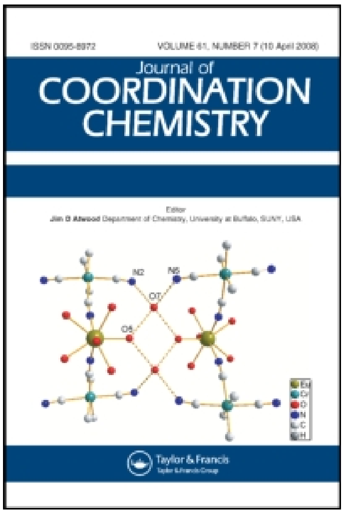

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Two extended organic-inorganic hybrids based on sandwich tungstogermanates

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Two extended organic–inorganic hybrids based on sandwich tungstogermanates

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Two inorganic–organic composite polyoxotungstates, $[Cu(en)_2(H_2O)]_2[Cu(en)_2(H_2O)_2]$-$\{[Cu(en)_2]_3[Cu_4(GeW_9O_{34})_2]\} \cdot 10H_2O$ (**1**, en = ethylenediamine) and $(H_2en)\{[Zn(en)_2]_4$-$[Zn_4(Hen)_2(GeW_9O_{34})_2]\} \cdot 10H_2O$ (**2**), were hydrothermally synthesized and their structures determined by single-crystal X-ray diffraction. Compounds **1** and **2** consist of sandwich polyanions $[Cu_4(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{12-}$ or $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$ linked by $[M(en)_2]^{2+}$ bridges to form 2-D networks, which are further packed into a 3-D supramolecular porous framework *via* extensive hydrogen bonding interactions. Their IR and UV spectra, thermal stabilities, and cyclic voltammograms were also investigated.

Keywords: Organic–inorganic hybrids; Polyoxometalates; Sandwich; Structure

1. Introduction

Polyoxometalates (POMs) have attracted interest in solid-state materials chemistry because of their structural diversity and potential applications in catalysis, medicine, and material sciences [1]. An important advance is decoration of polyoxoanions with various organic and/or transition metal complexes linking into 1-, 2-, even 3-D extended solid materials [2]. The introduction of transition metal complexes enrich the frameworks of polyoxometalates and ameliorate their electronic and magnetic properties [3]. Efforts have focused on transition metal complexes linking well-known POMs, such as Keggin-, Anderson-, Lindqvist-type, and Wells–Dawson type anions into high-dimensional networks under hydrothermal conditions [4]. Transition metal substituted sandwich-type polyoxoanions are an important subclass and may be ideal candidates because they have much more negative charge than the mother polyanions; the greater the charge density on the surface oxygens of POMs, the more metal–organic complex units coordinate to the POMs. However, almost all the reported sandwiched

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POMs are discrete structures, or high-dimensional structures constructed from sandwich clusters and sodium or potassium hydrated complexes; high-dimensional solid-state materials based on sandwiched POMs, and transition metal complexes are rare [5]. Considering hydrothermal synthesis techniques have been demonstrated to be a powerful tool for making extended POM-based solids [6–14], we thus attempted to make such solids by using trilacunary Keggin GeW_9O_{34} fragments as precursors under hydrothermal conditions. In this article, we report the hydrothermal syntheses and structures of two new extended organic–inorganic hybrids based on sandwich tungstogermanates and transition metal complexes.

2. Experimental

2.1. *Materials and instruments*

All reagents were used as purchased without purification. The trilacunary precursor $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}] \cdot 14H_2O$ was synthesized according to a procedure given in [15]. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. UV–Vis absorption and IR spectra were performed on a SHIMADZU UV–2550 visible spectrophotometer and a EQUINOX55 FT-IR spectrophotometer from 400–4000 cm^{-1} using KBr pellets. TG analyses were performed on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10°C min^{-1}. Cyclic voltammograms were performed on Chi660A software, the working electrode was GC and the reference electrode was SCE.

