

Four di-Cu^{II}-substituted sandwich-type germanomolybdates obtained under different reaction conditions: from zero-dimensional to two-dimensional structure†Suzhi Li,^{a,b} Yuan yuan Guo,^a Dongdi Zhang,^a Pengtao Ma,^a Xiaoyang Qiu,^b Jingping Wang^{*a} and Jingyang Niu^{*a}

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Four di-Cu^{II}-substituted sandwich-type germanomolybdates, (H₂en)₂H₇{[Na_{0.5}(H₂O)_{3.5}]₂-[Cu₂(β-Y-GeMo₉O₃₃)₂]}·6H₂O (**1**), (H₂en)₂H{[Na_{2.5}(H₂O)₁₂]₂[Cu(en)₂][Cu₂(β-Y-GeMo₉O₃₃)₂]}·8H₂O (**2**), [Na₄(H₂O)₁₂]₂H₄[Cu₂(β-Y-GeMo₉O₃₃)₂]}·11H₂O (**3**) and [Cu(en)₂]₂[Cu(en)₂(H₂O)₂]{[Cu(en)₂]₂-[Cu₂(β-Y-GeMo₉O₃₃)₂]}·8H₂O (**4**) (en = ethylenediamine), have been prepared. It is interesting that **1–3** were obtained in the same aqueous solution reaction system but exhibited different structures: **1** displays a 0D structure, **2** shows an organic–inorganic 1D chain structure, while **3** displays a 2D network. **4** was synthesized under hydrothermal condition by the same reagents, which represents the first transition metal-sandwiched organic–inorganic 2D heteropolymolybdate.

Introduction

The design and synthesis of novel transition-metal (TM) substituted sandwich-type polyoxometalates (POMs) based on trivalent Keggin polyoxoanions have attracted considerable attention in the last 20 years for their potential applications in the fields of magnetism, electrochemistry, optics, medicine, catalysis and functional materials.¹ To our knowledge, most of the reported compounds are TM-substituted sandwich-type heteropolytungstates (HPTs). The sandwich types include mononuclear,² dinuclear,³ trinuclear,^{3b,4} tetra-nuclear,^{4b,5} penta-nuclear,⁶ hexa-nuclear,⁷ hepta-nuclear,^{7d} even octa-nuclear⁸ and nenea-nuclear.⁹ Recently, Kortz's group, Wang's group and Yang's group have done a lot of work on the preparations and properties of sandwich-type HPTs. Compared with the extensive reports of TM-substituted sandwich-type HPTs, the molybdate analogues

are very limited, due to the structural lability of trivalent heteropolymolybdates (HPMs) in aqueous solution, resulting in saturated or monovacant Keggin polyoxoanions. In 1981, Fukushima reported the first di-Cu^{II}-substituted sandwich-type silicomolybdate [Cu₂(SiMo₉O₃₃)₂]^{12–};¹⁰ in 2007, Xu *et al.* addressed two di-TM-substituted sandwich-type arsenomolybdates [(CH₃)₄N]_{8n}[M(H₂O)₅]_{2n}(H₃O)_{2n}[M₂(H₂O)₁₀(MAS^VMo₉O₃₃)_{2n}][M(H₂O)₄(MAS^VMo₉O₃₃)₂]_n·20nH₂O (M = Mn²⁺–Co²⁺);¹¹ recently, they also synthesized a di-Mn^{II}-substituted sandwich-type vanadium molybdate [HN(CH₃)₃]₁₀[Mn₂(V^VMo₉O₃₃)₂]₁₀·10H₂O;¹² very recently, our lab reported several di/tetra-TM-substituted sandwich-type germanomolybdates.¹³ In the above compounds, the organic sections only act as counter cations. However, almost no pure organic–inorganic analogue has been reported; only one organic–inorganic one-dimensional (1D) chain HPM was reported in 2010, which consisted of the sandwich-type germanomolybdate polyoxoanions and the copper complex linkers.¹⁴ In this communication, we report the syntheses and characterizations of four di-Cu^{II}-substituted sandwich-type germanomolybdates, (H₂en)₂H₇{[Na_{0.5}(H₂O)_{3.5}]₂-[Cu₂(β-Y-GeMo₉O₃₃)₂]}·6H₂O (**1**), (H₂en)₂H{[Na_{2.5}(H₂O)₁₂]₂-[Cu(en)₂][Cu₂(β-Y-GeMo₉O₃₃)₂]}·8H₂O (**2**), [Na₄(H₂O)₁₂]₂H₄-[Cu₂(β-Y-GeMo₉O₃₃)₂]}·11H₂O (**3**) and [Cu(en)₂]₂[Cu(en)₂(H₂O)₂]{[Cu(en)₂]₂-[Cu₂(β-Y-GeMo₉O₃₃)₂]}·8H₂O (**4**) (en = ethylenediamine). It is interesting that the four compounds were obtained by the same reagents but exhibit different structures: **1**, **2**, **3** and **4** display a 0D, an organic–inorganic 1D chain, a 2D network and an organic–inorganic 2D network structure, respectively. To date, the di-TM-substituted sandwich-type germanomolybdates are rather rare.^{13,14} To our knowledge, **4** represents the first TM-sandwiched organic–inorganic 2D HPM.

