Combination between lacunary polyoxometalates and high-nuclear transition metal clusters under hydrothermal conditions: first (3,6)-connected framework constructed from sandwich-type polyoxometalate building blocks containing a novel $\{Cu_8\}$ cluster†

Jun-Wei Zhao, Jie Zhang, Shou-Tian Zheng and Guo-Yu Yang*

Received (in Cambridge, UK) 4th September 2007, Accepted 7th November 2007
First published as an Advance Article on the web 21st November 2007
DOI: 10.1039/b713510f

An unprecedented (3,6)-connected 3-D framework constructed from sandwich-type polyoxometalate building blocks containing a $\{Cu_8\}$ cluster, $[Cu(H_2O)_2]H_2[Cu_8(dap)_4(H_2O)_2(\alpha\text{-B-GeW}_9O_{34})_2]$ (dap = 1,2-diaminopropane) has been hydrothermally made, which provides a novel topological structure in transition metal substituted polyoxometalates.

The continuous interest in designing and making novel transition metal substituted polyoxometalates (TMSPs) has persisted because of their impressive compositional diversity and versatile applications in catalysis, medicine and material science.[1] Since the first sandwich-type $[Co_4(H_2O)_2(\alpha\text{-B-PW}_9O_{34})_2]^{10-}$ was found in 1973,[2] sandwiched TMSPs have developed as one of the most important subfamily in polyoxometalate (POM) chemistry.[3] So far, many sandwiched TMSPs have been reported, however, only 2- to 6-nuclear coplanar sandwiched TM clusters in sandwich belts were found (Fig. 1a–g). Although several inorganic–organic composite sandwiched TMSPs containing 2- to 4-nuclear TM clusters have been made,[4] the design and synthesis of novel inorganic–organic composite sandwiched POMs incorporating more TM centers remain less explored. Recently, we developed an effective strategy of using (a) the lacunary sites of the XW_9O_{34} (X = P/Si/Ge) fragments as structure-directing agents to induce the formation of large oligomers of TM clusters and (b) multidentate amines as structure-stabilizing agents to capture and stabilize TM oligomers formed *in situ*, to construct further novel inorganic–organic composite POMs under hydrothermal conditions. In this way, we obtained a series of POMs based on a single trivacant Keggin fragment capped by a $\{Ni_6\}$ cluster.[5] In the realization of these TMSPs, if two trivacant XW_9O_{34} fragments simultaneously interact with the TM oligomers generated *in situ*, novel sandwiched TMSPs may be formed under hydrothermal conditions. Great efforts have been made to attain this target and, fortunately, a novel $\{Cu_6\}$ sandwiched silicotungstate was first isolated (Fig. 1g).[6] As a continuance of our work, a novel 3-D (3,6)-connected $\{Cu_8\}$ sandwiched germanotungstate $[Cu(H_2O)_2]H_2[Cu_8(dap)_4(H_2O)_2(\alpha\text{-B-GeW}_9O_{34})_2]$ (**1**) with a $(4{\cdot}6^2)(4^2{\cdot}6^4{\cdot}8^7{\cdot}10^2)$ topological net was made. Similarly, an isomorphous $[Cu(H_2O)_2]H_2[Cu_8(en)_4(H_2O)_2(\alpha\text{-B-SiW}_9O_{34})_2]$[7] (**2**) was also obtained by using ethylenediamine (en) as a structure-stabilizing agent in our lab.

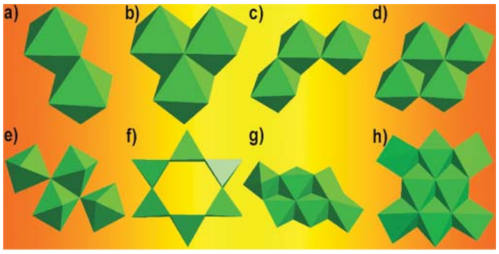

Fig. 1 Polyhedral views of some coplanar TM cluster units previously reported (a)–(g) and herein investigated (h) in the sandwich belts.

