bridges, whereas the 1-D chains of the latter are built by 1:2-type [Ln^{III}(α-PW₁₁O₃₉)₂]^{11–} units and dinuclear [Cu₂(bpy)₂(μ-ox)]²⁺ linkers.

3.3. IR spectra

In the low-wavenumber region, IR spectra of **1** and **2** display the characteristic vibrations of Keggin-type polyoxoanions (Supplementary material). Four groups of characteristic vibrations, ν(W–O_t), ν(P–O_a), ν(W–O_b), and ν(W–O_c), are observed at 938; 1099, 1050; 882; and 841, 777, 713 cm^{–1} for **1**, and 946; 1098, 1050; 881; and 833, 777, 728 cm^{–1} for **2**. In comparison with those of Na₃[α-PW₁₂O₄₀] · xH₂O [995, 1081, 900, and 805 cm^{–1} for ν(W–O_t), ν(P–O_a), ν(W–O_b), and ν(W–O_c)] [55], the ν(P–O_a) vibration splits into two vibrations while ν(W–O_c) splits into three vibrations, related to the lower symmetry of [α-PW₁₁O₃₉]^{7–} in **1** and **2** in contrast to [α-PW₁₂O₄₀]^{3–}. To compare with the IR spectrum of α-Na₇PW₁₁O₃₉ · nH₂O [954; 1099, 1042; 906, 865; and 809, 728 cm^{–1} for ν(W–O_t); ν(P–O_a); ν(W–O_b); and ν(W–O_c)], the ν(W–O_t) vibrations for **1** and **2** have red-shifts of 8–12 cm^{–1}, possibly from cations having stronger interactions to terminal oxygen of polyoxoanions, reducing the W–O_t bond force constant and leading to decrease of the W–O_t vibration frequency [47, 56]. Stretching absorptions of the –NH₂ and –CH₂ are observed at 3319–3142 and 2965–2868 cm^{–1} for **1**, and 3311–3134 and 2941–2884 cm^{–1} for **2**; bending vibrations of –NH₂ and –CH₂ appear at 1589 and 1461 cm^{–1} for **1** and 1573 and 1469 cm^{–1} for **2**, confirming the presence of organoamine ligands in **1** and **2**. The occurrence of vibration at 3472 cm^{–1} for **1** and 3464 cm^{–1} for **2** suggests the presence of lattice or coordination water.

3.4. TG analysis

The thermal stabilities of **1** and **2** were investigated on crystalline samples under air from 25°C to 800°C (Supplementary material). Compounds **1** and **2** undergo a two-step weight loss from 30°C to 800°C. For **1**, the weight loss of 4.22% from 25°C to 273°C corresponds to loss of three lattice water molecules, one coordination water, and 2.5 dap ligands (calcd 3.97%). On further heating, the second weight loss is 6.89% between 273°C and 800°C, assigned to removal of the remaining six dap ligands and two protons (calcd 7.12%). For **2**, the first weight loss is 5.72% from 25 °C to 297°C, corresponding to the release of 10 lattice water molecules, two coordination water molecules, and two en ligands (calcd 5.26%). The second weight loss of 4.72% from 297°C to 800°C is attributed to the removal of five en ligands and four protons (calcd 5.31%).

4. Conclusions

Two 3d–4f heterometallic monovacant Keggin phosphotungstates [Cu(dap)(H₂O)₂]_{0.5}[Cu(dap)₂]₄H₂[Pr(α-PW₁₁O₃₉)₂]·3H₂O (**1**) and [Cu(en)(H₂O)₂]₂[Cu(en)₂]_{1.5}H₄[Pr(α-PW₁₁O₃₉)₂]·10H₂O (**2**) have been hydrothermally synthesized and structurally characterized. Both **1** and **2** display organic–inorganic hybrid 2-D sheet architectures built by classic mono-Pr^{III} sandwiched dimeric moieties [Pr(α-PW₁₁O₃₉)₂]¹¹⁻ through [Cu(L)₂]²⁺ bridges (L = dap, en), representing rare organic–inorganic hybrid 2-D 3d–4f heterometallic monovacant Keggin POM species. Very recently, a photoluminescent 3d–4f heterometallic monovacant Keggin phosphotungstate [Cu(dap)₂(H₂O)] [Cu(dap)₂]_{4.5}[Dy(α-PW₁₁O₃₉)₂]·4H₂O was obtained to be published in due time. Other 4f metal cations are being introduced to this system, and we believe that more 3d–4f heterometallic POTs will be obtained. We are trying to exploit the reaction of other monovacant, trivacant and multivacant Keggin/Dawson POM precursors with 3d–4f heterometallic cations. We believe that this study will be important in expanding POM-based materials.

Supplementary material

CCDC nos 794868 and 794869 contain the supplementary crystallographic data for this article. 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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