^aInstitute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, P. R. China. E-mail: jpwang@henu.edu.cn, jyniu@henu.edu.cn; Fax: (+86) 378-3886876; Tel: (+86) 378-3886876

^bDepartment of Chemistry, Shangqiu Normal University, Shangqiu Henan 476000, P. R. China

†Electronic supplementary information (ESI) available: The unusual [β-Y-GeMo₉O₃₃]⁸⁻ unit derives from the well-known [β-GeMo₁₂O₄₀]⁴⁻, the space packing diagram of **4**, the IR spectra of **1–4**, the UV spectra of **1–4**, the TG curve of **4**, (a) temperature dependence of the χ_M and χ_{MT} for polycrystalline samples of **1** at a 2 kOe applied field; (b) The temperature evolution of the inverse magnetic susceptibility χ_M^{-1} for **1** between 50 and 300 K. CCDC reference numbers 859976, 859977, 861299 and 721330. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12491b

Experimental

Materials and measurements

All chemicals are commercially available and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. Inductively coupled plasma (ICP) analyses were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. IR spectra were obtained from a solid sample pelletized with KBr on a Nicolet 170 SXFT-IR spectrometer in the range 400–4000 cm^{-1} . UV absorption spectra were obtained with a U-4100 spectrometer at room temperature. TG analysis was performed in N_2 on a Perkin-Elmer-7 instrument. X-ray powder diffraction (XRPD) measurements were performed on a Philips X'Pert-MPD instrument with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the range $2\theta = 10\text{--}40^\circ$ at 293 K.

Syntheses of 1–3. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2.08 g, 8.60 mmol) and GeO_2 (0.10 g, 0.96 mmol) were successively dissolved in 40 mL HAc-NaAc buffer solution ($\text{pH} = 4.8$, 0.5 mol L^{-1}), and then $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (0.38 g, 1.92 mmol) and en (0.10 mL, 1.48 mmol) were added successively. The resulting mixture was heated in a water bath (80°C) for 1 hour and filtered after cooling. Evaporation at room temperature led to green crystals of **1** suitable for X-ray diffraction after 12 hours, which were collected by filtration and dried in air (Yield: *ca.* 35% based on Mo). Five days later, light purple crystals of **2** (Yield: *ca.* 25% based on Mo) and green crystals of **3** (Yield: *ca.* 20% based on Mo) formed in the filtrate. IR (KBr pellets, ν/cm^{-1} , Fig. S2†) for **1**: 3449 (s), 1626 (s), 1517 (s), 1402 (m), 1321 (w), 1043 (w), 928 (m), 883 (s), 845 (m), 766 (s), 675 (s), 526 (w). IR (KBr pellets, ν/cm^{-1} , Fig. S2†) for **2**: 3456 (s), 3298 (s), 3242 (w), 2954 (w), 2892 (w), 1628 (s), 1584 (s), 1463 (w), 1407 (w), 1276 (w), 1165 (w), 1097 (w), 1041 (s), 928 (s), 885 (s), 847 (s), 766 (s), 687 (s), 544 (m), 524 (m), 447 (w), 414 (m). IR (KBr pellets, ν/cm^{-1} , Fig. S2†) for **3**: 3524 (s), 1619 (s), 1519 (m), 1402 (w), 1206 (w), 1073 (w), 924 (m), 890 (s), 854 (m), 763 (s), 678 (s), 531 (m). Anal. Calcd (%) for **1**: C, 1.40; H, 1.55; N, 1.63; Na, 0.67; Cu, 3.69; Ge, 4.22; Mo, 50.15. Found: C, 1.45; H, 1.67; N, 1.57; Na, 0.60; Cu, 3.76; Ge, 4.26; Mo, 50.09. Anal. Calcd (%) for **2**: C, 3.86; H, 4.09; N, 4.50; Na, 4.62; Cu, 7.66; Ge, 5.84; Mo, 69.42. Found: C, 3.80; H, 4.01; N, 4.55; Na, 4.66; Cu, 7.62; Ge, 5.89; Mo, 69.37. Anal. Calcd (%) for **3**: H, 1.93; Na, 4.75; Cu, 3.28; Ge, 3.75; Mo, 44.58. Found: H, 1.99; Na, 4.70; Cu, 3.24; Ge, 3.81; Mo, 44.53.

