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Syntheses, structures and electrochemical properties of a class of 1-D double chain polyoxotungstate hybrids [H₂dap][Cu(dap)₂]₀.₅[Cu(dap)₂(H₂O)][Ln(H₂O)₃(α-GeW₁₁O₃₉)]·3H₂O

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A series of novel organic–inorganic hybrid 1-D double chain germanotungstates [H₂dap][Cu(dap)₂]₀.₅[Cu(dap)₂(H₂O)][Ln(H₂O)₃(α-GeW₁₁O₃₉)]·3H₂O [Ln = La III (1), Pr III (2), Nd III (3), Sm III (4), Eu III (5), Tb III (6), Er III (7)] (dap = 1,2-diaminopropane) have been hydrothermally prepared and structurally characterized by elemental analyses, powder X-ray diffraction (PXRD), IR spectra, thermogravimetric (TG) analyses, X-ray photoelectron spectroscopy (XPS) and single-crystal X-ray diffraction. The most prominent structural feature of 1–7 is that the [Ln(H₂O)₃(α-GeW₁₁O₃₉)]⁵⁺ moieties are firstly connected with each other via the W–O–Ln–O–W bridges creating a 1-D {[(Cu(dap)₂(H₂O)]}[Ln(H₂O)₃(α-GeW₁₁O₃₉)]}ₙ⁺ polymeric chain and then two adjacent antiparallel 1-D polymeric chains are linked together through [Cu(dap)₂]²⁺ linkages giving rise to the rare organic–inorganic hybrid 1-D Cu²⁺–Ln³⁺ heterometallic double-chain architectures. To the best of our knowledge, 1–7 represent the first 1-D double-chain Cu²⁺–Ln³⁺ heterometallic germanotungstates. The variable-temperature magnetic susceptibilities of 2, 4 and 7 have been investigated. Furthermore, the solid-state electrochemical and electro-catalytic properties of 3 and 4 have been carried out in 0.5 mol·L⁻¹ Na₂SO₄ + H₂SO₄ aqueous solution by entrapping them in a carbon paste electrode. 3 and 4 display apparent electro-catalytic activities for the nitrite, bromate and hydrogen peroxide reduction.

Introduction

Polyoxometalates (POMs) are polynuclear metal–oxo complexes with unique physical and chemical performances. The oxygen-rich surface of defect or lacunary POMs renders them become potential candidates to integrate transition-metal (TM) cations to form novel complexes such as luminescence, magnetism or Lewis acid catalysis can be also delivered to the desired outcomes during the course of derivatization or functionalization. Therefore, in recent years, a large number of Ln-containing POTs have been obtained. For instance, in 1997, Pope and co-workers reported a Ce₁₀-containing huge POT [As₂₂Ce₇₉W₁₄₈O₄₃₆(OH)₃₀]⁷⁶⁻. In 2001, an europium containing tetrameric phosphotungstate [{Eu(W₁₀O₃₃)₁₄(W₄O₁₄)}²₁]⁻ was discovered by Francesconi’s group. In 2002, Gouzerh et al. described two cerium-containing POTs [Ce(H₂O)₅As₄W₄₀O₁₄₀]²⁵⁻ and [(SbW₉O₃₃)₄{Sb₉O₃₃}₄]⁴₅⁻. In 2003, two crown-shaped europium containing arsenotungstates {K₂[Eu(H₂O)₂(α-As₂₉W₂₃O₇₆)O]₆}³⁵⁻ and {Cs₂[Eu(H₂O)₂(α-As₂₉W₂₃O₇₆)O]₄}²¹⁻ were separated. In 2007, an unprecedented Ce₂₀-containing gigantic germanotungstate (GT) [Ce₂₀Ge₁₀W₁₀₀O₃₇₄(OH)₃₀]⁵₆⁻ was prepared. Later, the longest Ln substituted POT molecule [Gd₃As₁₃₉₉₁₂₅₉₂₃(OH)₃₈₀]⁶₀⁻ was discovered. With the rapid development of POM chemistry, the first POM-based TM–Ln heterometallic derivative (PBTLHD) was reported in 2004. From then on, the design and synthesis of PBTLHDS have gradually become an emerging research field of POM chemistry owing to their potential applications in magnetism and catalysis as well as their intriguing architectures and topologies. However, as previously reported, there are unavoidable competitive reactions among highly negative POM precursors, strongly oxophilic Ln cations and less active TM cations in the reaction system, so the simultaneous combinations of lacunary POMs with TM and Ln components are comparatively difficult in the same system, which seems to be the key factor of the small number of reports on PBTLHDS. So,
currently, great efforts have been devoted to exploitation of novel PBTLHDs and some typical species have been successively synthesized (Fig. 1). Among PBTLHDs, only minority of TM–Ln-containing GTs have been reported. For example, Reinoso et al. prepared two Weakley-type heterometallic Cu/Mn–Ce substituted GTs \([\text{Ce}^{III}(\text{H}_2\text{O})_2]\_2\text{Mn}^{III} (\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2\] and \([\text{Cu}^{II}\text{(OAc)}]\_2\text{Mn}^{III} (\text{B-}\alpha\text{-GeW}_9\text{O}_{34})_2\] by reactions of \(\text{Ce}^{IV}\) cations with the synthons \([\text{Mn}^{II} (\text{H}_2\text{O})_2]\_2\text{B-}\alpha\text{-GeW}_9\text{O}_{34}\] and \([\text{Cu}^{II} (\text{H}_2\text{O})_2]\_2\text{B-}\alpha\text{-GeW}_9\text{O}_{34}\] in 2010 and 2011, respectively. Furthermore, a giant crown-shaped GT \(\text{Na}_4\text{K}_6 [\text{Ni}(\text{H}_2\text{O})_6] [\text{K}_{10} \text{Ce}_{24}\text{Ge}_{12}\text{W}_{12}0_{456}(\text{OH})_{12}(\text{H}_2\text{O})_{64}] \cdot 178\text{H}_2\text{O}\) was also obtained by them. As a result, the search and exploration on novel TM–Ln-containing GTs are still an incipient field. Under this background, we began to explore this challengeable area. Three organic–inorganic hybrid \(\{\text{Cu}_3\text{LnO}_4\}\) cubane inserted GTs \(\{[\text{Cu}^{II}(\text{en})_2]\_2 [\text{Cu}_3\text{Ln}(\text{en})_3(\text{OH})_2]\_2 [\text{Cu}(\text{H}_2\text{O})_2]_2 (\alpha\text{-GeW}_{11}\text{O}_{39})\}_2 \cdot 3\text{H}_2\text{O}\) (Ln = Eu\(^{III}\), n = 1; Ln = Tb\(^{III}\), n = 11; Ln = Dy\(^{III}\), n = 10) and three Cu–Ln-containing GT tetramers \(\text{Na}_2\text{H}_6 [\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2] [\text{Cu}^{II}(\text{en})_2 [\text{Pr}(\alpha\text{-GeW}_{11}\text{O}_{39})_2]_2 \cdot 1\text{H}_2\text{O}\). Very recently, we separated two unusual 1-D copper–bridged tetrahedral POM nanoclusters with tetrameric rare earth cores and GT vertexes \(\text{Na}_3\text{H}_7 [\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2] [\text{Pr}(\alpha\text{-GeW}_{11}\text{O}_{39})_2]_2 \cdot 3\text{H}_2\text{O}\) (RE = La\(^{III}\), n = 25; RE = Pr\(^{III}\), n = 2; RE = Nd\(^{III}\), n = 3; RE = Sm\(^{III}\), n = 4; RE = Eu\(^{III}\), n = 5; RE = Tb\(^{III}\), n = 6; RE = Er\(^{III}\), n = 7). In order to profoundly explore this research domain, we used dap \((\text{dap} = 1,2\text{-diaminopropane})\) instead of en, and finally, we made a series of novel organic–inorganic hybrid 1-D double chain GTs \([\text{H}_2\text{dap}][\text{Cu}(\text{dap})_2]_2 [\text{Cu}(\text{dap})_2] [\text{H}_2\text{O}] [\text{Ln}(\text{H}_2\text{O})_2] (\alpha\text{-GeW}_{11}\text{O}_{39})_2 \cdot 3\text{H}_2\text{O}\) (Ln = La\(^{III}\), Pr\(^{III}\), Nd\(^{III}\), Sm\(^{III}\), Eu\(^{III}\), Tb\(^{III}\), Er\(^{III}\)) by reactions of Ce\(^{IV}\) cations with the synthons \([\text{Mn}^{II} (\text{H}_2\text{O})_2]\_2\text{B-}\alpha\text{-GeW}_9\text{O}_{34}\] and \([\text{Cu}^{II} (\text{H}_2\text{O})_2]\_2\text{B-}\alpha\text{-GeW}_9\text{O}_{34}\] in 2010 and 2011, respectively.

