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Combination of Lacunary Polyoxometalates and High-Nuclear Transition-Metal Clusters under Hydrothermal Conditions. 5. A Novel Tetrameric Cluster of $[\{\mathrm{Fe^{II}Fe^{III}_{12}}(\mu_3\text{-OH})_{12}(\mu_4\text{-PO}_4)_4\}(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_4]^{22-}$

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

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, People's Republic of China

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A novel tetrameric cluster, $(\mathrm{enH_2})_{3.5}\mathrm{H}_{15}[\{\mathrm{Fe^{II}Fe^{III}_{12}}(\mu_3\text{-OH})_{12}(\mu_4\text{-PO}_4)_4\}(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_4]\cdot 83\mathrm{H_2O}$ (**1**; en = ethylenediamine), has been hydrothermally synthesized and characterized by IR, optical diffuse reflectance, thermogravimetric analysis, and single-crystal X-ray diffraction. The skeleton of **1** is composed of four tri-$\mathrm{Fe^{III}}$-substituted $[\mathrm{Fe^{III}_3}(\mu_3\text{-OH})_3(\text{B-}\alpha\text{-PW}_9\text{O}_{34})]^{3-}$ Keggin moieties fused together through a $\mathrm{Fe^{II}_2O_2}$ unit and four μ_4-$\mathrm{PO_4}$ bridges, resulting in a unique tetramer with C_2 symmetry. Magnetic measurements indicate that **1** reveals the antiferromagnetic interactions between $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ centers.

The family of transition-metal-substituted polyoxometalates (TMSPs) has been known for several decades; however, many new members of this unique class of metal−oxygen clusters remain to be discovered.[1] Increasing interest in TMSPs mainly stems from their accompanying multitude of potential applications in catalysis, medicine, magnetism, and material science,[1,2] although their formation mechanisms are still not well understood and commonly described as self-assembly. Recently, the assembly of small lacunary polyoxometalate (POM) moieties into larger oligomers or aggregates by the incorporation of transition metals (TMs) into the skeletons of POMs attracts growing attention owing to its potential applications besides the highly attractive feature of the symmetry and molecular nature of POMs. Thus, di-, tri-, hexa-, or multivacant POM precursors are constantly employed as candidates to obtain such oligomers or aggregates with the largest number of TM cations in close proximity, which may exhibit exchange-coupled spins, leading to large-spin ground states. In this way, except those familiar dimeric sandwich-type TMSPs,[1b,3] trimeric $[\mathrm{M_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3}]^{16-}$ ($\mathrm{M = Ni^{2+}/Co^{2+}}$),[4] $[\mathrm{Zr_6O_2(OH)_4(H_2O)_3}(\beta\text{-SiW}_{10}\mathrm{O}_{37})_3]^{14-}$,[5] $[\{\mathrm{SiW_8O_{31}Cu_3(OH)(H_2O)_2(N_3)}\}_3(\mathrm{N_3})]^{19-}$,[6] and $[\mathrm{Co_6(H_2O)_{30}}\{\mathrm{Co_9Cl_2(OH)_3(H_2O)_9}(\beta\text{-SiW}_8\mathrm{O}_{31})_3\}]^{5-}$ [7] and tetrameric $[\{(\mathrm{SiW_9O_{34}})(\mathrm{SiW_9O_{33}(OH)})(\mathrm{Cu(OH)})_6\mathrm{Cu}\}_2\mathrm{X}]^{23-}$ ($\mathrm{X = Cl^-/Br^-}$),[8] $[\mathrm{Nb_4O_6}(\alpha\text{-Nb}_3\mathrm{SiW_9O_{40}})_4]^{20-}$,[9] $[\{\mathrm{Ti_3P_2W_{15}O_{57.5}(OH)_3}\}_4]^{24-}$,[10] $[\{\beta\text{-Ti}_2\mathrm{SiW_{10}O_{39}}\}_4]^{24-}$,[11] $[\mathrm{Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})}]^{25-}$,[12] $[\mathrm{P_8W_{48}O_{184}Cu_{20}(N_3)_6(OH)_{18}}]^{24-}$,[13] $[\mathrm{H_{56}P_8W_{48}Fe_{28}O_{248}}]^{28-}$,[14] and $[\mathrm{H_{55}P_8W_{49}Fe_{27}O_{248}}]^{26-}$ [14] have been obtained. Participation of tin or lanthanide ions in this system has also resulted in larger aggregates,[15] such as tetrameric $[\mathrm{PM_2W_{10}O_{38}}]_4(\mathrm{W_3O_{14}})]^{30-}$