Synthesis of 4. $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2.08 g, 8.60 mmol), GeO_2 (0.10 g, 0.96 mmol), $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (0.38 g, 1.92 mmol) were successively dissolved in 15 mL HAc-NaAc buffer solution ($\text{pH} = 4.8$, 0.5 mol L^{-1}), and then en (0.10 mL, 1.48 mmol) was added. The resulting mixture was stirred for 2 h, sealed in a Teflon-lined steel autoclave (30 mL), kept at 170°C for 5 days and then cooled to room temperature. Dark purple crystals (Yield: $\approx 35\%$, based on Mo) were obtained by filtering, washed with distilled water and dried in air. IR (KBr pellets, ν/cm^{-1} , Fig. S2†) for **4**: 3447 (s), 3294 (s), 3246 (w), 2955 (w), 2892 (w), 1632 (w), 1587 (s), 1461 (w), 1391 (w), 1323 (w), 1280 (w), 1167 (w), 1097 (m), 1046 (s), 921 (m), 879 (s), 849 (m), 764 (s), 679 (s), 529 (m), 450 (w), 418 (w). Anal. Calcd (%) for

1: C, 6.65; H, 2.70; N, 7.75; Cu, 11.72; Ge, 3.35; Mo, 39.81. Found: C, 6.59; H, 2.69; N, 7.71; Cu, 11.80; Ge, 3.29; Mo, 39.92.

X-ray crystallography

Intensity data for **1–4** were collected on Bruker CCD Apex-II diffractometer with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The structures **1–4** were resolved by direct methods using the SHELXTL-97 program package.¹⁵ The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Lorentz polarization and empirical absorption corrections were applied. No hydrogen atoms associated with the water molecules were located from the difference Fourier map. Positions of the hydrogen atoms attached to the carbon and nitrogen atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. Absorption effects were empirically applied. Crystallographic data and structural refinements for **1–4** are summarized in Table 1. Absorption effects were empirically applied. CCDC reference no. 859976, 859977, 861299 and 721330 are for **1**, **2**, **3** and **4**, respectively.†

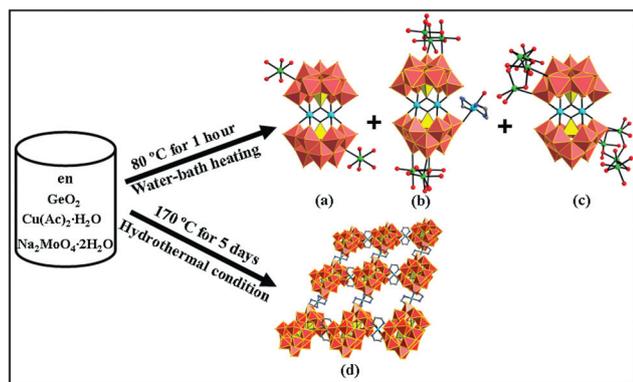
Results and discussion

Synthesis

1 was synthesized in HAc-NaAc solution by the direct reaction of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, GeO_2 , $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ and en using water-bath heating conditions, and light green crystals of **1** were obtained after 12 hours (Scheme 1a), which displayed a 0D structure. Light purple crystals of **2** (Scheme 1b) and green crystals of **3** (Scheme 1c) were found in the same solution five days later, which showed an organic–inorganic 1D chain structure and an inorganic 2D network, respectively. **4** was prepared under hydrothermal condition from the same reagents and displayed an organic–inorganic 2D network. As is well known, it is difficult to isolate trivacant HPMs and their sandwich-type species because lacunary HPM polyoxoanions generally show more structural lability in aqueous solution. The successful syntheses of **1–3** were achieved probably because: (1) sodium acetate buffer solution with optimum pH is favourable to the formation of lacunary germanomolybdate units in aqueous solution; (2) water-bath heating is milder than direct heating. In addition, the reason that **2** and **3** formed significantly later than **1** is that the solubilities of **2** and **3** are greater than that of **1**, owing to the existence of sodium clusters in **2** and **3**. To isolate di- Cu^{II} -sandwiched organic–inorganic high-dimensional structures, we attempted to change reaction conditions, such as temperatures, pH values of buffer solution and ratios of starting materials, but we were unsuccessful. By trial and error, we found that the hydrothermal method could prepare **4** (Scheme 1d). So, we presume that the high temperature and high pressure are crucial for the formation of high-dimensional structures. In addition, persistent attempts to prepare other first-row TM-sandwiched germanomolybdates using HAc-NaAc solution method and hydrothermal method were unsuccessful. Therefore, the nature of the TMs is crucial for the formation of **1–4**.