Experimental

Materials and physical measurements

All chemicals were commercially purchased and used without further purification. \(\text{K}_2\text{Na}_3 [\alpha\text{-GeW}_{11}\text{O}_{34}] \cdot 25\text{H}_2\text{O}\) was synthesized according to the literature and characterized by IR spectra. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400–II CHNS/O analyzer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a
Preparations of 1–7

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{La}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (1). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.304 g, 0.099 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.083 g, 0.487 mmol), LaCl\(_3\) (0.097 g, 0.399 mmol), dap (0.10 mL, 1.201 mmol) and H\(_2\)O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 30% (based on K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O).

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{Pr}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (2). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.366 g, 0.119 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.109 g, 0.639 mmol), PrCl\(_3\) (0.083 g, 0.336 mmol), dap (0.10 mL, 1.201 mmol) and H\(_2\)O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 26% (based on K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O).

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{Nd}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (3). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.362 g, 0.118 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.088 g, 0.516 mmol), NdCl\(_3\) (0.095 g, 0.379 mmol), dap (0.10 mL, 1.201 mmol) and H\(_2\)O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 32% (based on K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O).

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{Sm}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (4). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.308 g, 0.100 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.086 g, 0.504 mmol), SmCl\(_3\) (0.084 g, 0.327 mmol), dap (0.10 mL, 1.201 mmol) and H\(_2\)O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 35% (based on K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O).

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{Eu}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (5). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.302 g, 0.098 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.098 g, 0.575 mmol), EuCl\(_3\) (0.089 g, 0.345 mmol), dap (0.10 mL, 1.201 mmol) and H\(_2\)O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 33% (based on K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O).

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{Gd}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (6). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.287 g, 0.093 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.065 g, 0.381 mmol), TbCl\(_3\) (0.086 g, 0.324 mmol), dap (0.10 mL, 1.201 mmol) and H\(_2\)O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 33% (based on K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O).

[\( \text{[H}_2\text{dap}][\text{Cu(dap)}(\text{H}_2\text{O})][\text{Cu(dap)}]_2\text{Er}(\text{H}_2\text{O})(\alpha\text{-GeW}_{11} \text{O}_{39})] \cdot 3\text{H}_2\text{O} \) (7). A mixture of K\(_8\)Na\(_2\)[A-\(\alpha\)-GeW\(_{34}O\(_{112}\)] 25H\(_2\)O (0.307 g, 0.099 mmol), CuCl\(_2\cdot2\)H\(_2\)O (0.098 g, 0.575 mmol),
ErCl₄ (0.107 g, 0.391 mmol), dap (0.10 mL, 1.201 mmol) and H₂O (5 mL, 278 mmol) was stirred for 2 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 5 d and then cooled to room temperature. Purple prismatic crystals were obtained by filtering, washed with distilled water and then dried in air at ambient temperature. Yield: ca. 33% (based on K₈Na₂[La₈(N₂O₁₄)₉].25H₂O]. Anal. calcd. (found %) for C₃₃H₂₄Cu₁₅Ge₈N₈O₄₆=W₁₁·H₂O (5.6): C 4.23 (4.34), H 1.66 (1.81), N 3.29 (3.14), Cu 2.80 (2.91), Er 4.91 (4.80), Ge 2.13 (2.04), W 59.37 (59.03). IR (KBr pellets, cm⁻¹): 3486(vs), 3307(w), 3258(w), 3143(w), 2970(w), 2942(w), 1620(m), 1587(m), 1461(w), 1384(w), 1175(w), 1065(m), 1019 (m), 944(s), 879(vs), 812(vs), 767(vs), 695(s) (Fig. S1A, S1B).