2.2. *Synthesis of $[Cu(en)_2(H_2O)]_2[Cu(en)_2(H_2O)_2]\{[Cu(en)_2]_3[Cu_4(GeW_9O_{34})_2]\} \cdot 10H_2O$ (1)*

A mixture of $Na_9[A\text{-}\alpha\text{-}GeW_9O_{34}] \cdot 14H_2O$ (0.80 g, 0.36 mmol), $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.00 mmol), en (0.10 mL), and H_2O (14 mL) was stirred for 30 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25 mL), kept at 180°C for 4 days and then the temperature was lowered to room temperature for 2 days. The pH values before and after the reaction were 6.0 and 5.5, respectively. Purple flake crystals were collected (0.25 g, 43% yield based on Cu). IR (KBr, cm^{-1}): 3444(s), 3240(s), 2946(m), 1587(m), 1457(w), 1395(w), 1332(w), 1278(w), 1182(w), 1108(w), 1048(m), 930(s), 881(s), 773(s), 708(s), 507(s), 447(s). Elemental analysis: Calcd (%) for $C_{24}H_{124}Cu_{10}Ge_2N_{24}O_{82}W_{18}$: C, 4.69; H, 2.03; N, 5.47; Cu, 10.33; W, 53.80. Found: C, 4.81; H, 1.88; N, 5.26; Cu, 10.19; W, 53.64.

2.3. *Synthesis of $(H_2en)\{[Zn(en)_2]_4[Zn_4(Hen)_2(GeW_9O_{34})_2]\} \cdot 10H_2O$ (2)*

A mixture of $Na_9[A\text{-}\alpha\text{-}GeW_9O_{34}] \cdot 14H_2O$ (0.80 g, 0.36 mmol), $ZnCl_2$ (0.136 g, 1.0 mmol), en (0.10 mL), and H_2O (12 mL) was stirred for 30 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25 mL), kept at 160°C for 4 days and then cooled to room temperature for 2 days. The pH values before and after the reaction were 6.2 and 6.0, respectively. The single crystals in the form of

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$H_{124}N_{24}C_{24}Ge_2Cu_{10}O_{82}W_{18}$	$C_{22}H_{112}N_{22}Ge_2W_{18}O_{78}Zn_8$
Formula weight	6151.35	5910.78
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group		
Unit cell dimension (Å, °)		
a	12.982(3)	12.376(3)
b	13.837(3)	13.468(3)
c	17.107(4)	17.536(5)
α	94.744(4)	109.167(5)
β	110.148(4)	94.446(5)
γ	101.066(4)	113.898(4)
$V(\text{Å}^{3)}$	2794.2(10)	2448.0(10)
Z	1	1
$D_{\text{Calcd}}/\text{g cm}^{-3}$	3.656	4.009
Goodness-of-fit on F^2	0.934	0.956
R_1, wR_2 $[I > 2\sigma(I)]$	0.0660, 0.1468	$R_1 = 0.0610$, $wR_2 = 0.1368$
R_1, wR_2 (all data)	0.1116, 0.1597	$R_1 = 0.1128$, $wR_2 = 0.1727$

$R_1 = \Sigma(|F_o| - F_c)/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$.

achromatous flakes were collected (0.28 g, 37% yield based on Zn). IR (KBr, cm^{-1}) for **2**: 3421(s), 1590(m), 1512(m), 1277(w), 1177(w), 1102(w), 1044(w), 929(s), 871(s), 767(s), 678(s), 514(s), 453(s). Elemental analysis: Calcd (%) for $C_{22}H_{112}N_{22}Ge_2O_{78}W_{18}Zn_8$: C, 4.47; H, 1.91; N, 5.21; Zn, 8.85; W, 55.98. Found: C, 4.53; H, 1.70; N, 5.11; Zn, 8.69; W, 55.83.

2.4. *Crystallography*

The X-ray crystallographic data of **1** and **2** were collected on a BRUKER SMART APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package. Heavy atoms (W, Zn, Cu, and Ge) were refined with anisotropic displacement parameters. Other atoms (O, C, and N) were refined isotropically. Hydrogen atoms were not included. Some water molecules exhibit disorder in **2** as often the case with polyoxometalates, and only 8 of the 10 water molecules indicated by elemental analyses and thermal analysis in **2** could be located. Crystal data and structure refinement for **1** and **2** are given in table 1. Selected bond lengths are listed in table 2.