The phase purity of **1** was made by hydrothermal reaction of $K_8Na_2[\alpha\text{-A-GeW}_9O_{34}]\cdot 25H_2O$ (α-A-GeW$_9$) and $CuCl_2\cdot 2H_2O$ in the presence of dap at 100 °C for 5 days.‡ Notice that the α-A-GeW$_9$ unit in the starting material was transformed to the α-B-GeW$_9$ unit in **1**, mostly because the α-A-GeW$_9$ unit has six exposed surface oxygen atoms in the vacant site while the α-B-GeW$_9$ unit has seven exposed surface oxygen atoms, which favors the case that the α-B-GeW$_9$ unit can work as a heptadentate ligand to coordinate to the $\{Cu_8\}$ cluster and enhance the stability of **1** (Scheme S1†). The structural unit of **1** consists of a dimer $[Cu_8(dap)_4(H_2O)_2(\alpha\text{-B-GeW}_9O_{34})_2]^{4-}$, $\{Cu_8(GeW_9)_2\}$ and one $[Cu(H_2O)_2]^{2+}$ cation (Fig. 2a).§ A crystallographically imposed C_4 axis passes through (0, 1/2, 0). The dimer of $\{Cu_8(GeW_9)_2\}$ is built by two trivacant Keggin α-B-GeW$_9$ fragments in a staggered pattern linked by a $\{Cu_8\}$ cluster unit, $\{[Cu(dap)]_4Cu_4O_{14}(H_2O)_2\}$(Fig. 1h, Fig. 2b), *via* eight μ_3-O and four μ_4-O atoms from the lacunae of two α-B-GeW$_9$ units and two central μ_4-O atoms from two GeO_4 groups. In comparison with the classical $\{Cu_4\}$ sandwiched cluster $[Cu_4(H_2O)_2(\alpha\text{-B-GeW}_9O_{34})_2]^{12-}$,[8] the $\{Cu_8\}$ sandwiched $\{Cu_8(GeW_9)_2\}$ unit can be viewed as a derivative of the $[Cu_4(H_2O)_2(\alpha\text{-B-GeW}_9O_{34})_2]^{12-}$ cluster (Fig. S2†). The $\{Cu_8\}$ cluster in **1** (Fig. 2b) can be considered as four five-coordinate $[Cu(dap)]^{2+}$ groups that are grafted onto four corners of the rhombic $\{Cu_4O_{14}(H_2O)_2\}$ unit in $[Cu_4(H_2O)_2(\alpha\text{-B-GeW}_9O_{34})_2]^{12-}$ *via* twelve O atoms from the lacunae of two α-B-GeW$_9$ fragments. To our knowledge, **1** represents the first 3-D inorganic–organic composite $\{Cu_8\}$ sandwiched POM, although a $\{Co_8\}$ POM $K_8Na_8[(\alpha\text{-A-SiW}_9O_{34})_2Co_8(OH)_6(H_2O)_2(CO_3)_3]$ was recently reported,[3m] in which two $\{Co_4O_9(OH)_3(H_2O)\}$ units are linked *via* three carbonato groups (Fig. S3†). Moreover, the nearly coplanar $\{Cu_8\}$ cluster in **1** is unprecedented in coordination

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State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter and Graduate School of the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: ygy@fjirsm.ac.cn; Fax: (+86) 591-83710051

† Electronic supplementary information (ESI) available: Synthetic discussion and related figures. See DOI: 10.1039/b713510f