Preparations of 3- and 4-CPE

3-modified CPE (3-CPE) was fabricated as follows: 30 mg of graphite powder and 10 mg of 3 were mixed and ground together by an agate mortar and pestle to achieve a uniform mixture, and then 0.05 mL of paraffin oil was added with stirring. The homogenized mixture was packed into a glass tube with a 3.0 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with a Cu rod through the back of the electrode. In a similar manner, 4-CPE was made with 4.

X-ray crystallography

Intensity data for 1–7 were collected on a Bruker APEX-II CCD detector at 296(2) K with Mo Kα radiation (λ = 0.71073 Å). Direct methods were used to solve their structures and to locate the heavy atoms using the SHELXTL–97 program package.¹⁴ The remaining non-hydrogen atoms were found from successive difference Fourier syntheses and full-matrix least-squares refinements on F². Lorentz polarization and empirical absorption corrections were applied. No hydrogen atoms associated with water molecules were located from the difference Fourier map. The positions of hydrogen atoms attached to carbon and nitrogen atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding model using the default SHELXTL parameters. All the non-hydrogen atoms were anisotropically refined except for some water molecules, oxygen, carbon and nitrogen atoms (details are seen in ESI). Crystallographic data and structure refinements for 1–7 are summarized in Table 1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with CCDC 967043, 967044, 967045, 967046, 967047 and 967048 for 1, 2, 3, 4, 5, 6 and 7, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 X-ray diffraction crystallographic data and structure refinements for 1–7

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α = [∑||Fobs|| - |Fcalc||/∑||Fobs||]², β = [∑w(Fobs² - Fcalc²)²/∑w(Fobs²)²]²/2, w = 1/[σ²(Fobs²) + σ²(Fcalc²) + 1], P(F) = (F² + 2Fcalc²)/3, where x = 0.0099, y = 0.0000 for 1; x = 0.0601, y = 0.0000 for 2; x = 0.1070, y = 0.0000 for 3; x = 0.0368, y = 0.0000 for 4; x = 0.0267, y = 0.0000 for 5; x = 0.0958, y = 0.0000 for 6; x = 0.1413, y = 0.0000 for 7.
Results and discussion

Syntheses

1–7 were obtained from the reaction of lacunary GT precursor [α-A-GeW9O34]\(^{10–}\) with Cu\(^{II}\) and Ln\(^{III}\) cations in the participation of dop under hydrothermally conditions. Though the trivacant Keggin [α-A-GeW9O34]\(^{10–}\) precursor has been intensively exploited since 2004,\(^{11}\) investigations on the reactions of the [α-A-GeW9O34]\(^{10–}\) precursor, TM and Ln cations are rare. Considering the advantages of hydrothermal conditions, the flexibility of various coordination modes and the Jahn-Teller effect of Cu\(^{II}\) ions, and the expoxilibity and high coordination numbers of Ln\(^{III}\) cations, the system including [α-A-GeW9O34]\(^{10–}\), Cu\(^{II}\) and Ln\(^{III}\) was developed and some neoteric Cu–Ln containing GTs were made.\(^{12}\) Three double {Cu\(_3\)LnO\(_4\)} cubane inserted GTs [{Cu(en)}\(_2\){Cu\(_2\)(en)}\(_2\)O\(_2\)]\(^{10–}\) were first obtained.\(^{12a}\) When Gd\(^{III}\) or Y\(^{III}\) cations \(n = 11\); Ln = Tb\(^{III}\), \(n = 11\); Ln = Dy\(^{III}\), \(n = 10\) and three tetrameric architectures {Cu(en)}\(_2\){Ln(α-GeW\(_9\)O\(_{34}\))}\(_2\)\(^{24–}\) (Ln = La\(^{III}\), Pr\(^{III}\), Er\(^{III}\)) built by two 1:2-type [ Ln(α-GeW\(_9\)O\(_{34}\))]\(^{13–}\) moieties via a [Cu(en)]\(_2\)\(^{2+}\) bridge were first obtained.\(^{12a}\) When Gd\(^{III}\) or Y\(^{III}\) cations were introduced to the system, two tetrahedral PTBLHD nanoclusters Na\(_8\)K\(_2\)Cu\(_{10}\)La\(_{10}\)O\(_{33}\)\(_{10}\) [Cu(en)]\(_2\){Cu\(_2\)(en)}\(_2\)O\(_2\)]\(_{10}\) [RE=GeW\(_{11}\)O\(_{39}\)]\(_{10}\) \(n = 25\); RE = Eu\(^{III}\), \(n = 3\) were synthesized.\(^{12b}\) As ongoing efforts to this branch, when dop replaced en, seven isomorphous Cu\(^{II}\)–Ln\(^{III}\) containing GTs 1–7 were sequentially separated, whose main skeletons are constructed from the 1-D Cu\(^{II}\)–Ln\(^{III}\) heterometalllic GT double-chains by means of the bridging role of [Cu(dap)]\(^{2+}\) cations. From the above results, several points can be mentioned here: (a) All Cu\(^{II}\)–Ln\(^{III}\) containing GTs prepared by dop consist of [α-GeW\(_9\)O\(_{34}\)]\(^{10–}\) fragments although we used the [α-A-GeW\(_9\)O\(_{34}\)]\(^{10–}\) precursor, indicating that it is favorable for conversion from [α-A-GeW\(_9\)O\(_{34}\)]\(^{10–}\) to [α-GeW\(_9\)O\(_{34}\)]\(^{10–}\) during the course of formation. When K\(_8\)Na\(_2\)[α-GeW\(_9\)O\(_{34}\)]\(_{25}\)H\(_2\)O replaced K\(_8\)Na\(_2\)[α-A-GeW\(_9\)O\(_{34}\)]\(_{25}\)H\(_2\)O under similar conditions, the same target products can be not afforded, which can further support this proposal. (b) Organic ligands have an important influence on the structural constructions of the outcomes. When dop replaced en, we obtained 1-D double-chain Cu\(^{II}\)–Ln\(^{III}\) heterometallic GTs reported in this paper. (c) The nature of Ln\(^{III}\) ions greatly affects structural constructions in the [α-A-GeW\(_9\)O\(_{34}\)]\(^{10–}\), Cu\(^{II}\), Ln\(^{III}\) and en system whereas the nature of Ln\(^{III}\) ions has no obvious effect on structural constructions in the [α-A-GeW\(_9\)O\(_{34}\)]\(^{10–}\), Cu\(^{II}\), Ln\(^{III}\) and dop system. For example, in the presence of en, double {Cu\(_2\)LnO\(_4\)} cubic inserted GTs were made for Eu\(^{III}\), Tb\(^{III}\) and Dy\(^{III}\) cations, tetrameric {Cu(en)}\(_2\){Ln(α-GeW\(_9\)O\(_{34}\))}\(_2\)\(^{24–}\) were formed for La\(^{III}\), Pr\(^{III}\) and Er\(^{III}\) cations while copper-bridged tetrahedral PTBLHD nanoclusters are only formed by virtue of Gd\(^{III}\) or Y\(^{III}\) cations. In the participation of dop, only 1-D double-chain Cu\(^{II}\)–Ln\(^{III}\) heterometallic GTs were obtained. (d) The nature of TM cations can also influence the structural diversity of the products. Ni\(^{III}\) or Co\(^{III}\) were used in the presence of Ln\(^{III}\) ions under similar conditions, unfortunately, only organic–inorganic hybrid TM substituted GTs [enH\(_2\)]\(_{14}\), [Ni(en)]\(_2\){[Ni(en)]\(_2\)H\(_2\)O\(_2\)}\(_{2}\)[B–GeW\(_9\)O\(_{34}\)]\(_{2}\)\(_{14}\)H\(_2\)O\(_{15}\) and [[Co\(_{2}\)(dap)]\(_2\)(H\(_2\)O)]\(_{2}\)[Co(dap)]\(_2\)[Co(Hdap)]\(_2\)[B–GeW\(_9\)O\(_{34}\)]\(_{14}\)H\(_2\)O\(_{15}\) were obtained. When other TM ions such as Ti\(^{IV}\), Cr\(^{III}\), Fe\(^{II}\) and Cd\(^{II}\) ions were used, however, amorphous powders were obtained. In the future, we will introduce other functional organic ligands such as aliphatic polycarboxylic acid and aromatic polycarboxylic acid ligands to the system to prepare much more TM–Ln containing GTs with excellent properties and novel architectures.