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* To whom correspondence should be addressed. E-mail: ygy@fjirsm.ac.cn. Fax: (+86) 591-83710051.

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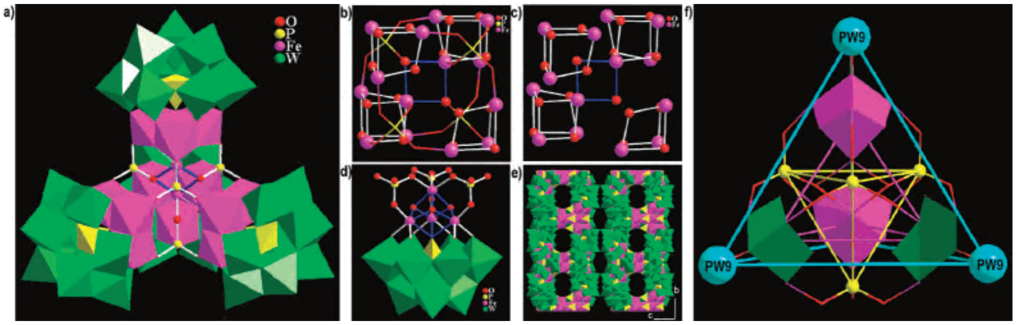

Figure 1. (a) Polyhedral/ball-and-stick representation of the tetramer **1**. The water and en molecules were omitted for clarity. (b) Combination of four $\{Fe_3\}$ trimers from four $\{Fe_3PW_9\}$ units, the central $Fe^{II}{}_2O_2$ unit, and four PO_4 bridges. (c) Distribution fashion of four $\{Fe_3\}$ trimers of four $\{Fe_3PW_9\}$ units and the central $Fe^{II}{}_2O_2$ unit. (d) Connection fashion of a $Fe^{III}{}_3Fe^{II}O(OH)_3$ cubane-substituted trivacant Keggin moiety and three PO_4 groups. (e) Packing of **1** along the *a* axis showing two types of elliptical channels. Color code: WO_6, green; FeO_6, purple; PO_4, yellow. (f) Linking model of $Fe^{III}{}_3Fe^{II}O(OH)_3$ cubanes (purple), $Fe^{III}{}_3O(OH)_3$-truncated (green), $[B\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ (cyan), and $PO_4{}^{3-}$ bridges (yellow) in **1**.

(M = Eu^{3+}/Y^{3+}),[15a] $[Ce(H_2O)_5As_4W_{40}O_{40}]^{25-}$,[15b] $[(SbW_9O_{33})_4\{WO_2(H_2O)\}_2Ce_3(H_2O)_8(Sb_4O_4)]^{19-}$,[15b] and $[Cs\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{23-}$,[15c] hexameric $[K\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$,[15c] decameric $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$,[15d] and dodecameric $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(AXW_9O_{34})_{12}]^{36-}$ (X = P^{5+}/As^{5+})[15e] and $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$.[15f] We recently initiate an investigation into the reaction of lacunary polyoxoanion nucleophilic ligands with electrophilic TM ions under hydrothermal conditions.[16a] Much motivation for this project arises from the fact that the lacunary sites of polyoxoanions are able to act as structure-directing agents and induce the formation of TM clusters to further construct larger oligomers or aggregates.[16a] Thus, we have successfully prepared several novel dimeric sandwich-type POMs.[16b−e] As our continuous work, we again isolated a novel tetramer, $(enH_2)_{3.5}H_{15}[\{Fe^{II}Fe^{III}{}_{12}(\mu_3\text{-}OH)_{12}(\mu_4\text{-}PO_4)_4\}(B\text{-}\alpha\text{-}PW_9O_{34})_4]\cdot 83H_2O$ (**1**). Notably, it is very rare that the $PO_4{}^{3-}$ ion simultaneously participates in linking several polyoxoanion fragments in POM chemistry.[4] As far as we know, **1** is the fourth-largest iron-containing POM except the three reported $\{Mo^{VI}{}_{72}Fe^{III}{}_{30}\}$,[17] $[H_{56}P_8W_{48}Fe_{28}O_{248}]^{28-}$,[14] and $[H_{55}P_8W_{49}Fe_{27}O_{248}]^{26-}$.[14]