3. Results and discussion

3.1. *Synthesis*

The pH of the reaction system and hydrothermal condition are crucial for formation and crystallization of the title compounds. The pH must be between 5.5 and 6.5; when pH was higher than 6.5 an unknown powder was the main product and when pH was

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

Bond	**1**	**2**
$W{=}O_t$	1.69(2)–1.79(2)	1.64(2)–1.733(18)
$W–O_b$	1.881(18)–2.02(2)	1.74(2)–2.07(2)
$W–O_c$	2.286(17)–2.39(2)	2.264(19)–2.374(18)
$Ge–O_c$	1.706(18)–1.739(19)	1.692(16)–1.787(19)

O_t = terminal oxygen atoms, O_b = bridging oxygen atoms, O_c = central oxygen atoms bridging with Ge.

lower than 5.5 ethylenediamine was protonated and could not coordinate to metal ions. As for many inorganic–organic hybrids of polyoxometalates and transition metal complexes, the title compounds could only be prepared under hydrothermal conditions, confirming that hydrothermal synthesis is a powerful tool for making extended POM-based solids.

3.2. *Structure description*

The X-ray crystallographic data for **1** and **2** reveal sandwich-type transition metal substituted tungstates and transition metal coordination fragments. The building unit of **1** can be described as a sandwich Cu_4-substituted polyoxoanions $[Cu_4(GeW_9O_{34})_2]^{12-}$ and copper complexes (figure 1a). $[Cu_4(GeW_9O_{34})_2]^{12-}$ is made up of two trilacunary $[B\text{-a-}GeW_9O_{34}]^{10-}$ moieties linked by four Cu^{2+} ions, of two types: part a is Cu1 and Cu1A bonded to six oxygens from $[Cu_4(GeW_9O_{34})_2]^{12-}$ to form a distorted octahedron and part b is Cu2 and Cu2A defined by five O atoms from $[Cu_4(GeW_9O_{34})_2]^{12-}$ moieties forming a distorted square pyramid. Thus, two CuO6 octahedra and two CuO5 square pyramids are linked by sharing edges to form an unexpected defective rhombic Cu4 unit (figure 1b), which differs from the usual rhombic M4 units with four edge-sharing MO_6 octahedra.

In **1**, $[Cu_4(GeW_9O_{34})_2]^{12-}$ units are linked through $[Cu6(en)_2]^{2+}$ complexes into a 1-D chain. In this chain, Cu's are octahedrally coordinated by two chelating en ligands and two trans–oxo (terminal oxygens) ligands from two adjacent $[Cu_4(GeW_9O_{34})_2]^{12-}$ clusters (Cu–O: 2.462(6) Å, Cu–N: 2.007(8) Å and 2.018(8) Å). For Cu3 and Cu3A as decorating atoms, each CuN_4O_1 square pyramid has two chelating en ligands and one terminal oxo ligand from $[Cu_4(GeW_9O_{34})_2]^{12-}$, Cu–O and Cu–N distances are 2.536(3) Å and 2.018(1)–2.046(3) Å, respectively.

Two adjacent $[Cu3(en)_2]^{2+}$ units as bridging bidentate ligand link two $[Cu(en)_2]_2[Cu_4(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$ clusters *via* weak Cu $\cdots$ O interactions (3.042(9) Å) to form a 2-D structure (figure 1c). On the basis of bond valence sum calculations, the oxidation states of Cu, W, and Ge are +2 (average value = 1.838), +6 (average value = 5.916), and +4 (average value = 4.24), respectively. The oxidation states of these atoms are consistent with the overall charge of **1**.