Table 1 Crystallographic data and structural refinements for 1–4

	1	2	3	4
Empirical formula	C ₄ H ₅₃ Cu ₂ Ge ₂ Mo ₁₈ N ₄ NaO ₇₉	C ₈ H ₁₀₁ Cu ₃ Ge ₂ Mo ₁₈ N ₈ Na ₅ O ₉₈	H ₇₄ Cu ₂ Ge ₂ Mo ₁₈ Na ₈ O ₁₀₁	C ₁₂ H ₅₈ Cu ₄ GeMo ₉ N ₁₂ O ₃₈
Formula weight	3443.72	4055.67	3873.74	2168.93
Temperature/K	296 (2)	296 (2)	296 (2)	296 (2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
a/Å	32.627 (8)	12.680 (6)	12.482 (7)	13.0503 (14)
b/Å	11.861 (3)	13.080 (7)	12.791 (8)	14.0662 (15)
c/Å	22.294 (6)	18.380 (9)	17.272 (15)	17.4386 (19)
V/Å ³	8580 (4)	2553 (2)	2343 (3)	2770.0 (5)
Z	4	1	1	2
F (000)	6476	1950	1844	2092
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.661	2.637	2.742	2.603
μ/mm^{-1}	3.821	3.461	3.558	4.097
Refl. collected	21 004	12 656	11 682	14 098
Independent refl.	7513	8839	8112	9575
GOOF	1.015	1.012	1.020	1.025
R(int)	0.0443	0.0388	0.0673	0.0212
Final R indices (I = 2σ(I))	R ₁ = 0.0489, wR ₂ = 0.1376	R ₁ = 0.0718, wR ₂ = 0.1985	R ₁ = 0.0538, wR ₂ = 0.1284	R ₁ = 0.0506, wR ₂ = 0.1398
R indices (all data)	R ₁ = 0.0785, wR ₂ = 0.1528	R ₁ = 0.1040, wR ₂ = 0.2134	R ₁ = 0.0671, wR ₂ = 0.1323	R ₁ = 0.0608, wR ₂ = 0.1454

**Scheme 1** Compounds **1** (a), **2** (b), **3** (c) and **4** (d) were obtained from the same reactants under different conditions. Isolated H₂en molecules, lattice water molecules and all H atoms were omitted for clarity.

Crystal structure

Structural analyses indicate that the skeletons of **1–4** are all made up of di-Cu^{II}-substituted sandwich-type germanomolybdate polyoxoanion [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻, which is constructed from the association of two unusual [β-Y-GeMo₉O₃₃]⁸⁻ fragments linked by two Cu^{II} ions leading to a sandwich-type structural assembly with C_{2h} point symmetry. The unusual [β-Y-GeMo₉O₃₃]⁸⁻ fragment can be viewed as a derivative of the well-known [β-B-GeMo₉O₃₃]⁸⁻ polyoxoanion by moving one MoO₆ octahedron on a Mo₃O₁₃ group of the [β-B-GeMo₉O₃₃]⁸⁻ polyoxoanion to the other side of itself, and capping to a window surrounded by another two Mo₃O₁₃ units (Scheme S1†). This structural feature is similar to the reported examples.^{10–14}

The molecular structure of **1** consists of a polyoxoanion unit {[Na_{0.5}(H₂O)_{3.5}]₂[Cu₂(β-Y-GeMo₉O₃₃)₂]}¹¹⁻, two isolated H₂en molecules, six lattice water molecules and seven protons based on charge balance (Scheme 1a). The polyoxoanion unit {[Na_{0.5}(H₂O)_{3.5}]₂[Cu₂(β-Y-GeMo₉O₃₃)₂]}¹¹⁻ is made up of a di-Cu^{II}-substituted sandwich-type germanomolybdate polyoxoanion

[Cu₂(β-Y-Ge Mo₉O₃₃)₂]¹²⁻ bonding two coordination cations [Na_{0.5}(H₂O)_{3.5}]^{0.5+} through two terminal oxygen atoms (Na–O: 2.353(16)–2.58(3) Å). In the polyoxoanion [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻, both equivalent Cu^{II} cations in the sandwich belt exhibit a six-coordinate distorted octahedral geometry defined by six oxygen atoms from two [β-Y-GeMo₉O₃₃]⁸⁻ fragments. The corresponding Cu–O distances range from 1.939(6) to 2.431(7) Å, and the Cu1...Cu1A separation is 2.968(2) Å.