1 was made in a good yield by the self-assembly reaction of $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ with $FeSO_4\cdot 7H_2O$ at 100 °C for 5 days in the presence of ethylenediamine under hydrothermal conditions[18] and not made by the conventional aqueous solution method (see the Supporting Information).

Single-crystal X-ray analysis[19] indicates that the skeleton of **1** is composed of four tri-Fe^{III}-substituted $[Fe^{III}{}_3(\mu_3\text{-}OH)_3(B\text{-}\alpha\text{-}PW_9O_{34})]^{3-}$ ($\{Fe_3PW_9\}$) Keggin moieties fused together by a $Fe^{II}{}_2O_2$ unit and four μ_4-PO_4 bridges, leading to a tetramer with C_2 symmetry (Figures 1a and S1a in the Supporting Information). The C_2 axis passes through the Fe9 and P6 atoms and is associated with the symmetrical plane defined by the Fe4, Fe8, and Fe9 atoms. Noticeably, the construction motif of **1** is significantly different from the reported tetramer containing tetradecacopper $[\{(A\text{-}\alpha\text{-}SiW_9O_{34})(A\text{-}\alpha\text{-}SiW_9O_{33}(OH))(Cu(OH))_6Cu\}_2X]^{23-}$ (X = Cl^-/Br^-), where four tri-Cu^{II}-substituted $[(A\text{-}\alpha\text{-}SiW_9O_{34})(Cu(OH))_3]^{7-}$ Keggin moieties are combined together via five μ_3-OH, four μ_2-O, and two Cu^{II} ions and a halogen ion (Figure S2 in the Supporting Information).[8] Alternatively, **1** may be also considered as a combination of four $[B\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ units anchored by a $[Fe^{II}Fe^{III}{}_{12}(\mu_3\text{-}OH)_{12}(\mu_4\text{-}PO_4)_4]^{14+}$ core; such a large Fe−P−O polymeric cation containing two $Fe^{III}{}_3Fe^{II}O(OH)_3$ cubanes, two $Fe^{III}{}_3O(OH)_3$ truncated cubanes, and four PO_4 groups is first observed in an isolated molecule (Figure 1b). However, when four PO_4 groups are removed, only two $\{Fe_3\}$ trimers of four $\{Fe_3PW_9\}$ units are linked together by the $Fe^{II}{}_2O_2$ unit (Figure 1c). Notice that two oxygen vertices of the $Fe^{II}{}_2O_2$ unit come from two μ_4-PO_4 bridges (Figure S1b in the Supporting Information). Bond valence sum calculations[20] of Fe and W centers reveal that the oxidation states of Fe1−Fe7 atoms located on $\{Fe_3PW_9\}$ moieties [Fe^{III}−O: 1.904(3)−2.352(3) Å] and Fe8−Fe9 bridges [Fe^{II}−O: 2.001(4)−2.175(3) Å] are 3+ and 2+, respectively; the oxidation states of all of the W atoms are 6+ (see the Supporting Information). The Fe^{III} centers are from the oxidation of the Fe^{II} centers. In **1**, two Fe^{II} vertices cap two $\{Fe_3PW_9\}$ moieties, forming two $Fe^{III}{}_3Fe^{II}O(OH)_3$ cubane-substituted Keggin moieties. This combination mode of a