A noteworthy feature of **1** is that the vacant sites of the unusual defective rhombic Cu_4 units may be good centers for further structural derivation, such as intramolecular decoration through organic amine ligands to form unique hybrid structures. $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$ in **2** is such an example. The building block $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$ can be derived from the well-known sandwich $[Zn_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ anion [16]

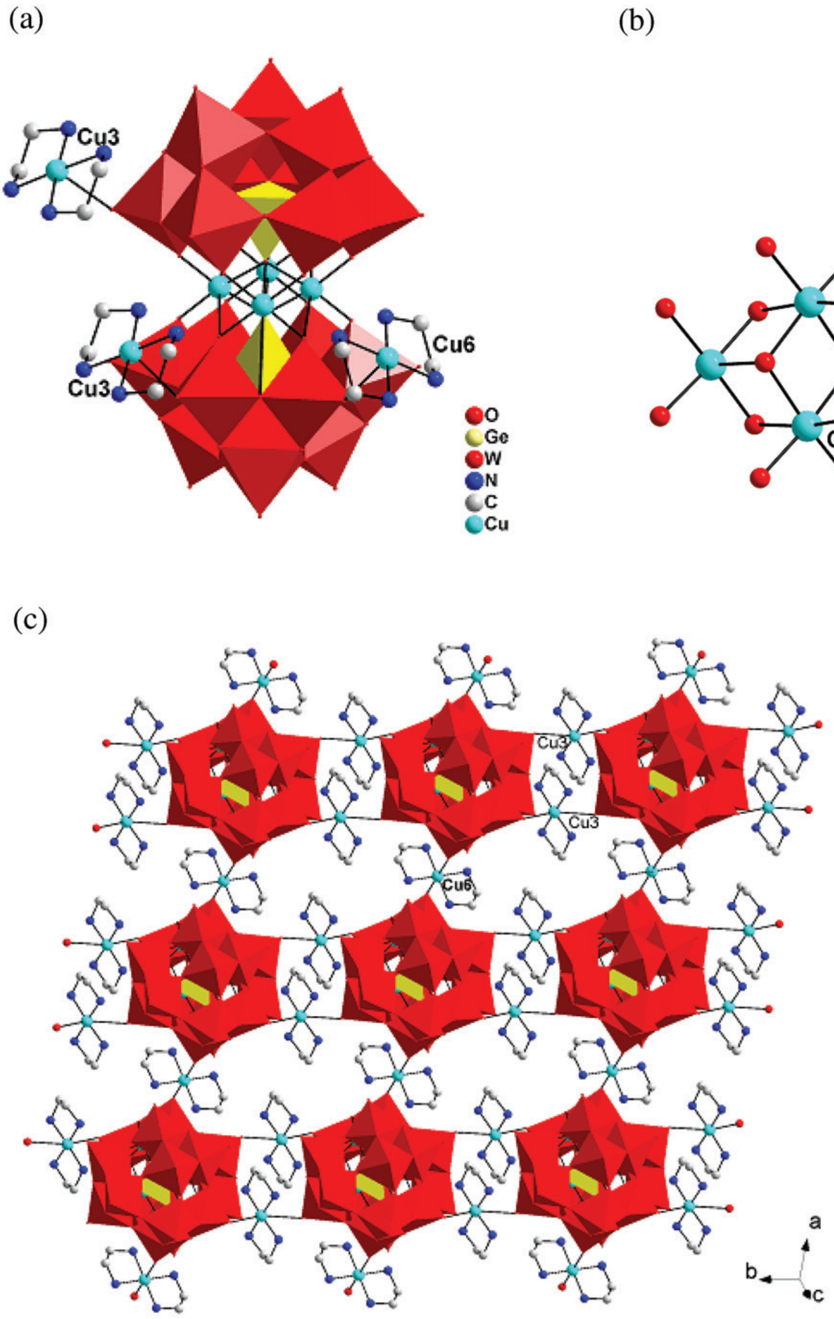

Figure 1. (a) Combined polyhedral/ball-and-stick representation of the hybrid unit $[Cu(en)_2]_3[Cu_4(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{6-}$; (b) defective rhombic Cu_4O_{14} cluster in $[Cu_4(GeW_9O_{34})_2]^{12-}$; (c) 2-D layer structure of **1**.

by replacing two water molecules of the central $Zn_4O_{14}(H_2O)_2$ fragment with two monoprotonated en. In $Zn_4O_{14}(Hen)_2$, all Zn centers have a distorted ZnO_6 or ZnO_5N octahedral environment with Zn–O (2.00(8)–2.19(6) Å) and Zn–N (2.19(0) Å) bond lengths in the usual range (figure 2b).