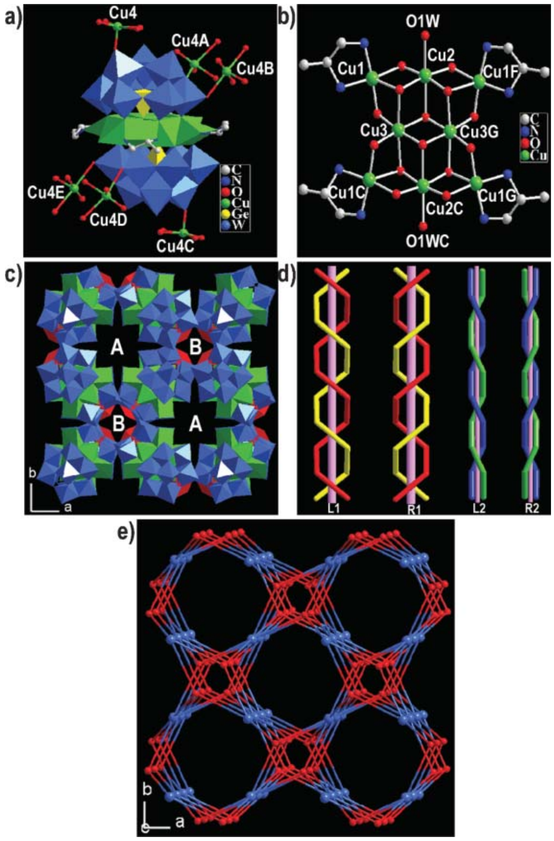

Fig. 2 (a) Coordination environment of the dimer $\{Cu_8(GeW_9)_2\}$. The $\{Cu_8\}$ cluster: green polyhedra; the $[Cu4(H_2O)_2]^{2+}$ bridges: green balls. (b) The linking mode of the $\{Cu_8(GeW_9)_2\}$ cluster. Atoms with "A–G" in their labels are generated by symmetry (A: y, $0.5 - I$, $-0.5 + I$; B: $0.5 - y$, x, $-0.5 + z$; C: $-0.5 + y$, $0.5 + x$, $-z$; D: $-0.5 + x$, $1 - y$, $0.5 - z$; E: $-x$, $0.5 + y$, $0.5 - z$; F: $0.5 - y$, $0.5 - x$, z; G: $-x$, $1 - y$, $-z$). (c) The 3-D framework viewed down the *c*-axis, showing two types of helical channels, A and B. The $[Cu4(H_2O)_2]^{2+}$ bridges: red polyhedra. The carbon and hydrogen atoms are omitted for clarity. (d) The dual left-/right-handed helices (L1/R1 and L2/R2) enclosing two different A and B channels, respectively. For clarity, L1/R1 helices are only shown in $\{Cu_8(GeW_9)_2\}$ nodes, and $[Cu4(H_2O)_2]^{2+}$ bridges are omitted, while L2/R2 helices are only shown in $[Cu4(H_2O)_2]^{2+}$ nodes, and $\{Cu_8(GeW_9)_2\}$ bridges are omitted. (e) The 3-D topological net along the *c*-axis. $\{Cu_8(GeW_9)_2\}$ nodes: blue; $[Cu4(H_2O)_2]^{2+}$ nodes: red.

chemistry. As shown in Fig. 2b, the 3 : 2 : 3 distribution of eight Cu^{2+} ions in the motif leads to three types of coordination environments: one type (Cu1/Cu1C/Cu1F/Cu1G) resides in a five-coordinate square pyramid, in which the basal plane is defined by two N atoms from a dap ligand [Cu–N: 1.975(10)–1.993(10) Å] and two μ_3-O atoms from the lacunae of two α-B-GeW_9 fragments [Cu-μ_3-O: 1.990(7)–2.015(7) Å], and one μ_4-O atom from the lacunae of a α-B-GeW_9 fragment occupies the apical position [Cu–O: 2.418(7) Å]; another (Cu2/Cu2C) is a six-coordinate octahedral geometry with two μ_3-O and two μ_4-O atoms from the lacunae of two α-B-GeW_9 fragments building the equatorial plane [Cu–μ_3-O: 1.979(7) Å and Cu–μ_4-O: 2.010 (7) Å], and one μ_4-O atom from a GeO_4 group and one water O atom standing on the axial positions [Cu–μ_4-O: 2.392(9) Å and Cu–O_W: 2.296(11) Å]; the other (Cu3/Cu3G) has two μ_3-O and two μ_4-O atoms from the lacunae of two α-B-GeW_9 units in approximately square-planar equatorial plane [Cu–μ_3-O: 1.951(7) Å and Cu–μ_4-O: 1.967(6) Å], and its coordination sphere is completed by two μ_4-O atoms from the lacunae of two α-B-GeW_9 fragments [Cu–μ_4-O: 2.446(7) Å]. The adjacent Cu···Cu distances are in 3.107(1)–3.224(1) Å. The $[Cu4(H_2O)_2]^{2+}$ bridge employs a square pyramidal geometry, in which the basal plane is defined by two H_2O ligands and two terminal oxygen (O_t) atoms from two α-B-GeW_9 units [Cu–O_w: 1.85(3)–2.07(4) Å and Cu–O_t: 2.805(8) Å], and one O_t atom from another α-B-GeW_9 unit occupies the apical position [Cu–O_t: 1.957(12) Å]. Owing to the coexistence of octahedral and square pyramidal geometries of Cu^{2+} ions, the Jahn–Teller effect of CuO_6 octahedra, the *pseudo*-Jahn–Teller effect of CuO_3N_2 square pyramids and the different linkage modes possibly lead to different isomers or configurations (see ESI†).

