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Synthesis, structure, and photocatalytic hydrogen evolution of a trimeric Nb/W addendum cluster†

Haiying Wang,[a] Lili Hou,[b] Chen Li,[a] Dongdi Zhang,*[a] Pengtao Ma,[a] Jingping Wang[a] and Jingyang Niu*[a]

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We present the second example of mixed Nb/W addendum based trimer, $Cs_{12}[(SiW_9Nb_3O_{38})_3WO_3(OH)_3]\cdot 33H_2O$ by utilizing *in situ* formed Keggin-type $\{SiW_9(NbO_2)_3\}$ unit as the secondary building block. The polyanion $[(SiW_9Nb_3O_{38})_3WO_3(OH)_3]^{12-}$ incorporates three saturated niobium-substituted tungstosilicate $\{SiW_9Nb_3\}$ clusters that are linked together by three Nb–O–Nb bridges and a tungsten joint. The compound has been thoroughly characterized by single crystal X-ray diffraction, UV-Vis spectroscopy, TG analysis, PXRD and FTIR spectra. In addition, the photocatalytic activities of the title compound and the two precursors A-α-$Na_{10}[SiW_9O_{34}]\cdot 23H_2O$ and $K_7HNb_6O_{19}\cdot 13H_2O$ for H_2 evolution were also evaluated.

Introduction

Polyoxoniobates (PONbs)[1,2] are a unique family of polynuclear anionic metal oxo clusters with properties suitable for many potential applications in catalysis, magnetism, biomedicine, materials science, and nanotechnology.[3–6] This family has accelerated dramatically over the last 15 years, and a vast expansion of available PONbs has been reported.[7–14] In this context, the class of Nb/W addendum heteropolyoxometalates develops slowly since the pioneering work reported by Finke and Droege in 1984.[15] Recently, some other Nb/W addendum heteropolyoxometalate clusters have been communicated.[16–37] However, most of them comprise a monomeric,[16–23] dimeric[18,24–27] or tetrameric[18,19,27–29] structure. Key efforts include the synthesis and physical characterization of the above-mentioned Keggin-type monomeric triniobium-substituted polytungstosilicate $[SiW_9Nb_3O_{40}]^{7-}$ and its dimeric form $[Si_2W_{18}Nb_6O_{77}]^{8-}$ by Finke *et al.*[15] and the extensive efforts with the preparation and single-crystal X-ray structure of the Keggin-type monomeric triperoxoniobium-substituted clusters $[XW_9(NbO_2)_3O_{37}]^{7-}$ (X = P,[16] Si,[17] Ge,[18] As[19]) and its peroxo-free clusters $[XW_9Nb_3O_{40}]^{7-}$ (X = Si,[15] Ge,[18] As[19]), dimeric tungstoniobates $[Si_2W_{18}Nb_6O_{77}]^{8-}$,[15,24] $[Si_2W_{18}Nb_6O_{78}]^{10-}$ (ref. 25) and $[Ge_2W_{18}Nb_8O_{88}]^{20-}$,[18] supramolecular tetra-Keggin clusters $[Nb_4O_6(Nb_3XW_9O_{40})_4]^{20-}$ (X = Si,[29,30] Ge,[18] As[19]) by Hill and Liu group, respectively. In 2012 and 2013, Liu and Su *et al.* reported the self-assembly of W/Nb mixed-addendum polyoxometalate and lanthanide/transition-metal-containing Keggin-type Nb/W mixed species, respectively.[31,32] On the other hand, several Wells-Dawson-type niobium-substituted tungstophosphates, $(P_2W_{15}Nb_3O_{62})^{9-}$,[20,21] $[P_2W_{17}NbO_{62}]^{7-}$ (ref. 22) and $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$,[23] $[H_6P_2W_{12}Nb_4O_{59}(NbO_2)_2]_2^{8-}$ (ref. 26) were successively communicated by Finke, Hill and Yue group, respectively. In 2012, Liu group also reported two Wells-Dawson-type Nb/W-based lanthanide derivatives, $[Ln_6(H_2O)_{38}(P_2W_{15}Nb_3O_{62})_4]^{18-}$ (Ln = Ce, Eu).[33]