In **2**, $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$ is linked to four $Zn(en)_2^{2+}$ through three bridging and one terminal oxo of the anion (figure 2a). The four $Zn(en)_2^{2+}$ can be divided into two classes according to their roles as bridging or decorating groups. The decorating groups, which include Zn4 and its symmetry-equivalent Zn4A, are defined by one bridging oxo from $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$ and two chelating en ligands (Zn–N: 1.92(3) Å and 2.06(3) Å). Crystallographically independent Zn3 and Zn5, in the bridging role, are octahedrally coordinated with two en ligands (Zn–N: 1.98(4)–2.09(5) Å) and two terminal oxo or bridging oxo from two adjacent $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$ clusters (Zn–O: 2.72(8) Å and 2.25(9) Å) to form a 2-D network, as shown in figure 2(c). On the basis of bond valence sum calculations, the oxidation states of Zn, W, and Ge atoms are +2 (average value = 1.908), +6 (average value = 5.898), and +4 (average value = 4.02), respectively. The oxidation states of these atoms are consistent with the overall charge of **2**.

Extensive hydrogen bonding exists in the crystal structures of **1** and **2**. $\{Cu(enMe)_2\}^{2+}$ and $\{Zn(enMe)_2\}^{2+}$ bridging groups and lattice waters are positioned within the interlayer region and interacted with neighboring layers through N–H···O and O–H···O hydrogen bonds, making the layers 3-D supramolecular networks.

3.3. *IR and UV spectra*

The IR spectra of **1** and **2** (figures S1 and S2, Supplementary material) are similar with four characteristic peaks of POMs at 929–930 cm^{-1} ascribed to $\upsilon(W\text{–}O_t)$, 871–881 cm^{-1} ascribed to $\upsilon(W\text{–}O_b\text{–}W)$, 806–814 cm^{-1} ascribed to $\upsilon(Ge\text{–}O_a)$, and 767–773 cm^{-1} ascribed to $\upsilon(W\text{–}O_c\text{–}W)$ (where O_t = terminal oxygen, O_b = bridged oxygen of two octahedra sharing a corner, and O_c = bridged oxygen of two octahedra sharing an edge). The characteristic bands from 1044 to 1590 cm^{-1} can be regarded as features of en. All correspond to the spectrum of the heteropoly complex of Keggin structure previously reported [17]. In the UV electronic spectra of **1** and **2**, two strong absorption bands with maxima around 210 and 255 nm are observed attributed to the charge transfer of O_d–W and O_b/O_c–W, respectively.

3.4. *Thermal analyses*

The thermal stabilities of **1** and **2** were investigated under N_2 from 40 to 750°C (Supplementary material). For **1**, the weight loss of 4.11% (Calcd 4.25%) below 150°C was attributed to the release of crystal water. According to the thermal analysis curve, the anhydrous compound began to decompose at 275°C. In the range 275–619°C, weight loss of 10.73% was assigned to the decomposition of en ligands and POMs. The whole weight loss (14.84%) is in good agreement with the calculated value (15.97%). The anhydrous **2** was stable up to 266°C. Upon further heating until *ca* 690°C, weight loss was caused by decomposition of en ligands and POMs. The whole weight loss (14.68%) is in good agreement with the calculated value (14.23%).