The most striking structural feature is that each dimer $\{Cu_8(GeW_9)_2\}$ joins six $[Cu4(H_2O)_2]^{2+}$ bridges (Fig. 2a), while each $[Cu4(H_2O)_2]^{2+}$ bridge links three dimers $\{Cu_8(GeW_9)_2\}$ (Fig. S4†), resulting in an unprecedented 3-D (3,6)-connected framework (Fig. 2c). The alignments of $\{Cu_8(GeW_9)_2\}$ units and $[Cu4(H_2O)_2]^{2+}$ bridges along the 4_2 screw axis form two types of helical channel, A and B, with cross-section dimensions of 2.7 × 2.7 Å and 1.4 × 1.4 Å, respectively (Fig. 2c, Fig. S5†). Noticeably, channels A and B are enclosed by two couples of interweaved dual left-/right-helices, L1/R1 and L2/R2, with a pitch of 18.85 Å (Fig. 2d). For L1/R1 chains, each chain is built by $\{Cu_8(GeW_9)_2\}$ units *via* $[Cu4(H_2O)_2]^{2+}$ bridges (Fig. S6a†). The dap ligands and the O_t atoms from the α-B-GeW_9 units protrude into the inner of A channels (Fig. S5†). Hydrogen-bonding interactions exist between N atoms of dap ligands and O atoms of α-B-GeW_9 units (N···O: 3.038(14)–3.283(13) Å). For L2/R2 chains, each chain is constructed from $[Cu4(H_2O)_2]^{2+}$ cations *via* $\{Cu_8(GeW_9)_2\}$ units (Fig. S6b†). Different from A channels, coordination water molecules from $[Cu4(H_2O)_2]^{2+}$ cations point to the inner of the B channels (Fig. S5†). Although 3-D frameworks with helical channels built by plenary Keggin units and amino acid complexes have been reported,[9] to the best of our knowledge, **1** still represents the first 3-D (3,6)-connected trivacant Keggin POM derivative with helical channels based on sandwich-type TMSP building blocks. Topologically, the 3-D architecture is a (3,6)-connected net (Fig. 2e), in which the dimer $\{Cu_8(GeW_9)_2\}$ and the $[Cu4(H_2O)_2]^{2+}$ group act as a 6- and 3-connected nodes, respectively. A topological analysis of this net was performed with OLEX.[10] The Schäfli symbol of this net is $(4{\cdot}6^2)(4^2{\cdot}6^4{\cdot}8^7{\cdot}10^2)$.

A plot of $\chi_M T$ *vs.* T and the fitting line under a 5 kOe external field for **1** are shown in Fig. 3. The $\chi_M T$ product of 3.43 emu mol^{-1} K at 300 K is in good agreement with the sum of the spin-only contribution (3.38 emu mol^{-1} K) for 9 Cu^{II} considering $g = 2$ per formula unit. Upon cooling, the $\chi_M T$ product gradually increases to a maximum of 3.84 emu mol^{-1} K at 12 K, and then sharply decreases to 2.44 emu mol^{-1} K at 2 K. The magnetic susceptibility can be well fitted by a Curie–Weiss expression with $C = 3.45$ emu mol^{-1} K and $\theta = 0.568$ K (Fig. S7†), indicative of the presence of weak ferromagnetic exchange interactions among the Cu^{II} centers. To analyze the observed magnetic data, a magnetic exchange model has been used for the $\{Cu_8\}$ cluster (Fig. 3). The isostropic spin Hamiltonian for the $\{Cu_8\}$ cluster is given as follows: $H = -2J_1(S_1S_2 + S_2S_3 + S_6S_7 + S_7S_8) - 2J_2(S_1S_4 + S_3S_5 + S_4S_6 + S_5S_8) - 2J_3(S_2S_4 + S_2S_5 + S_4S_7 + S_5S_7) - 2J_4S_4S_5$. The molar

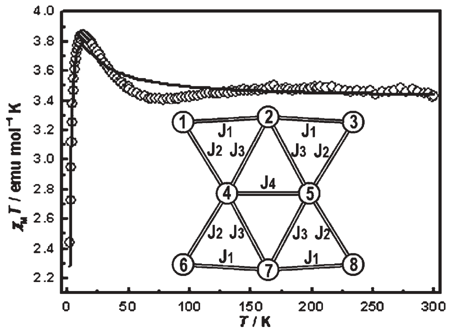

Fig. 3 The plot of the $\chi_M T$ *vs.* T for **1** between 2 and 300 K. The solid line represents the best fit to experimental data. The inset is a magnetic exchange model.