The structural unit of **2** contains a polyoxoanion unit {[Na_{2.5}(H₂O)₁₂]₂[Cu(en)₂][Cu₂(β-Y-GeMo₉O₃₃)₂]}⁵⁻, two isolated H₂en molecules, eight lattice water molecules and a proton based on charge balance (Scheme 1b). In the polyoxoanion unit {[Na_{2.5}(H₂O)₁₂]₂[Cu(en)₂][Cu₂(β-Y-GeMo₉O₃₃)₂]}⁵⁻, the di-Cu^{II}-sandwiched germanomolybdate polyoxoanion [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻ links a copper coordination cation [Cu(en)₂]²⁺ and two sodium cation clusters [Na_{2.5}(H₂O)₁₂]^{2.5+} through one and four terminal oxygen atoms, respectively. The Cu²⁺ in [Cu(en)₂]²⁺ exhibits a hexa-coordinate octahedral configuration defined by four N atoms from two en ligands for the basal plane (Cu–N_{en}: 1.999(14)–2.005(13) Å) and two terminal O atoms from two adjacent polyoxoanions [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻ for the two axial positions (Cu–O_{POM} = 2.657(8) Å). In [Na_{2.5}(H₂O)₁₂]^{2.5+}, Na1, Na2 and Na3 (with occupancy ratio of 0.5) are all hexa-coordinate octahedra formed by oxygen atoms from water molecules and polyoxoanions, which join together through edge-/corner-sharing to form a cluster. It is notable that the adjacent {[Na_{2.5}(H₂O)₁₂]₂[Cu₂(β-Y-GeMo₉O₃₃)₂]}⁷⁻ polyoxoanion units connect each other *via* [Cu(en)₂]²⁺ bridges constructing a 1D organic–inorganic shoulder to shoulder structure (Fig. 1), which is different from the reported 1D head to head structure in which [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻ polyoxoanions link to cations [Cu(im)₄]²⁺ (im = imidazole) through extreme oxygen atoms.¹⁴

Different from **1**, **2** and **3** is pure inorganic di-Cu^{II}-sandwiched germanomolybdate, whose structural unit is composed of di-Cu^{II}-substituted sandwich-type germanomolybdate polyoxoanion [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻ linking two sodium cation clusters [Na₄(H₂O)₁₂]⁴⁺ through four terminal oxygen atoms, eleven

lattice water molecules and four protons based on charge balance (Scheme 1c). The most intriguing feature of **3** is that each tetrameric $[\text{Na}_4(\text{H}_2\text{O})_{12}]^{4+}$ cluster connects three $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ polyoxoanions, meanwhile each $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ polyoxoanion is combined with six tetrameric $[\text{Na}_4(\text{H}_2\text{O})_{12}]^{4+}$ clusters. By this interconnection mode, the 2D network is constructed (Fig. 2a). From the viewpoint of topology, when the tetrameric $[\text{Na}_4(\text{H}_2\text{O})_{12}]^{4+}$ clusters and $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ polyoxoanions are respectively viewed as three-/six-connected nodes, the 2D network can be simplified to a (3,6)-connected 2D topology (Fig. 2b), which is different from the (6,6)-connected 3D topology in $[\text{Na}_{12}(\text{H}_2\text{O})_{36}][\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2] \cdot 3\text{H}_2\text{O}$ reported previously.¹³

Compound **4** exhibits an asymmetric structure consisting of a polyoxoanion unit $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]\}^{8-}$, two

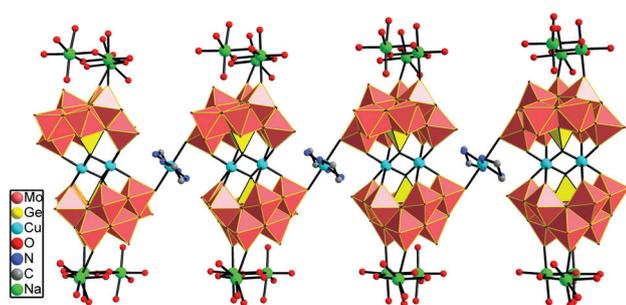


Fig. 1 The 1D chain structure of **2**. Isolated H_2en molecules, lattice water molecules and all H atoms were omitted for clarity.