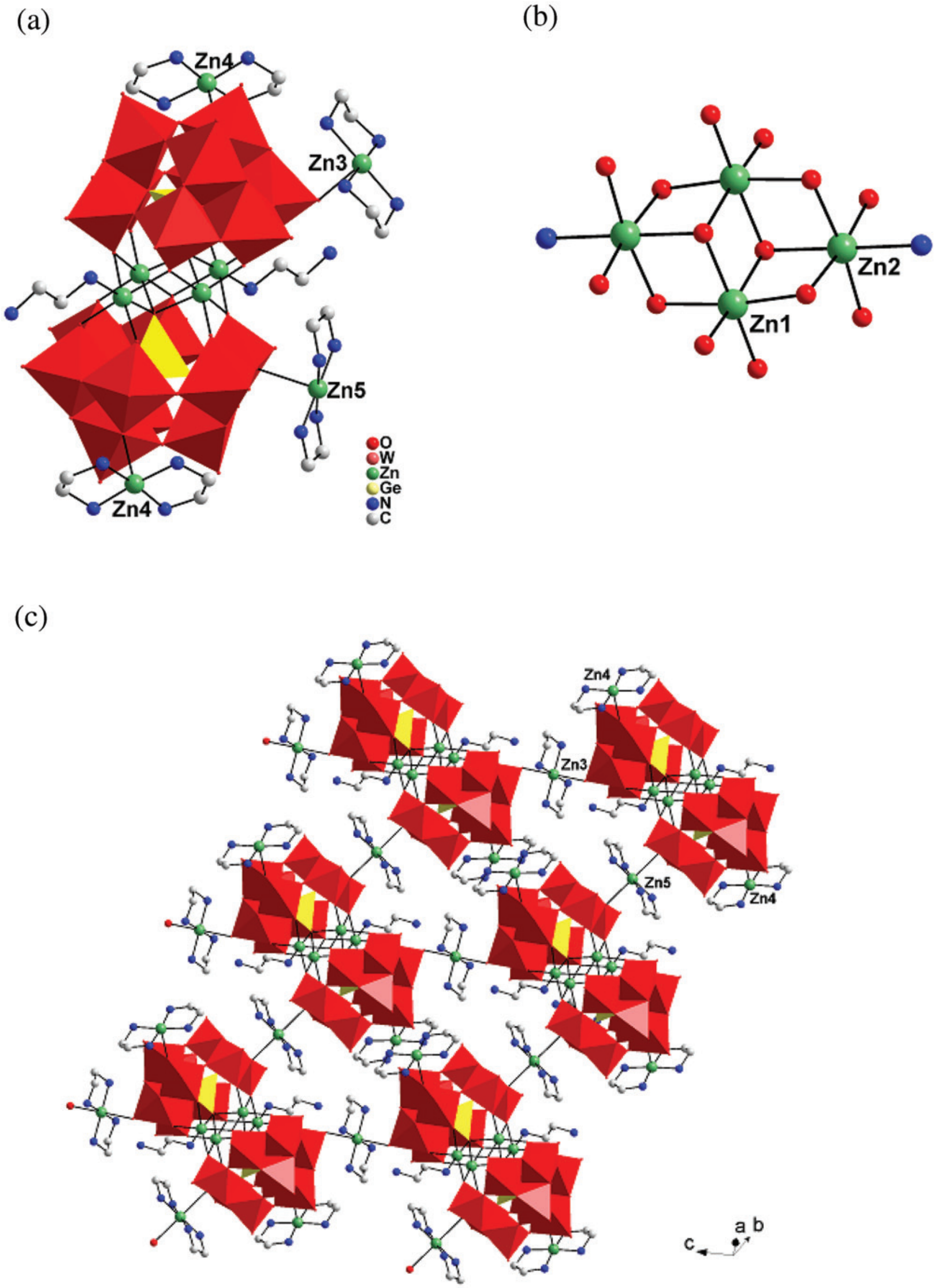

Figure 2. (a) Combined polyhedral/ball-and-stick representation of the hybrid unit for $[Zn(en)_2]_4[Zn_4(Hen)_2(GeW_9O_{34})_2]^{2-}$; (b) rhombic $Zn_4O_{14}N_2$ in $[Zn_4(Hen)_2(GeW_9O_{34})_2]^{10-}$; (c) 2-D layer structure of **2**.

3.5. *Cyclic voltammogram*

Cyclic voltammetry was carried out on pH = 6 solution (0.4 M CH_3COONa + CH_3COOH) at a scan rate of 10 mV s^{-1}. Compound **1** exhibits three redox pairs (figure 3a) with reduction peak potential values at −0.873, −0.711, and −0.123 V *versus* SCE, respectively, in the potential range of +1.2 to −1.2 V, assigned to the redox of W centers for I/I′ and II/II′ pairs, and the domain where the waves were located are similar