It should be noted that our group has developed a new synthetic strategy, utilizing peroxo-niobium-substituted POM formed *in situ* as a secondary building block, to construct giant Nb/W addendum polyoxoanions and their transition-metal derivatives in recent years.[27,28,34–36] In particular, the unprecedented hexameric cluster $\{Mn_{15}(Nb_6P_2W_{12}O_{62})_6\}$, in which the six polyanions $[Nb_6P_2W_{12}O_{61}]^{10-}$ are alternately connected by four intriguing trinuclear $\{Mn_3^{III}\}$ moieties and four $\{Mn^{II}\}$ linkers, represents the first example of niobotungstate with single-molecule magnet and also the largest cluster in niobotungstate chemistry.[35] The successful synthesis of these compounds has been thoroughly demonstrated that the NbO_2 groups are actually more basic and reactive than their oxotungsten counterparts. Therefore, $\{SiW_9(NbO_2)_3\}$ or $\{P_2W_{12}(NbO_2)_6\}$ formed *in situ* can indeed be regarded as a saturated building block to generate gigantic POM assemblies.

As our continuous work, herein we present the synthesis, structure of the second example of trimeric Keggin-type Nb/W mixed compound $Cs_{12}[(SiW_9Nb_3O_{38})_3WO_3(OH)_3]\cdot 33H_2O$ (**1**, Cs_{12}-**1a**$\cdot 33H_2O$), which has been characterized by single crystal X-ray diffraction, UV-Vis spectroscopy, TG analysis, PXRD and FTIR spectra. In addition, the photocatalytic H_2 evolution activity of compound **1** was also investigated.

[a] *Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China. E-mail: ddzhang@henu.edu.cn; jyniu@henu.edu.cn; Fax: +86-371-23886876*

[b] *Engineering Research Center for Nanomaterials, Henan University, Kaifeng, 475004, China*

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Results and discussion

Synthesis

Compound **1** was obtained by the addition of $Fe(NO_3)_3\cdot 9H_2O$ into $[SiW_9(NbO_2)_3O_{37}]^{7-}$ that was *in situ* formed from $K_7HNb_6O_{19}\cdot 13H_2O$ (abbreviated as $\mathbf{Nb_6}$)[37] and trilacunary A-α-$Na_{10}[SiW_9O_{34}]\cdot 23H_2O$ (abbreviated as $\mathbf{SiW_9}$)[38] in the presence of H_2O_2. The solution was adjusted to pH 2.3 and heated to 90 °C for 5 h, followed by the addition of CsCl (Scheme 1a). Interestingly, polyanion **1a** can be only crystallized with the need for Cs^+ cation (Scheme 1b). This is in agreement with the original report indicating an essential templating role of Cs^+ in the formation of Keggin-based analogues.[17–19,24,25] In addition, $Fe(NO_3)_3\cdot 9H_2O$ is essential for the formation of **1**, although it does not appear in the structure (Scheme 1c). Such observations have also been observed in the formation of previous POM clusters.[39,40]

Structural analysis

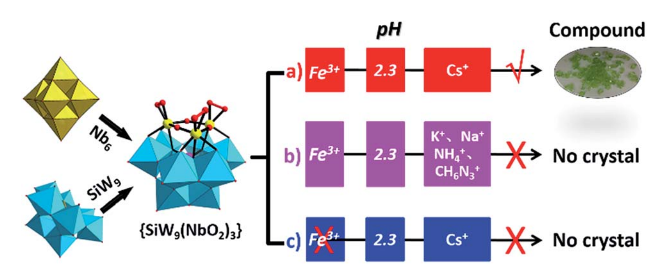
Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the trigonal space group *R*3*m*, exhibiting a trimeric cluster based on the classic Keggin-type unit $\{SiW_9Nb_3\}$ (Fig. 1a and b). As expected, the structure of $\{SiW_9Nb_3\}$ unit (Fig. 1c) comprises a trilacunary $\mathbf{SiW_9}$ fragment (Fig. 1d) with the vacant sites occupied by three NbO_6 groups. The three $\{SiW_9Nb_3\}$ units are linked to each other *via* two Nb–O_b–Nb (O_b: bridging oxygen atom) bridges and capped by an extra WO_6 octahedron, resulting in a rare trimeric assemble. Alternatively, **1a** can be viewed as three $\mathbf{SiW_9}$ fragments supporting an unprecedented $\{WNb_9\}$ core (Fig. 1e).