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(18) A mixture of $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ (0.246 g, 0.094 mmol), $FeSO_4\cdot 7H_2O$ (0.139 g, 0.500 mmol), en (0.05 mL, 0.740 mmol), HAc (0.10 mL, 1.748 mmol), and H_2O (5 mL, 277 mmol) was stirred for 1 h, sealed in a 20 mL Teflon-lined steel autoclave, kept at 100 °C for 5 days, and then cooled to room temperature. The red crystals were harvested. Yield: ca. 38% based on $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$. Anal. Calcd (%) for $C_7N_7H_{228}O_{247}P_8Fe_{13}W_{36}$: C, 0.70; H, 1.92; N, 0.82; P, 2.07; Fe, 6.07; W, 55.36. Found: C, 0.82; H, 2.20; N, 0.76; P, 1.99; Fe, 5.98; W, 55.52. The P:Fe:W ratio observed by energy-dispersive X-ray analysis: 1:1.70:4.80. Calcd: 1:1.63:4.50. IR (KBr pellet): 3467, 3137, 1611, 1507, 1048, 947, 871, 790, 730, 476 cm^{-1} (Figure S8 in the Supporting Information).

(19) Intensity data of **1** were collected at 293 K on a Rigaku Saturn 70 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL-97* program package. Routine Lorentz and polarization corrections and empirical absorption correction were applied. P4, P5, and P6 atoms were disordered over two positions; Fe8 and Fe9 atoms were also disordered with an occupancy of 0.25 for each. Crystal data for **1**: $C_7N_7H_{228}O_{247}P_8Fe_{13}W_{36}$, M_r = 11955.80, monoclinic, space group *C*2/*m*, a = 36.666(7) Å, b = 25.887(5) Å, c = 21.682(4) Å, β = 94.891(3)°, V = 20505(6) Å^3, Z = 4, S = 1.088, R1 = 0.0526, wR2 = 0.1327.

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metallic cubane group with a trivacant Keggin unit is very rare in TMSP chemistry.[21] Different from the Ni_4O_4 cubane-substituted polyoxoanion $[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ first reported by Kortz et al. in 1999 (Figure S3 in the Supporting Information),[21] the capped Fe^{II} (Fe8/Fe9) center in **1** links to three Fe^{III} centers via three PO_4 groups, respectively (Figure 1d). Because Fe8/Fe9 atoms are disordered and situated on the symmetrical plane, each of Fe8/Fe9 atoms has an occupancy of 0.25 according to the results of inductively coupled plasma and energy-dispersive X-ray analyses. Thus, each $Fe^{III}_3Fe^{II}O(OH)_3$ cubane only contains three Fe^{III} ions and a half Fe^{II} ion, further leading to 13 Fe atoms per molecular unit of **1**. Additionally, the coordination environments of four PO_4^{3-} bridges in **1** can be classified into two types: one [P5 and P5A ($x, -y, z$)] bonds to two $Fe^{III}_3Fe^{II}O(OH)_3$ cubane-substituted Keggin moieties and one $Fe^{III}_3O(OH)_3$-truncated cubane-substituted Keggin moiety (Figure S1c in the Supporting Information); the other (P4 and P6) links to one $Fe^{III}_3Fe^{II}O(OH)_3$ cubane-substituted Keggin moiety and two $Fe^{III}_3O(OH)_3$-truncated cubane-substituted Keggin moieties (Figure S1d in the Supporting Information). If each $[B\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ unit acts as a node, four $[B\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ units are just situated in four vertices of a tetrahedron. Inside this tetrahedron, two $Fe^{III}_3Fe^{II}O(OH)_3$ cubanes and two $Fe^{III}_3O(OH)_3$-truncated cubanes are just inhibited inside of four pyramidal angles. Intriguingly, four μ_4-PO_4 groups exactly locate the centers of four faces of the tetrahedron (Figure 4f). Interestingly, the stacking of **1** along the *a* axis creates two types of elliptical channels with sizes of 10.8 × 19.8 and 6.3 × 9.5 Å, respectively, in which en or water guest molecules are located (Figure 4e). The en, water molecules, and O atoms of POMs accommodated in the channels are hydrogen-bonded together [N−H···O: 2.684(12)−3.350(5) Å; C−H···O: 3.246(5)−3.401(6) Å]. The solvent-accessible volume of **1** calculated using *PLATON*[22] is 13.6%, indicating that it may be a potential porous material.