Structural descriptions

Bond valence sum (BVS) calculations\(^{17a–c}\) of 1–7 indicate that the oxidation states of all W, Cu and Ln atoms are +6, +2 and +3, respectively (Table S1) and 1, 3, 5 and 7 are further confirmed by XPS spectra (Fig. 2, S2). The W\(_{4f}\) and W\(_{4f}\) binding energies of 34.0 and 35.7 eV for 1, 33.5 and 35.6 eV for 3, 34.0 and 35.9 eV for 5, 33.8 and 35.9 for 7 are coincident with the previous results,\(^{18a–c}\) which indicate that all the W centers are +6 in 1, 3, 5, 7. The spin–orbit components (2p\(_{3/2}\) and 2p\(_{1/2}\)) of the Cu\(_{2p}\) peak are well deconvoluted by two curves at 932.9 and 952.6 eV for 1, 392.8 and 952.0 eV for 3, 932.8 and 953.2 eV for 5, 933.3 and 953.0 eV for 7. These values are in line with the reported values,\(^{18d}\) confirming the presence of the Cu\(^{II}\) cations in 1, 3, 5, 7. Two peaks at 833.4 and 853.6 eV correspond to the La\(_{3d\_2/2}\) and La\(_{3d\_3/2}\) of the La\(^{III}\) cation in 1.\(^{15a}\) The peaks at 979.9 and 1003.7 eV are ascribed to the Nd\(_{3d\_2/2}\) and Nd\(_{3d\_3/2}\) of the Nd\(^{III}\) cation in 3.\(^{15b}\) In 5, the XPS profile exhibits two peaks at 1132.3 and 1162.0 eV, which are assigned to the 3d\(_{2/2}\) and 3d\(_{3/2}\) levels of the Eu\(^{III}\) cation.\(^{18e}\) The Eu\(_{5d}\) peak is found at 170.4 eV.\(^{18f}\) This paper is consistent with BVS calculations from X-ray structural analysis data.

Fig. 2 a) The XPS spectrum for W\(_{4f}\) and W\(_{4f}\) in 1; b) The XPS spectrum for Cu\(_{2p}\) and Cu\(_{2p}\) in 1; c) The XPS spectrum for La\(_{3d\_2}\) and La\(_{3d\_3}\) in 1; d) The XPS spectrum for W\(_{4f}\) and W\(_{4f}\) in 3; e) The XPS spectrum for Cu\(_{2p}\) and Cu\(_{2p}\) in 3; f) The XPS spectrum for Nd\(_{3d\_2}\) and Nd\(_{3d\_3}\) in 3.
The phase purity of 1–7 is supported by the agreement of the PXRD patterns of the bulks with the calculated patterns from the single-crystal structural analyses (Fig. S3, S4). The intensity differences between experimental and simulated PXRD patterns are due to the variation in preferred orientation of the powder sample during collection of the experimental PXRD. Single-crystal X-ray structural analyses display that 1–7 are isomorphous and all crystallize in the triclinic space group P–1. 1–7 all display a 1-D double-chain architecture formed by two 1-D antiparallel CuII–LnIII heterometallic GT polymeric chains {[Cu(dap)2(H2O)][Ln(H2O)3(α-GeW11O39)]}n3n– by means of the bridging functionality of the [Cu(dap)]2+ cations. Herein, only the structure of 1 is described in details. Additionally, because of the existence of the Jahn–Teller effect of CuII ions in the ligand field resulting in the elongation of the Cu–O distances, the Cu–O weak interactions will be considered in the following description. The asymmetrical structural unit [H2dap][Cu(dap)2]0.5[Cu(dap)(H2O)][Ln(H2O)3(α-GeW11O39)]·3H2O of 1 (Fig. 3a) consists of a mono-LaIII substituted Keggin-type [Ln(H2O)3(α-GeW11O39)]5– subunit, half [Cu(dap)]2+ bridging cation, one pendant [Cu(dap)(H2O)]2+ cation, a diprotonated [H2dap]2+ and three lattice water molecules. In the asymmetrical structural unit, the pendant [Cu(dap)(H2O)]2+ cation links to the [Ln(H2O)3(α-GeW11O39)]5– subunit via a terminal oxygen atom and is embedded in a severely distorted octahedral geometry, in which four nitrogen atoms from two dap ligands occupy the basal plane [Cu–N: 1.993(19)–2.022(18) Å] and a terminal oxygen atom [Cu–O: 3.277(11) Å] and a water ligand [Cu–O: 2.321(16) Å] stand on two axial positions. The bridging [Cu2(dap)]2+ cation is located on the special site with the atomic coordinate (0.5, 0.5, 0) leading to an occupancy of 50% and inhabits in an elongated octahedron defined by four nitrogen atoms from two dap ligands with Cu–N distances of 1.97(3)–1.99(3) Å building the equatorial plane and two oxygen atoms from two adjacent [Ln(H2O)3(α-GeW11O39)]5– subunits with long Cu–O distances of 3.310(42) Å occupying two polar sites. The [Cu1(dap)2(H2O)]2+ and [Cu2(dap)]2+ cations display elongated octahedral geometries, proving the occurrence of Jahn–Teller distortion of the copper cations in the ligand field, which can be inferred that both Cu1 and Cu2 cations adopt the electron configuration of (t2g)6(dx2-y2)1(dz2)2. The LaIII cation is captured by the monovacant [α-GeW11O39]8– fragment and resides in an eight-coordinate distorted square antiprismatic geometry (Fig. 3b). The LaIII cation is coordinated by eight oxygen atoms, four of which come from one [α-GeW11O39]8– fragment [La–O: 2.428(14)–2.488 (13) Å], one from the other neighboring [α-GeW11O39]8– fragment [La–O: 2.526(15) Å]. In the coordinate polyhedron around the LaIII cation, the O7, O2W, O3W and O4W group and the O30, O33, O35 and O39 group constitute two bottom planes of the square antiprism and the average deviations from their ideal planes are 0.1012 and 0.0072 Å, respectively. The distances between the La cation and two bottom planes are 1.4911 and 1.1312 Å, respectively. Especially, the La–O7 distance of 2.526(15) Å is much longer than those of the other La–O bonds (La–O30, La–O33, La–O35, La–O39) distances because the W–O–La–O7–W linkage participates in the construction of the 1-D chain (Fig. 4a). More interesting is that two asymmetrical structural units of 1 are joined together by means of the [Cu2(dap)]2+ cation constructing the dimeric structural unit {[Cu(dap)2(H2O)][La(H2O)3(α-GeW11O39)]}2+ (Fig. 3c). The most remarkable structural characteristic of