In **1a**, each of the Nb and W atoms is coordinated by six oxygen atoms, resulting in an octahedral coordination geometry, whereas all the Si atoms exhibit conventional tetrahedral coordination polyhedra. In **1a**, the W–O, Nb–O and Si–O bond lengths are in the range of 1.70(2)–2.368(19), 1.82(3)–2.32(3) and 1.61(2)–1.65(3) Å, respectively.

As shown in Table S1,† bond valence sum (BVS) calculations for **1a** are consistent with Si, W and Nb being in the +4, +6 and +5 oxidation states, respectively.[41] BVS calculations for all oxygen atoms in **1a** indicate that three terminal oxygen atoms (O25) on the W6 site (Fig. S1†) are mono-protonated with the value of 1.27, resulting in an $\{WO_3(OH)_3\}$ unit.

IR spectra

The Fourier transform infrared spectra (FTIR) of **1**, $\mathbf{SiW_9}$ and $\{SiW_9(NbO_2)_3\}$ are shown in Fig. 2 and S2.† They all show strong bands in the range of 1050–950 cm^{-1}, as well as medium or strong bands in the range of 950–850 cm^{-1}, associated with antisymmetric stretching vibrations of the Si–O and the terminal W=O bonds, respectively. The medium bands at 850–680 cm^{-1} correspond to the antisymmetric stretching vibrations of the M–O_b bridges. These results confirm that the Keggin-type framework remains intact under the condition of the synthesis. Compared with that of $\{SiW_9(NbO_2)_3\}$, the significant changes in FTIR spectrum of **1** are the disappearance of weak intensity band between 860 and 870 cm^{-1} and the appearance of medium intensity band at 749 cm^{-1}, which is characteristic of the antisymmetric stretching vibrations of peroxo groups[18,29] and Nb–O–Nb bridges,[15,18,19] respectively. This is in good agreement with the solid-state structure.



Scheme 1 Synthetic routes leading to the isolation of polyanion **1a**, highlighting the effect of cesium countercation and $Fe(NO_3)_3\cdot 9H_2O$.

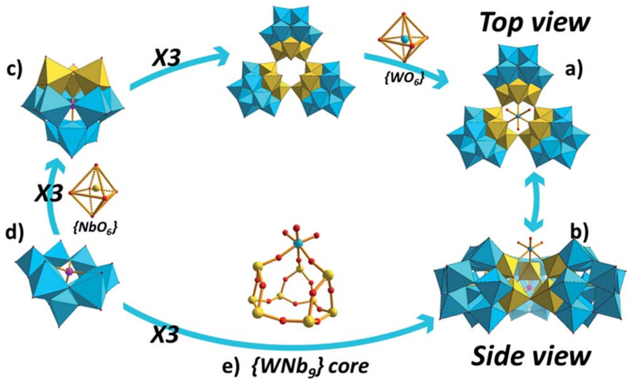


Fig. 1 Combined polyhedral/ball-and-stick representation of polyanion **1a** in different direction (a and b); the $\{SiW_9Nb_3\}$ unit (c); the $\{SiW_9\}$ fragment (d); the $\{WNb_9\}$ core (e). All cations and solvent water molecules have been omitted for clarity. WO_6 octahedra (blue), NbO_6 octahedra (yellow), Si balls (pink), Nb balls (yellow), and O balls (red).