1 is highly hydrated and exposure to the X-ray beam on collecting intensity data results in spontaneous dehydration of lattice water molecules. Thus, some lattice water molecules cannot be directly determined by single-crystal structural analysis. The combination of elemental and thermogravimetric (TGA) analyses allows us to identify the number of lattice water molecules. Such a determination method of the lattice water molecules is commonly used in giant POM species.[8,23] TGA shows a total weight loss of 16.86% between 30 and 1000 °C, corresponding to the removal of 3.5 diprotonated en and 83 lattice water molecules and the dehydration of 15 protons and 12 hydroxyl groups (calcd 16.83%) (Figure S4 in the Supporting Information).

The value of χ_M slowly increases from 0.10 emu mol^{-1} at 300 K to 0.31 emu mol^{-1} at 24 K and then exponentially to the maximum of 1.21 emu mol^{-1} at 2 K (Figure 2). At 300 K, the $\chi_M T$ value of 31.87 emu mol^{-1} K is much lower than the theoretical value (55.5 emu mol^{-1} K) for 12 noninteracting Fe^{III} ($S = {}^5/_2$) and 1 Fe^{II} ($S = 2$) ions with $g = 2.00$. Upon cooling, the $\chi_M T$ value continuously decreases to 2.42 emu mol^{-1} K at 2 K, which is characteristic of the antiferromagnetic behavior. In 70−300 K, the magnetic data obey the Curie−Weiss law [$\chi_M = C/(T - \theta)$], affording $C = 54.88$ emu K mol^{-1} and $\theta = -226.61$ K (Figure S5 in the Supporting Information) and confirming the presence of the strong antiferromagnetic couplings between Fe centers. Such strong antiferromagnetic couplings can be observed in some Fe−O clusters.[14,24] According to the relationship between the Fe−O−Fe angles and the coupling constants within polynuclear iron compounds, when the Fe−O−Fe angles are larger than 90°, the compound reveals antiferromagnetic couplings.[25a] Meanwhile, using the formulation $J = A(B + C\cos\varphi + \cos^2\varphi)\exp(Dr)$ (φ = Fe−O−Fe angle; r = Fe−O distance) based on the angular overlap model[25b] can also confirm this conclusion.[25a] In **1**, except only one Fe8−O66−Fe9 angle equal to 86.7(1)°, other Fe−O−Fe angles range from 90.3(1) to 113.7(1)°; therefore, the antiferromagnetic couplings are expected in **1** (Figures S6 and S7 in the Supporting Information).

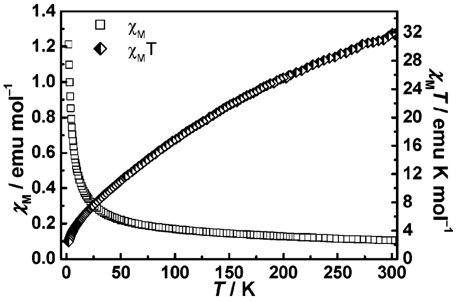

Figure 2. Temperature variation of the magnetic susceptibility of **1** as χ_M and $\chi_M T$ vs T between 2 and 300 K.

In summary, a novel tetrameric POM cluster has been made by a combination of the mild hydrothermal conditions with trivacant Keggin POM precursors. Especially, **1** is one new member of the largest iron-containing poly(POM).[14,17] The successful synthesis of **1** enlightens us to further exploit this system and provides us with a possible method that can construct the high-nuclear poly(POM) clusters.

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Supporting Information Available: Figures of the IR spectra, optical diffuse-reflectance spectra, TGA, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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