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

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We present the second example of mixed Nb/W addendum based trimer, Cs12[(SiW9Nb3O40)3WO3(OH)3]:33H2O by utilizing in situ formed Keggin-type (SiW9O40)2−单元 as the secondary building block. The polyanion (SiW9Nb3O40)2−incorporates three saturated niobium-substituted tungstosilicate (SiW9Nb3) 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−x−Na80[SiW9O34]:23H2O and K7HNB6O19:13H2O for H2 evolution were also evaluated.

Introduction

Polyoxoniobates (PONbs)12−14 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.15−17 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.16−19 It should be noted that our group has developed a new synthetic strategy, utilizing perxo-niobium-substituted POM incorporated as a secondary building block, to construct giant Nb/W addendum polyoxoanions and their transition-metal-containing derivatives in recent years.20−24 In particular, the unprecedented hexameric cluster {Mn15(Nb6P2W12O62)6}, in which the six polyanions [Nb8P2W12O64]10− are alternately connected by four intriguing trinuclear [Mn11] moieties and four {Mn11} linkers, represents the first example of niobotungstate with single-molecule magnet and also the largest cluster in niobotungstate chemistry.25 The successful synthesis of these compounds has been thoroughly demonstrated that the NbO2 groups are actually more basic and reactive than their oxotungsten counterparts. Therefore, [SiW6(NbO3)3] or [P2W12(NbO3)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 Cs12[(SiW9Nb3O40)3WO3(OH)3]:33H2O (1) has been characterized by single crystal X-ray diffraction, UV-Vis spectroscopy, TG analysis, PXRD and FTIR spectra. In addition, the photocatalytic H2 evolution activity of compound 1 was also investigated.

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Results and discussion

Synthesis

Compound 1 was obtained by the addition of Fe(NO$_3$)$_3$·9H$_2$O into [SiW$_9$(NbO$_2$)$_3$O$_{27}$]$^{7-}$ that was in situ formed from K·H$_2$Nb$_6$O$_{19}$·13H$_2$O (abbreviated as Nb$_6$) and trilacunary A·Cs·Na$_{10}$[SiW$_9$O$_{37}$]·23H$_2$O (abbreviated as SiW$_9$)$_{38}$ in the presence of H$_2$O$_2$. 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$_3$)$_3$·9H$_2$O 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.$^{26,29}$

Structural analysis

Single crystal X-ray diffraction analysis reveals that 1 crystallizes in the trigonal space group R3m, exhibiting a trimeric cluster based on the classic Keggin-type unit [SiW$_9$Nb$_3$] (Fig. 1a and b). As expected, the structure of [SiW$_9$Nb$_3$] unit (Fig. 1c) comprises a trilacunary SiW$_9$ fragment (Fig. 1d) with the vacant sites occupied by three NbO$_6$ groups. The three [SiW$_9$Nb$_3$] units are linked to each other via two Nb-O$^-$–Nb (O$^-$: bridging oxygen atom) bridges and capped by an extra WO$_6$ octahedron, resulting in a rare trimeric assembly. Alternatively, 1a can be viewed as three 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,$^\dagger$ bond valence sum (BVS) calculations for 1a are consistent with Si, W and Nb being in the +4, +6 and +5 oxidation states, respectively.$^{11}$ BVS calculations for all oxygen atoms in 1a indicate that three terminal oxygen atoms (O25) on the W6 site (Fig. S1)$^\dagger$ are mono-protonated with the value of 1.27, resulting in an [WO$_3$(OH)$_2$]$_3$ unit.

IR spectra

The Fourier transform infrared spectra (FTIR) of 1, SiW$_9$ and [SiW$_9$(NbO$_2$)$_3$]$_3$ are shown in Fig. 2 and S2.$^\dagger$ 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$_6$ 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 peroxy groups.$^{16,29}$

Photocatalytic studies

To demonstrate the photocatalytic H$_2$ evolution activity of 1, 100 mg 1 and 5.2 mL H$_2$PtCl$_6$ (1 mM) were dissolved in 100 mL.