Photocatalytic studies

To demonstrate the photocatalytic H_2 evolution activity of **1**, 100 mg **1** and 5.2 mL H_2PtCl_6 (1 mM) were dissolved in 100 mL

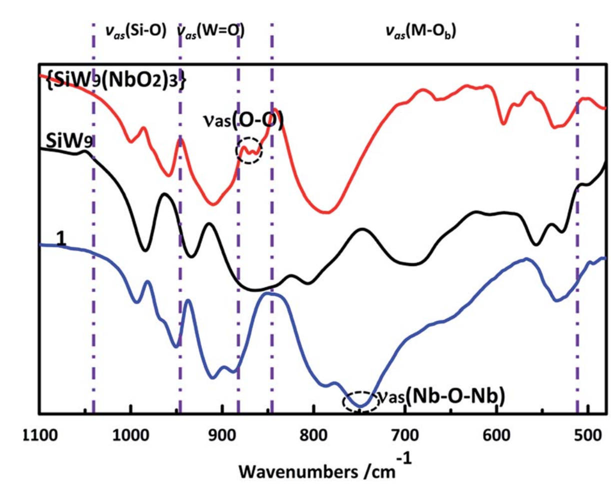


Fig. 2 FTIR spectra of **1**, $\mathbf{SiW_9}$ and $\{SiW_9(NbO_2)_3\}$ in the region between 1100 to 450 cm^{-1}.

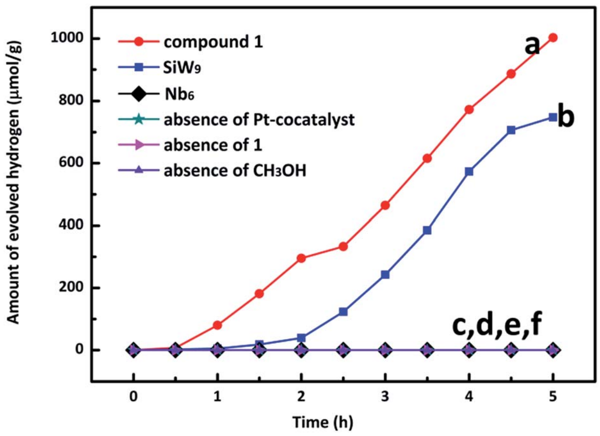


Fig. 3 Time dependence of photocatalytic H_2 production over different system: (line (a)) compound **1** (red), (line (b)) **SiW$_9$** (blue) and (line (c)) **Nb$_6$** (black); (lines (d–f)) the absence of Pt-cocatalyst (cyan), **1** (rose red), CH_3OH (purple).

of 20% methanol–water mixed solution (4/1, volume ratio), which was irradiated under full spectrum using a 300 W Xe lamp in a quartz cell. In this system, **1** was used as light photosensitizer and catalyst in the presence of a Pt co-catalyst, while methanol was acted as a sacrificial electron donor, which is the source of the electrons required in the reduction semi-reaction of water. As shown in Fig. 3, the amount of the evolved H_2 for compound **1** increased continuously, and the total evolved H_2 over 5 h was 1003.0 μmol g^{-1} (line (a)), and the average H_2 evolution rate was 200.6 μmol h^{-1} g^{-1}.

For comparison, the use of the precursors **SiW$_9$** or **Nb$_6$** was also investigated under otherwise identical reaction conditions (lines (b) and (c) in Fig. 3), the total evolved H_2 of **SiW$_9$** over 5 h was 747.6 μmol g^{-1}, whereas the **Nb$_6$** is almost inactive. To investigate the important roles of Pt co-catalyst, **1** and CH_3OH in the photocatalytic process, three blank experiments were carried out with no H_2 evolution observed (lines (d–f) in Fig. 3), indicating that Pt co-catalyst, **1** and CH_3OH play an indispensable role in light harvesting for photocatalysis. On the other hand, the increase in H_2 evolution of **1** compared to **SiW$_9$** may be attributed to the introduction of niobium, which is in agreement with our previous result.[27] Furthermore, the band gap is reduced from 3.51 eV for **SiW$_9$** to 2.74 eV for **1**, in turn, indicating a positive photocatalytic effect (Fig. S3†).

Conclusion

In summary, a new Keggin-type based trimeric Nb/W mixed cluster $Cs_{12}[(SiW_9Nb_3O_{38})_3WO_3(OH)_3]\cdot 33H_2O$ (**1**, Cs_{12}-**1a**$\cdot 33H_2O$) has been synthesized by utilizing the *in situ* formed saturated Keggin-type $\{SiW_9(NbO_2)_3\}$ unit as the secondary building block. Polyanion **1a** incorporates three Keggin-type saturated niobium-substituted tungstosilicate $\{SiW_9Nb_3\}$ clusters that are linked to each other by Nb–O–Nb linkages and a tungsten joint. Again, the successful synthesis of **1** demonstrated that the oxoniobium(V) surface is more basic and reactive than its oxotungsten(VI) counterpart and may reactive to transition-metal or lanthanide, providing an alternative perspective for the assemble of novel polyoxometalate derivatives. In addition, **1** exhibits photocatalytic H_2 evolution activity.