Fig. 3 a) The asymmetrical structural unit of 1 with the selected numbering scheme; b) The eight-coordinate distorted square antiprism of the LaIII cation; c) The dimeric structural unit made up of two {[Cu(dap)2(H2O)][La(H2O)3(α-GeW11O39)]}2+ moieties through a [Cu2(dap)]2+ linker. The atoms with “A, B” labels are symmetrically generated (A: 1 + x, y, z; B: 1 – x, 1 – y, –z). Hydrogen atoms, protons and lattice water molecules are omitted for clarity.

Fig. 4 a) The 1-D chain constructed by the W–O–La–O7–W linkers in 1;
b) The 1-D organic–inorganic hybrid double-chain architecture of 1; c) Arrangement of 1-D double-chains in the crystallographic ac plane in 1 showing the mode of −AAA−.

I is that each dimeric structural unit \([\{\text{Cu(dap)}_2(\text{H}_2\text{O})\}\{\text{La(H}_2\text{O})_3\}(\alpha-\text{GeW}_{11}\text{O}_{39})\}]^{16\text{−}}\) connects two adjacent identical units through four W–O–La–O–W bridges and construct the beauteous 1-D antiparallel double-chain motif (Fig. 4b). Alternatively, the 1-D antiparallel double-chain structure can be also viewed as a fusion of two 1-D linear chains \([\{\text{Cu(dap)}_2(\text{H}_2\text{O})\}\{\text{La(H}_2\text{O})_3\}(\alpha-\text{GeW}_{11}\text{O}_{39})\}]^{16\text{−}}\) via \([\text{Cu}2(\text{dap})_2]^{2+}\) linkers (Fig. 4a,4b). Actually, other 1-D polymeric chains created by mono-La substituted Keggin moieties have been previously observed. For example, in 2000, Pope and co-workers communicated two 1-D inorganic zigzag chain-like Ln-containing monovacant Keggin silicotungstates \([\text{Ln}-(\alpha-\text{SiW}_{11}\text{O}_{39})](\text{H}_2\text{O})_1]^{12\text{−}}\) (Ln = CeIII; LaIII);20a In 2003, Mialane et.al. discovered a 1-D inorganic linear \([\text{Yb}(\alpha-\text{SiW}_{11}\text{O}_{39})](\text{Na}_3\text{SiW}_{10}\text{O}_{36})\text{[Cu}_2(\text{dap})_2])^{2−}\) (Fig. 4c, S5). It should be pointed out that the design and assembly of metal-involved supramolecular architectures are currently of great interest in supramolecular chemistry and crystal engineering because they can provide novel topology and functional materials.21 Moreover, Keggin-based supramolecular architectures are regarded as one of the most promising materials potentially applied in the field of chemistry, biology and material sciences.22 From the viewpoint of supramolecular chemistry, supramolecular structures are also present in 1–7 considering hydrogen bonding interactions between nitrogen atoms of dap ligands and surface oxygen atoms of POM units and water molecules. Specifically speaking, dap ligands work as the proton donors, surface oxygen atoms of mono-RE substituted Keggin GTs and water molecules function as the proton acceptors, and then donors and acceptors are hydrogen-bonded together generating the infinitely 3-D supramolecular architectures (Fig. 6). The N–H⋯O distances are in the range of 2.67(3)–3.48(4) Å for 1, 2.859(19)–3.51(2) Å for 2, 2.87(3)–3.54(3) Å for 3, 2.83(4)–3.41(4) Å for 4, 2.64(6)–3.43(5) Å for 5, 2.59(3)–3.47(3) Å for 6, and 2.90(2)–3.35(4) Å for 7, respectively.