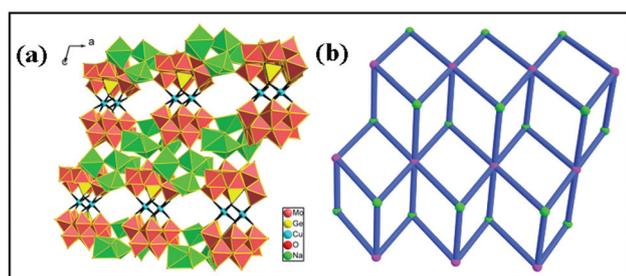


Fig. 2 The 2D network structure (a) and the (3,6)-connected 2D topology (b) of **3**. The $[\text{Na}_4(\text{H}_2\text{O})_{12}]^{4+}$ clusters and $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ polyoxoanions are respectively viewed as purple balls and green balls. Isolated H_2en molecules, lattice water molecules and all H atoms were omitted for clarity.

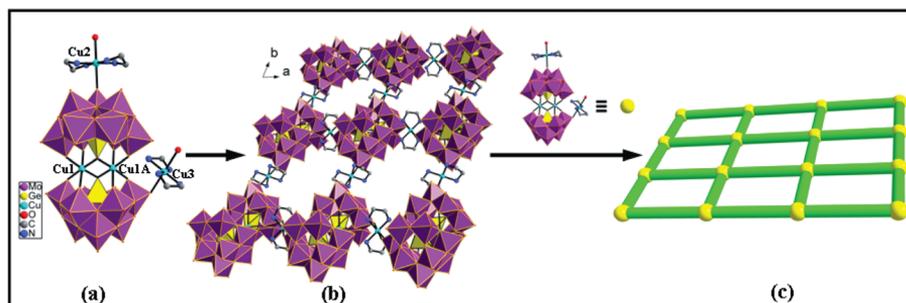
isolated $[\text{Cu}(\text{en})_2]^{2+}$ cations and two isolated $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ cations as charge balance ions and eight lattice water molecules. The polyoxoanion unit $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]\}^{8-}$ (Scheme 2a) consists of a di- Cu^{II} -substituted sandwich-type germanomolybdate polyoxoanion $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ and two $[\text{Cu}(\text{en})_2]^{2+}$ bridging cations of $[\text{Cu}_2(\text{en})_2]^{2+}$ and $[\text{Cu}_3(\text{en})_2]^{2+}$. Cu2 and Cu3 atoms are located on the special sites (0.5, 0.5, 0) and (0, 1, 0.5), respectively, which exhibit the elongated octahedral geometries defined by four N atoms from two en ligands for the basal plane (Cu–N_{en}: 2.007(8)–2.021(7) Å) and two terminal O atoms from two adjacent polyoxoanions $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ for the two axial positions (Cu–O_{POM} = 2.419(6) and 2.489(6) Å). Particularly, **4** shows a beautiful 2D network structure, in which the polyoxoanion $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ acts as a tetradentate ligand, bridging four adjacent polyoxoanions, forming a 2D window-like layer (Scheme 2b). By this interconnection mode, a fascinating ring with dimensions approximately 14.5×7.5 Å comes into being (Fig. S1†). From the viewpoint of topology, when the di- Cu^{II} -substituted sandwich-type germanomolybdate polyoxoanions $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$ are viewed as four-connected nodes, the 2D window-like layer can be simplified to a (4,4)-connected 2D topology net with Schläfli symbol $(4^4 \cdot 6^2)$ (Scheme 2c), in which each coordination cation $[\text{Cu}(\text{en})_2]^{2+}$ acts as a bidentate ligand linking two polyoxoanions $[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]^{12-}$. Although the TM-sandwiched 2D HPTs have been reported,^{5b,16} as far as we know, **4** represents the first di-TM-sandwiched inorganic–organic 2D HPM.

XRPD

The experimental XRPD patterns of the bulk products of **1–4** are in good agreement with the simulated XRPD patterns, indicating the phase purity of the samples of **1–4** (Fig. 3). The intensity differences between them are attributed to the variation in preferred orientation of the powder samples during collection of the experimental XRPD.

IR spectra

The IR spectra of **1** and **3** in the 400–1000 cm^{-1} range are similar and those of **2** and **4**, indicating the structural type of the polyoxoanions of **1** and **3** are almost the same, and those of **2** and **4** are also similar, which are in good agreement with the



Scheme 2 The polyhedral and ball-and-stick illustration of the polyoxoanion units $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2(\beta\text{-Y-GeMo}_9\text{O}_{33})_2]\}^{8-}$ in **4** (a), the 2D window-like layer (b) and (4,4)-connected 2D topology net (c) of **4**.