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Visual Elements:
- **Scheme 1**: Synthetic routes leading to the isolation of polyanion 1a, highlighting the effect of cesium counterionation and Fe(NO$_3$)$_3$·9H$_2$O.
- **Fig. 1**: Combined polyhedral/ball-and-stick representation of polyanion 1a in different direction (a and b); the (SiW$_9$Nb$_3$) 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).
- **Fig. 2**: FTIR spectra of 1, SiW$_9$ and [SiW$_9$(NbO$_2$)$_3$] in the region between 1100 to 450 cm$^{-1}$.
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 photocatalyst and at 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 H2 for compound 1 increased continuously, and the total evolved H2 over 5 h was 1003.0 μmol g⁻¹ (line (a)), and the average H2 evolution rate was 200.6 μmol h⁻¹ g⁻¹. For comparison, the use of the precursors SiW₉ or Nb₆ was also investigated under otherwise identical reaction conditions (lines (b) and (c) in Fig. 3), the total evolved H2 of SiW₉ over 5 h was 747.6 μmol g⁻¹, whereas the Nb₆ is almost inactive. To investigate the important roles of Pt co-catalyst, 1 and CH₃OH in the photocatalytic process, three blank experiments were carried out with no H2 evolution observed (lines (d-f) in Fig. 3), indicating that Pt co-catalyst, 1 and CH₃OH play an indispensable role in light harvesting for photocatalysis. On the other hand, the increase in H2 evolution of 1 compared to SiW₉ may be attributed to the introduction of niobium, which is in agreement with our previous result. Furthermore, the band gap is reduced from 3.51 eV for SiW₉ 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 Cs₁₂[SiW₆Nb₃O₁₈OH]·3H₂O (1, Cs₁₂·1a·3H₂O) has been synthesized by utilizing the in situ formed saturated Keggin-type (SiW₆Nb₃O₁₈) unit as the secondary building block. Polyanion 1a incorporates three Keggin-type saturated niobium-substituted tungstosilicate [SiW₆Nb₃] 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 oxoniobiomalysodium(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 assembly of novel polyoxometalate derivatives. In addition, 1 exhibits photocatalytic H2 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. K₃H[SiW₉O₃₄]·13H₂O and A-α-Na₁₀[SiW₉O₃₄]·23H₂O were prepared by 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 N₂ 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-SHP28 reaction vessel with a magnetic stirrer at room temperature. The produced H2 was analyzed by a GC-7920 instrument with N₂ as a carrier gas.

Synthesis of 1. K₃H[SiW₉O₃₄]·13H₂O (0.5 g, 0.36 mmol) was dissolved in a solution consisting of 7.5 mL of 30% aqueous H₂O₂ and 60 mL of water. Under rapidly stirring, 6 mL HCl (1.0 M) was added dropwise, while powdered A-α-Na₁₀[SiW₉O₃₄].23H₂O (3.44 g, 1.20 mmol) was added in a single step. Ten minutes later, a solution of Fe(NO₃)₃·9H₂O (0.31 g, 1.1 mmol) in H₂O (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 | Cs₁₂H₄₀Nb₁₀O₄₈Si₃W₂₈ |
| 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/Å³ | 12 806.8(15) |
| Z | 3 |
| D₄/g cm⁻³ | 3.798 |
| μ/mm⁻¹ | 21 980 |
| F₀₀₀ | 12 609 |
| Crystal size/mm³ | 0.37 × 0.25 × 0.21 |
| Refins collected | 21 257 |
| Indep refinns | 5324 |
| Rint | 0.0913 |
| Goodness-of-fit on F² | 1.058 |
| R₁ = | 0.0473, wR₁ = 0.1173 |
| R₁ | 0.0543, wR₁ = 0.1213 |
| Flack parameter | 0.535(19) |

### Notes

- **R₁** = \(\sum|F_o| - |F_c|/\sum|F_o|\)
- **wR₁** = \(\{\sum[w(F_o^2 - F_c^2)]^{1/2}\}/\sum[w(F_o^2)]\).
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): ν = 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 (λ = 0.71073 Å). Structure solution and refinement were carried out by using the SHELXS-97 and SHELXL-2014 program packages. 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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