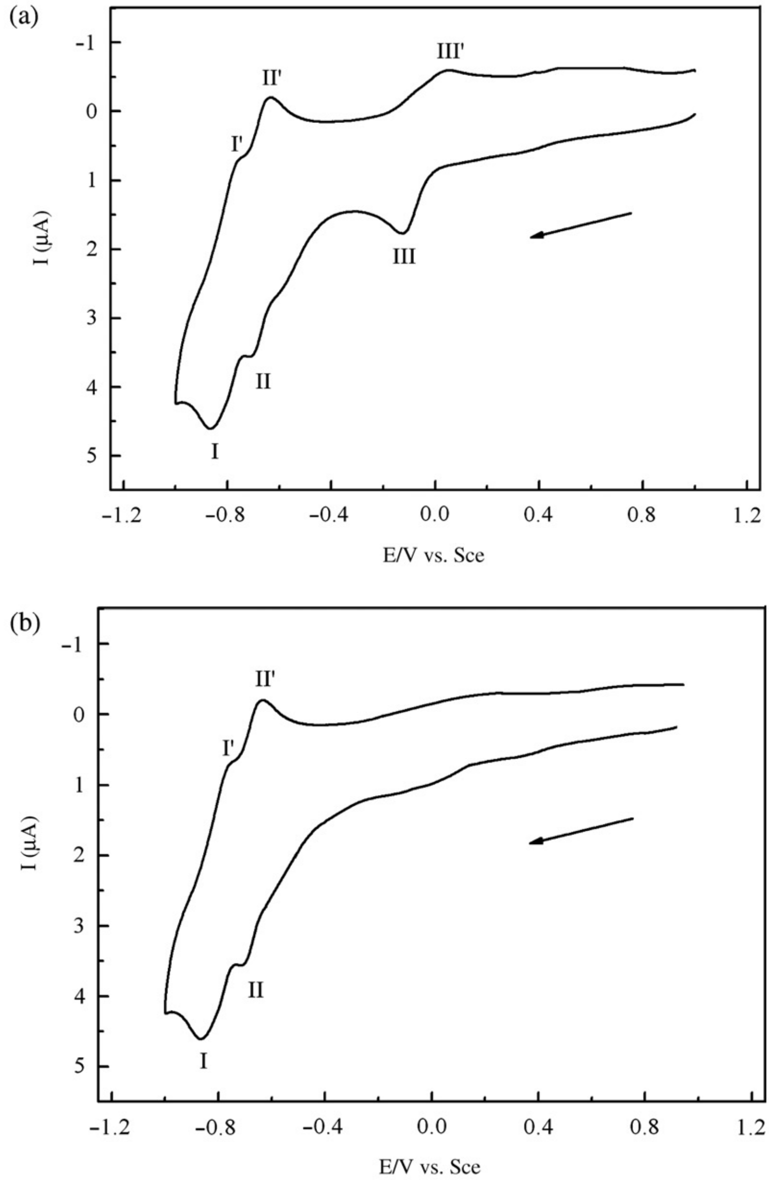

Figure 3. (a) CV curve of **1** in pH = 6 solution (0.4 M $CH_3COONa + CH_3COOH$). The scan rate was 10 mV/s^{-1}. (b) CV curve of **2** in pH = 6 solution (0.4 M $CH_3COONa + CH_3COOH$). The scan rate was 10 mV/s^{-1}.

to other tungsten-containing POMs [18–20], and the third pair associated a single oxidation process located at +0.044 V could be attributed to the redox processes of the Cu centers [18, 21]. The cyclic voltammogram of **2** is very similar as that of **1** in the negative potential domain and exhibits two redox pairs with reduction peak potential values at −0.866 and −0.696 V *versus* SCE (figure 3b), respectively, both assigned to the redox processes of the W centers.

4. Conclusion

Two sandwich M_4-substituted POM-based 2-D hybrid materials were synthesized under hydrothermal conditions. The successful synthesis of **1** and **2** enrich the diversity of sandwich-type TMSP chemistry and also provide an effective way for making unique inorganic–organic composite TMSPs, suggesting that preparation of 2-D and even 3-D extended solid frameworks consisting of transition metal substituted POMs and transition coordination fragments will be feasible under hydrothermal conditions.

Supplementary material

Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No: 705798 for $C_{24}H_{124}Cu_{10}Ge_2N_{24}O_{82}W_{18}$ (**1**) and 705799 for $C_{22}H_{112}N_{22}Ge_2O_{78}W_{18}Zn_8$ (**2**).

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