magnetic susceptibility of the $\{Cu_8\}$ cluster (χ_c) is described as $\chi_c = (Ng^2\beta^2/3kT)\{\sum S_n^T(S_n^T + 1)(2S_n^T + 1)\exp[-E_n/kT]\}/\{\sum(2S_n^T + 1)\exp[-E_n/kT]\}$.[11] Considering the contribution of a paramagnetic $[Cu4(H_2O)_2]^{2+}$ bridge, the molar magnetic susceptibility (χ) of **1** is discribed as $\chi = \chi_c + (1/2)(3/2)Ng^2\beta^2/3kT$. A molecular field correction in the form of $\chi_M = \chi/(1 - zJ'\chi_c/Ng^2\beta^2)$ is introduced to describe the intercluster interactions. The best-fitting parameters obtained using the MAGPACK program package[12] are $J_1 = -2.36$ cm^{-1}, $J_2 = 4.45$ cm^{-1}, $J_3 = 3.03$ cm^{-1}, $J_4 = -2.23$ cm^{-1}, $g = 1.98$ and $zJ' = -0.01$ cm^{-1}. The agreement factor R, defined as $\sum[(\chi_M)_{obs} - (\chi_M)_{cal}]^2/\sum(\chi_M)_{obs}{}^2$, is equal to 2.52×10^{-4}. The negative zJ' value accounts for the very small antiferromagnetic phenomenon observed below 12 K. Note that the magnitudes of all J values are comparable, so the $\{Cu^{II}{}_8\}$ cluster in **1** is a frustrated system with many low-lying excited states.[13]

The work was supported by the National Natural Science Fund for Distinguished Young Scholars of China (grant 20725101), the 973 program (grant 2006CB932904), the NNSF of China (grant 20473093), and the NSF of Fujian Province (grant E0510030).

Notes and references

‡ Synthesis of **1**: $K_8Na_2[\alpha\text{-A-GeW}_9O_{34}]\cdot 25H_2O^{3m}$ (0.246 g, 0.08 mmol), $CuCl_2\cdot 2H_2O$ (0.128 g, 0.75 mmol), dap (0.05 mL, 0.589 mmol) were suspended in H_2O (5 mL, 278 mmol), and then K_2CO_3 (2 M, 0.05 mL) was added (starting pH 4.5). The resulting mixture was stirred for 2 h, sealed in a Teflon-lined bomb (20 mL), kept at 100 °C for 5 days and then cooled to room temperature (end pH 3.6). Dark green prismatic crystals were obtained by filtration, washed with distilled water and dried in air. Yield: *ca* 50% (based on $K_8Na_2[\alpha\text{-A-GeW}_9O_{34}]\cdot 25H_2O$). Anal. calcd (%): C, 2.63; H, 0.92; N, 2.04; Cu, 10,43; Ge, 2.65; W, 60.33. Found: C, 2.73; H, 0.75; N, 2.12; Cu, 10.14; Ge, 2.57; W, 60.39.

§ Crystal data for **1**: $C_{12}H_{50}N_8O_{72}Cu_9Ge_2W_{18}$, $Mr = 5484.94$, tetragonal, $P4_2/ncm$, $a = 21.6769(2)$, $c = 18.8529(3)$ Å, $V = 8858.75(18)$ Å^3, $Z = 4$, $\rho = 4.113$ g cm^{-3}, $\mu = 26.137$ mm^{-1}, $F(000) = 9644$, $GOF = 1.121$. A total of 44138 reflections were collected, 4235 of which were unique ($R_{int} = 0.0763$). R_1 (wR_2) = 0.0308 (0.0596) for 299 parameters and 3404 reflections ($I > 2\sigma(I)$). The intensity data were collected on a Siemens Smart diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Direct methods were used to solve the structure and to locate the heavy atoms using the SHELXTL-97 program package. The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Routine Lorentz polarization corrections and an absorption correction were applied. The hydrogen atoms attached to the carbon and nitrogen atoms were geometrically placed except for the C2 atom. All non-hydrogen atoms were refined anisotropically except for the C3 atom. The C3 atom was disordered over two positions with occupancies of 0.15 and 0.85, respectively. CCDC 644937 for **1**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713510f

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7 $[Cu(H_2O)_2]H_2[Cu_8(en)_4(H_2O)_2(\alpha\text{-B-SiW}_9O_{34})_2]$ (**2**): $Mr = 5339.84$ tetragonal, $P4_2/ncm$, $a = 21.3874(13)$, $c = 18.634(2)$ Å, $V = 8523.4(12)$ Å^3, $Z = 4$, $\rho = 4.161$ g cm^{-3}, $\mu = 26.499$ mm^{-1}, $GOF = 1.059$. A total of 51668 reflections were collected, 3859 of which were unique ($R_{int} = 0.2017$). R_1 (wR_2) = 0.0719 (0.1774). CCDC 663471 (Fig. S13). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713510f.

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