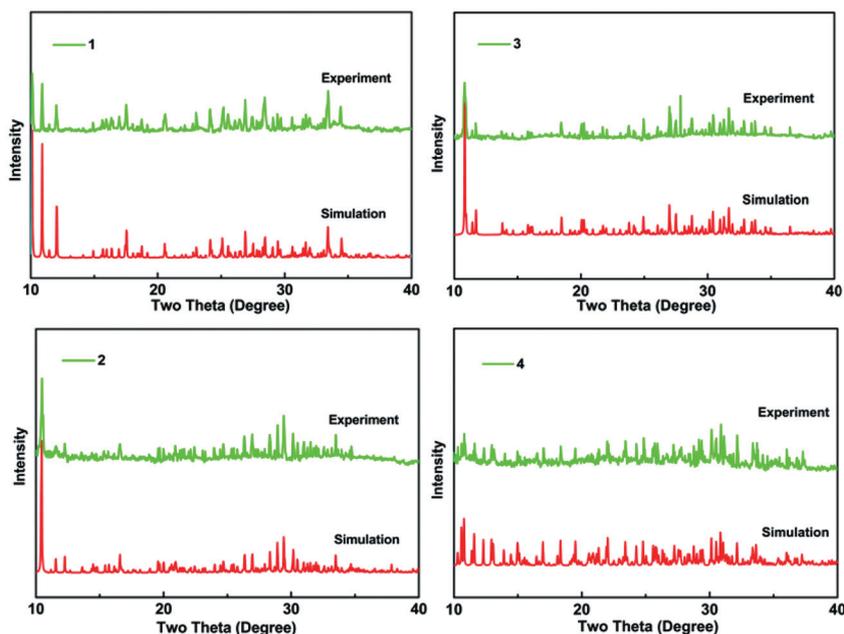


Fig. 3 Comparison of the simulated and experimental XRPD patterns of 1–4.

results of X-ray diffraction structural analyses. The IR spectra of 1–4 (Fig. S2†) in the low-wavenumber region all display four characteristic vibration patterns derived from the Keggin framework at 928, 883/845, 766 and 675 cm^{-1} for 1; 928, 885/847, 766 and 687 cm^{-1} for 2; 924, 890/854, 763 and 678 cm^{-1} for 3; and 921, 879/849, 764 and 679 cm^{-1} for 4, namely, $\nu(\text{Mo}-\text{O}_t)$, $\nu(\text{Ge}-\text{O}_a)$, $\nu(\text{Mo}-\text{O}_b)$ and $\nu(\text{Mo}-\text{O}_c)$, respectively.¹³ In addition, in 1, the vibration bands at 3449, 1626 and 1517 cm^{-1} can be assigned to the stretching bands of $-\text{OH}$ groups and the bending vibration bands of $-\text{NH}_2$ and $-\text{CH}_2$ groups, respectively. The stretching bands of $-\text{OH}$, $-\text{NH}_2$ and $-\text{CH}_2$ groups are observed at 3456, 3298 and 2954 cm^{-1} for 2, and 3447, 3294 and 2955 cm^{-1} for 4, respectively; and the bending vibration bands of $-\text{NH}_2$ and $-\text{CH}_2$ groups appear at 1584 and 1463 cm^{-1} for 2, and 1587 and 1461 cm^{-1} for 4, respectively. The occurrence of these resonance signals confirms the presence of en ligands in 1, 2 and 4.

UV spectra

The UV spectra of 1–4 in aqueous solution all display two similar absorption peaks at 206 and 233 nm for 1, 205 and 231 nm for 2, 208 and 232 nm for 3, and 206 and 231 nm for 4, respectively (Fig. S3†). The higher energy spectral band can be assigned to the charge transfer transitions of the $\text{O}_t \rightarrow \text{Mo}$ band, whereas the lower can be attributed to those of $\text{O}_{b,c} \rightarrow \text{Mo}$ band, suggesting the presence of polyoxoanions. In order to investigate the influences of the pH value on the stability of 4 in aqueous solution, *in situ* UV spectroscopic measurement of 4 was performed in aqueous solution. The pH values in the acidic direction and the alkaline direction were adjusted using diluted HCl solution and diluted NaOH solution, respectively. The pH value of 4 that was dissolved in water was 6.0. As shown in Fig. 4a, the UV spectrum of 4 in aqueous solution displays two