IR spectra

IR spectra for 1–7 were recorded as KBr pellets in the range of 4000–400 cm−1 (Fig. S1A, S1B). Their IR spectra display the characteristic vibration patterns resulting from the Keggin POT framework in the region of 1100–600 cm−1. Four characteristic vibration bands attributable to \(v_{ad}(\geq\text{O})\), terminal \(v_{ad}(\text{W}–\text{O})\), corner-sharing

Fig. 6 The 3-D extended supramolecular architecture of 1.
\( \nu_{\text{v}}(\text{W–O}) \), and edge-sharing \( \nu_{\text{v}}(\text{W–O}) \) asymmetric vibrations derived from the Keggin GT framework, appear at 879–873, 944–940, 814–810, 769–766 and 697–692 cm\(^{-1} \), respectively. Specifically, four groups of characteristic vibration bands corresponding to \( \nu(\text{Ge–O}) \), \( \nu(\text{W–O}) \), \( \nu(\text{W–O}) \), and \( \nu(\text{W–O}) \) are observed at 873; 940; 811; 767; and 692 cm\(^{-1} \) for 1, 876; 939; 813; 767; and 693 cm\(^{-1} \) for 2, 876; 941; 814; 769; and 695 cm\(^{-1} \) for 3, 876; 941; 814; 769; and 695 cm\(^{-1} \) for 4, 875; 942; 810; 766; and 693 cm\(^{-1} \) for 5, 877; 943; 813; 768; and 697 cm\(^{-1} \) for 6, 879; 944; 812; 767; and 695 cm\(^{-1} \) for 7, respectively. In general, these characteristic bands can be easily assigned in comparison with the corresponding bands of monovacant Keggin POT clusters.\(^{15,16a} \) Compared with the K\(_{6}\)Na\(_{3}\)[\( \alpha\)-GeW\(_{11}\)O\(_{39}\)]\(^{13}\)H\(_{2}\)O precursor,\(^{16b} \) the \( \nu(\text{W–O}) \) vibration bands for 1–7 are almost not shift, suggesting the weak influence of [Cu(dap)]\(^{2+}\) and [Cu(dap)]\(^{2+}\) (H\(_{2}\)O)\(^{3-}\) cations on the terminal oxygen atoms on the \( [\alpha\text{-GeW}_{11}\text{O}_{39}]^{8-} \) skeletons. This phenomenon can be also confirmed by the long Cu–O\(_{t}\) distances (> 2.5 Å) from the X-ray single crystal analyses. Furthermore, the possible major reason that the \( \nu(\text{W–O}) \) split into two bands may be related to the fact that the incorporation of the Ln cations to the defect sites of \( [\alpha\text{-GeW}_{11}\text{O}_{39}]^{8-} \) fragments lead to the deformation and distortion of the \( [\alpha\text{-GeW}_{11}\text{O}_{39}]^{8-} \) skeletons. In addition, the stretching bands of –OH, –NH\(_{2}\), and –CH\(_{2}\) groups are observed at 3486–3461, 3308–3140 and 2971–2928 cm\(^{-1} \), respectively. The bending vibration bands of –NH\(_{2}\) and –CH\(_{2}\) groups appear at 1621–1522 and 1493–1461 cm\(^{-1} \), respectively. The occurrence of these characteristic bands provides evidence of the incorporation of Ln cations into the defect sites of \( [\alpha\text{-GeW}_{11}\text{O}_{39}]^{8-} \) skeletons.

![Fig. 7](image_url)

**Fig. 7** a) Temperature dependence of magnetic susceptibility for 2 between 2 and 300 K; b) Temperature evolution of the inverse magnetic susceptibility for 2 between 80 and 300 K; c) Temperature dependence of magnetic susceptibility for 4 between 2 and 300 K; d) Temperature evolution of the inverse magnetic susceptibility for 4 between 100 and 300 K; e) Temperature dependence of magnetic susceptibility for 7 between 2 and 300 K; f) Temperature evolution of the inverse magnetic susceptibility for 7 between 80 and 300 K. The red solid lines were generated from the best fit by the Curie–Weiss expression.

### Magnetic Properties

Recently, the research and discovery of TM–Ln containing complexes with magnetic interactions in the solid-state chemistry and material science have been attracting increasing attention.\(^{23} \) Though lots of TM–Ln containing complexes have been reported, except for the isotropic Gd\(^{3+}\) cation having an \( f^7 \) electron configuration and an orbitally non-degenerate ground state, not much is known about the nature and magnitude of the exchange interaction of Ln cations between themselves and with other magnetic groups and the evolution of the magnetic properties along the Ln series,\(^{24a} \) because the magnetic properties of Ln cations are strongly influenced by spin–orbit couplings and in particular the magnetocrystalline anisotropy is generally large.\(^{24b,c} \) Generally, the orbital component of the magnetic moment is much more important for Ln cations compared to TM cations, since ligand-field effects are smaller and spin–orbit couplings larger for f electrons of Ln cations.\(^{25} \) Under the influence of the interelectronic repulsion and spin–orbit couplings, the \( 2^{5/2} \)–L group term of the \( 4f^n \) configuration of Ln cations is split into \( 2^{2S+1}L \) spectroscopic levels. Each of these states is further split into Stark sublevels by the ligand-field perturbation.\(^{24b} \) Although the theory of the paramagnetic properties of Ln cations has long been investigated, the presence of the large unquenched orbital angular momentum has not allowed the development of simple models for a rational analysis of the structural magnetic correlations.\(^{25c} \) Since there are Cu\(^{3+}\) and Ln\(^{3+}\) centers in 1–7, the magnetic susceptibilities of 2, 4 and 7 have been measured on their polycrystalline samples in an applied magnetic field of 2000 Oe in the temperature range of 2–300 K (Fig. 7) on a Quantum Design MPMS XL–7 magnetometer.