Experimental section

Materials and methods

All the reagents were obtained from commercial sources and used as received. All solvents were used without further purification. $K_7H[Nb_6O_{19}]\cdot 13H_2O$[37] and A-α-$Na_{10}[SiW_9O_{34}]\cdot 23H_2O$[38] were prepared using literature methods. The IR spectra (using KBr in pellets) were recorded on a Bruker VERTEX 70 IR spectrometer (4000–450 cm^{-1}). X-ray powder diffraction (PXRD) spectral data was recorded on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation in the angular range 2θ = 5–45° at 293 K. UV-Vis spectra were obtained with a U-4100 spectrometer at room temperature. Thermogravimetric (TG) analysis was performed under N_2 atmosphere on a NETZSCH STA 449 F5 Jupiter thermal analyzer with the heating rate of 10 °C min^{-1} from 30 to 600 °C. Photocatalytic reactions were carried out in a CEL-SPH2N reaction vessel with a magnetic stirrer at room temperature. The produced H_2 was analyzed by a GC-7920 instrument with N_2 as a carrier gas.

Synthesis of 1. $K_7H[Nb_6O_{19}]\cdot 13H_2O$ (0.5 g, 0.36 mmol) was dissolved in a solution consisting of 7.5 mL of 30% aqueous H_2O_2 and 60 mL of water. Under rapidly stirring, 6 mL HCl (1.0 M) was added dropwise, while powdered A-α-$Na_{10}[SiW_9O_{34}]\cdot 23H_2O$ (3.44 g, 1.20 mmol) was added in a single step. Ten minutes later, a solution of $Fe(NO_3)\cdot 9H_2O$ (0.31 g, 1.1 mmol) in H_2O (2 mL) was added. The pH of the resulting mixture was adjusted to 2.3 and then heated to 90 °C for 5 hours. After this period, the mixture was cooled to room temperature and

Table 1 Crystal data and structure refinement

	1
Empirical formula	$Cs_{12}H_{69}Nb_9O_{153}Si_3W_{28}$
Formula weight	10 180.26
Crystal system	Trigonal
Space group	*R3m*
a/Å	30.4555(13)
b/Å	30.4555(13)
c/Å	15.9433(13)
γ/deg	120
V/Å^3	12 806.8(15)
Z	3
D_c/g cm^{-3}	3.798
μ/mm^{-1}	21.980
F_{000}	12 609
Crystal size/mm^3	0.37 × 0.25 × 0.21
Reflns collected	21 257
Indep reflns	5324
R_{int}	0.0913
Goodness-of-fit on F^2	1.058
$R_1[I > 2\sigma(I)]^a$	$R_1 = 0.0473$, $wR_2 = 0.1173$
wR_2 (all data)^b	$R_1 = 0.0543$, $wR_2 = 0.1213$
Flack parameter	0.535(19)

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

filtered, followed by the addition of CsCl (0.3 g, 1.9 mmol). The solution was then stirred for 35 minutes and filtered. The resulting filtrate was kept at room temperature to allow slow evaporation for about five weeks (yield 0.29 g, 12% based on Nb). IR (KBr, cm^{-1}): $\nu = 997$ (s), 950 (m), 910 (w), 881 (m), 749 (m).

X-ray crystal-structure analyses

Suitable single crystals were selected from their respective mother liquors and placed in a thin glass tube. X-ray diffraction intensity was recorded on a Bruker Apex-II CCD diffractometer at 296(2) K with MoKα monochromated radiation ($\lambda = 0.71073$ Å). Structure solution and refinement were carried out by using the SHELXS-97 and SHELXL-2014 program packages[42,43] for **1**. Selected details of the data collection and structural refinement of compound **1** can be found in Table 1. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 433156.

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