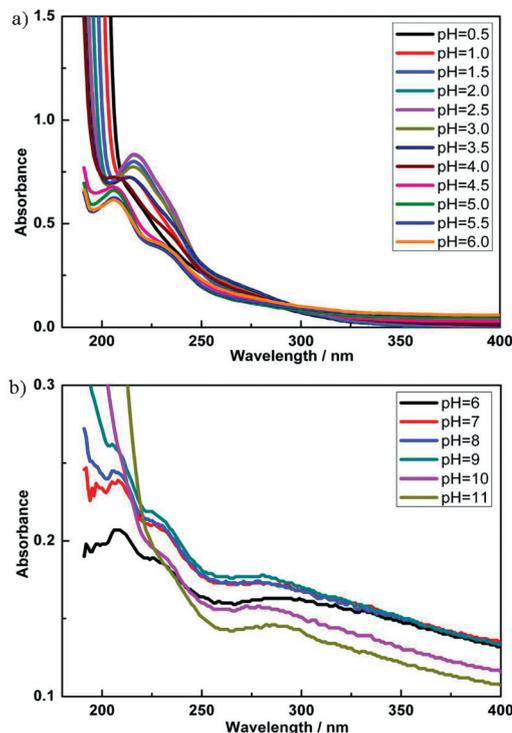


Fig. 4 The influence of the pH values on the stability of 4 in aqueous solution: (a) The UV spectral evolution with increasing acidity; (b) the UV spectral evolution with increasing alkalinity.

absorption bands at *ca.* 206 and 231 nm at pH = 6.0; when the pH value gradually decreases to near 4.5, there are no obvious changes. With the pH value further decreased, the absorption band at 206 nm is gradually red-shifted, while the absorption band at 231 nm slowly disappears. The reason for the red-shift of the $\text{O}_t \rightarrow \text{Mo}$ band may be that the terminal oxygen atoms of

polyoxoanions protonate. In contrast, when the pH value of **4** increases (Fig. 4b), both bands at 206 and 231 nm become weaker until they vanish, suggesting the decomposition of the skeleton of **4**. The above discussion indicates that the skeleton of **4** has been destroyed at pH lower than 4.5 and higher than 10, that is, the pH stable ranges of aqueous solution of **4** are *ca.* 4.0–9.0.

TG analysis

The thermal stability of **4** was investigated on crystalline samples under an N₂ atmosphere from 25 to 800 °C (Fig. S4†). The TG curve of **4** shows two steps of weight loss, giving a total loss of 20.23% (calc. 20.78%). The weight loss of 3.75% during the first step from 25 to 136 °C involves the release of eight lattice water molecules (calc. 3.32%). On further heating, the materials lose weight continuously during the second step with combined weight loss of 16.48% from 136 to 800 °C, corresponding to the removal of two coordinated water molecules and the decomposition of twelve en ligands (calc. 17.46%).

Conclusions

In conclusion, four di-Cu^{II}-substituted sandwich-type germanomolybdates, (H₂en)₂H₇{[Na_{0.5}(H₂O)_{3.5}]₂[Cu₂(β-Y-GeMo₉O₃₃)₂]}·6H₂O (**1**), (H₂en)₂H{[Na_{2.5}(H₂O)₁₂]₂[Cu(en)₂][Cu₂(β-Y-GeMo₉O₃₃)₂]}·8H₂O (**2**), [Na₄(H₂O)₁₂]₂H₄[Cu₂(β-Y-GeMo₉O₃₃)₂]}·11H₂O (**3**) and [Cu(en)₂]₂[Cu(en)₂(H₂O)]₂{[Cu(en)₂]₂[Cu₂(β-Y-GeMo₉O₃₃)₂]}·8H₂O (**4**), have been synthesized from the same reactants under different reaction conditions. It is interesting that **1–3** were obtained in the same aqueous solution reaction system but exhibited different structures: **1** displays a 0D structure, **2** shows an organic–inorganic 1D chain structure, while **3** is a 2D network structure. **4** was synthesized under the hydrothermal condition, which represents the first TM-sandwiched organic–inorganic 2D HPM in which each sandwiched polyoxoanion [Cu₂(β-Y-GeMo₉O₃₃)₂]¹²⁻ acts as a tetradentate ligand bridging four adjacent polyoxoanions through four [Cu(en)₂]²⁺ bridges. Magnetic measurement indicates **1** demonstrates antiferromagnetic exchange interactions. Further work in this area will be focused on making other novel multi-dimensional compounds by appropriate reaction conditions.

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