In the case of 2, the magnetic data for 2 are plotted in the form of \( \chi_M \) and \( \chi_M T \) versus \( T \) (Fig. 7a). The temperature dependence of \( \chi_M \) exhibits a slightly increases from 0.01 emu mol\(^{-1} \) at 300 K to 0.05 emu mol\(^{-1} \) at 36 K. This tendency becomes more pronounced below 36 K, exponentially reaching 0.42 emu mol\(^{-1} \) at 2 K. Correspondingly, the \( \chi_M T \) product at 300 K of 2.29 emu K mol\(^{-1} \) is consistent with the theoretical value (2.16 emu K mol\(^{-1} \)) expected for 1.5 non-interacting Cu\(^{II}\) cations (\( S = 1/2 \)) considering \( g = 2 \) and 1 isolated Pr\(^{III}\) cations (\( H_a, J = 4, g = 4/5 \)).\(^{25b} \) The \( \chi_M T \) value declines gradually between 300 and 34 K, where the \( \chi_M T \) value is 1.69 emu K mol\(^{-1} \). Below 34 K, it falls sharply to 0.82 emu K mol\(^{-1} \) at 2 K. This decline phenomenon is related to the depopulation of the Stark levels of Pr\(^{III}\) cations upon cooling. It is well known that ligand-field effects can split the 9-fold degenerate \( ^3H_4 \) ground state of the Pr\(^{III}\) cation into Stark levels and the value of \( \chi_M T \) mainly depends on the populations of those Stark levels.\(^{25c} \) As for 2, at 300 K, all the Stark levels from the 9-
fold degenerate $^3\text{H}_4$ ground states are populated, such that $\chi M T$ is equal to the value expected for one free Pr$^{III}$ ion and one and a half isolated Cu$^{II}$ cations, however, as temperature drops, the progressive depopulation of higher Stark levels occurs, leading to the decrease of the $\chi M T$ value. The curve of $\chi M T$ versus $T$ between 80 and 300 K (Fig. 7b) follows the Curie–Weiss expression $[\chi M = C/(T–\theta)]$ with $C = 2.44$ emu K mol$^{-1}$ and $\theta = –15.05$ K for 2. The larger $\theta$ value also indicates the importance of ligand-field effects in 2. In the meantime, the progressive depopulation of higher Stark levels can also result in the deviation of the curve of $\chi M T$ versus $T$ to the Curie–Weiss law.

For 4, the magnetic data are plotted in Fig. 7c in the form of $\chi M$ and $\chi M T$ versus $T$. The temperature dependence of $\chi M$ exhibits a slight increase from 0.003 emu mol$^{-1}$ at 300 K to 0.019 at 36 K and then exponentially to the maximal value of 0.321 emu mol$^{-1}$ at 2 K. The $\chi M T$ product at 300 K is 0.81 emu K mol$^{-1}$, being higher than the expected value of 0.65 emu K mol$^{-1}$ for 1.5 isolated Cu$^{II}$ cations with $S = 1/2$ and $g = 2$ and one free Sm$^{III}$ cation ($^4\text{H}_{5/2}$, $J = 5/2$, $g = 2/7$). This suggests the existence of the thermal population of the higher energy state of the free Sm$^{III}$ ion at room temperature. In general, the $^3\text{H}_4$ ground term for the free Sm$^{III}$ ion in the crystal field is split into six states by spin–orbit coupling and the spin–orbit coupling parameter is 1200 cm$^{-1}$, which often lead to the thermal population of the high energy states. The $\chi M T$ value decline from 300 to 2 K, finally reaches the minimum value of 0.64 emu K mol$^{-1}$, which illustrates the occurrence of the depopulation of the Kramers doublets of higher energy. Similar phenomenon have been observed in the Sm$^{III}$-containing complexes such as [Sm$_2$(4-cba)$_6$(phen)$_2$(H$_2$O)$_2$] and [(α-PW$_{11}$O$_{39}$)Ln(H$_2$O)(η$_3$-μ$_4$-1,1)-CH$_3$COO]$^{2-}$. Actually, the curve of $\chi M T$ versus $T$ in 100–300 K for 4 can be described using the Curie–Weiss law with the $C = 0.88$ emu K mol$^{-1}$ and $\theta = 33.89$ K (Fig. 7d), but the depopulation of the Kramers doublets of higher energy upon cooling results in the deviation of the relation of $\chi M T$ versus $T$ between 100 and 2 K.

With respect to 7, the $\chi M$ value slowly increase from 0.04 emu mol$^{-1}$ at 300 K to 0.42 emu mol$^{-1}$ at 40 K and then exponentially reaches the maximum of 8.50 emu mol$^{-1}$ at 2 K (Fig. 7e). The value of $\chi M T$ at 300 K of 12.33 emu K mol$^{-1}$ is in line with the sum (12.04 emu K mol$^{-1}$) of the contribution attributable to one and a half free Cu$^{II}$ cations ($S = 1/2$) with $g = 2.00$ and one free Er$^{III}$ cation in the $^4\text{I}_{15/2}$ group state ($J = 15/2$, $g = 6/5$). The $\chi M T$ value increase to a maximum of 18.85 emu K mol$^{-1}$ at 14 K upon cooling (Fig. 7e). This behavior may indicate that the $S_{D_{11/2}}$ = 11/2 local spins somewhat tend to align along the same direction. The $\chi M T$ decreases on the decreasing temperature from 14 to 2 K. This behavior suggests the intermolecular interactions. The relationship of $\chi M T$ versus $T$ in 80–300 K can be described by the Curie–Weiss law with $C = 11.60$ emu K mol$^{-1}$ and $\theta = –19.63$ K (Fig. 7f). However, as the temperature decreases from 80 to 2 K, the relation of $\chi M T$ versus $T$ does not follow the Curie–Weiss law.

Electrochemical and electrocatalytic properties

POMs, as a large and rapidly growing class, can undergo reversible multi-electron redox process, and can be utilized as the chemically bulk-modified CPEs with many advantages of inexpensive, easy to handle, easy to prepare, so they have attracted much attention in electrochemical applications and the manufacture of chemically modified electrodes. By means of cyclic voltammetry (CV), the solid-state electrochemical and electrocatalytic properties of 3 and 4 have been carried out in 0.5 mol·L$^{-1}$ Na$_2$SO$_4$ + H$_2$SO$_4$ aqueous solution (a medium suitable for testing electro-catalytic processes) by entrapping them in a carbon paste electrode (CPE). The reproducibility of cyclic voltammograms indicates that 3-
CPE and 4-CPE are stable in this medium. Since 3 and 4 are isostructural, their electrochemical and electro-catalytic properties are very similar (Fig. 8, S6). Since the pH value of the supporting electrolyte has a marked effect on the electrochemical behavior, we find that the best pH values of 3 and 4 are 1.34 and 1.35, respectively (Fig. S7, S8). Fig. 8a shows the typical CV behavior of 3 in a pH 1.34 sulfate medium (0.5 mol·L−1 Na2SO4 + H2SO4) at a scan rate of 50 mV s−1 at room temperature. The same to 4, its typical CV behavior is illustrated in Fig. S6a. It can be clearly seen that in the potential range of −0.8 to 0.4 V, the CV patterns are restricted to two pairs of redox waves and their mean peak potentials E1/2 = (Epa + Epc) / 2 are −0.613 V and −0.023 V (vs the Ag/AgCl electrode) for 3, and −0.548 V and 0.007 V (vs the Ag/AgCl electrode) for 4, respectively. As expected, the WVI-based wave is located at a more negative potential than that attributable to the CuII center. The former features the redox process of the WVI centers and the latter is attributed to the redox process of the CuII center in the polyoxoanion framework.12,26e

Previous studies have shown that POMs are capable of delivering the electrons to other species, thus serving as the powerful electron reservoirs for multi-electron reductions and electrocatalytic processes.27a For example, Toth and Anson applied the iron47-substituted Keggin type POMs as catalysts to the reductions of hydrogen peroxide and nitrite.29a Dong et al. observed that [SiW12O40]4− could be acted as an electrocatalyst for the reduction of nitrite.27b Here, 3-CPE and 4-CPE are employed to probe the electro-catalytic reductions of hydrogen peroxide, bromate and nitrite in 0.5 mol·L−1 Na2SO4 + H2SO4 aqueous solution (pH = 1.34 for 3 and pH = 1.35 for 4). The H2O2 electro-activity improvement is of special interest for applications such as chemical industry, biosensors and fuel cells.28 Thus, the electro-catalytic investigations on the reduction of hydrogen peroxide catalyzed by other POMs have been performed. For instance, in 2004, Wang’s group firstly reported the high electrocatalytic reduction activity of hydrogen peroxide catalyzed by the Keggin-type phosphomolybdate (PMo12)3-doped polypyrrole (PPy) CPE.28b In order to evaluate the electrocatalytic activity, 3-CPE and 4-CPE are employed to probe the electrocatalytic reduction of hydrogen peroxide (Fig. 8b, S6b). As shown in Fig. 8b and S6b, with the addition of hydrogen peroxide, the WVI-based reduction peak currents increase, while the corresponding oxidation peak currents decrease. However, the CuII reduction wave is almost unaffected by addition of hydrogen peroxide. The results show that the reduction of nitrite is mainly mediated by the reduced species of tungsten-oxo clusters in 3 and 4. To further illustrate their electrocatalytic potential, the reduction procedures of bromate catalyzed by them have been also carried out. The monitoring or removal of bromate species is interesting as it is present in drinking water samples as a byproduct of ozone disinfection and is often used as food additive.12b Moreover, the negative impacts of bromate on human body have been confirmed.26 As a result, developing new the rapid and inexpensive analytic methods to detect the presence of bromate is indispensable. So the electrocatalytic abilities of 3-CPE and 4-CPE toward the reduction of BrO3− have been studied in 0.5 mol·L−1 Na2SO4 + H2SO4 aqueous solution containing various NaBrO3 concentrations at room temperature. Fig. 8c and S6c show the cyclic voltammograms for the electrocatalytic reduction of bromate by 3-CPE and 4-CPE. The catalytic effects of BrO3− are similar to the H2O2 for 3 and 4, with addition of NaBrO3, the reduction peak currents of the CuII-based wave is less affected whereas the WVI-based reduction peak currents increase gradually and the corresponding oxidation peak currents gradually decrease, suggesting that the bromate is reduced by the species of tungsten components.28d Actually, such phenomenon has been previously encountered.12b,26c-f In addition, the electrocatalytic reduction of nitrite on 3-CPE and 4-CPE are also measured. The catalytic reduction evolution of nitrite on 3-CPE and 4-CPE can be seen clearly in Fig. 8d and S6d. Unlike the electrocatalytic reductions of hydrogen peroxide and bromate, the electrocatalytic reductions not only occur on the WVI-based wave obviously, but also appear on the CuII-based wave. With addition of NaN3, the reduction peak currents of the the WVI-based wave and CuII-based wave increase steadily and their corresponding oxidation peak currents decrease. The results show that the electrocatalytic reduction of nitrite is simultaneously mediated by the WVI-based wave and CuII-based wave in 3 and 4. As discussed above, 3 and 4 display apparent electro-catalytic activities for the nitrite, bromate and hydrogen peroxide reduction.

Conclusions

In conclusion, we have synthesized a family of 1-D double chain organic–inorganic hybrid Cu–Ln heterometalllic GTS [H2dap]4[Cu(dap)2(H2O)][Cu(dap)2]6[Ln(H2O)3(a−GeW12O40)]·3H2O [Ln = LaIII (1), PrIII (2), NdIII (3), SmIII (4), EuIII (5), TbIII (6), ErIII (7)] under hydrothermal conditions, which are structurally characterized by elemental analyses, IR spectra, PXRD, TG analyses XPS and single-crystal X-ray diffraction. X-ray diffraction structural analyses indicate that 1–7 are isomorphic and adopt novel 1-D double-chain architectures constructed by two antiparallel 1-D polymeric chains linked through [Cu(dap)]2+ linkages. As far as we know, they exemplify a scarce type of organic–inorganic hybrid 1-D double chain Cu–Ln heterometalllic GTS. The magnetic properties of 2, 4 and 7 have been measured and their magnetic behaviors are mainly affected by Ln centers with strong spin–orbit coupling contribution and /or the ligand-field perturbation. The TG curves of 2, 5, 6 and 7 show two steps of weight loss between 25 and 700 °C. Furthermore, the solid-state electrochemical and electro-catalytic properties of 3 and 4 have been evaluated. The electrocatalytic reductions of hydrogen
peroxide and bromate are principally mediated by the WVI-based wave while the reduction of nitrite is simultaneously mediated by the WVI-based wave and CuII-based wave. In short, 3-CPE and 4-CPE have obvious electro-catalytic activities for the reductions of hydrogen peroxide, bromate and nitrite. The key points of the other functional organic ligands such as aliphatic polycarboxylic wave while the reduction of nitrite is simultaneously mediated by WVI-based

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References


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Syntheses, structures and electrochemical properties of a class of 1-D double chain polyoxotungstate hybrids \([\text{H}_2\text{dap}]\text{[Cu(dap)]}_2\text{[Cu(dap)(H}_2\text{O)}][\text{Ln(H}_2\text{O)}_3(\alpha-\text{GeW}_{11}\text{O}_{39})]·3\text{H}_2\text{O}\]

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A series of novel organic–inorganic hybrid 1-D double chain germanotungstates 1–7 are the first 1-D double-chain Cu\(^{II}\)–Ln\(^{III}\) heterometallic germanotungstates.