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Polyoxometalates

Tetradecacobalt(II)-Containing 36-Niobate $[Co_{14}(OH)_{16}(H_2O)_8Nb_{36}O_{106}]^{20-}$ and Its Photocatalytic H_2 Evolution Activity

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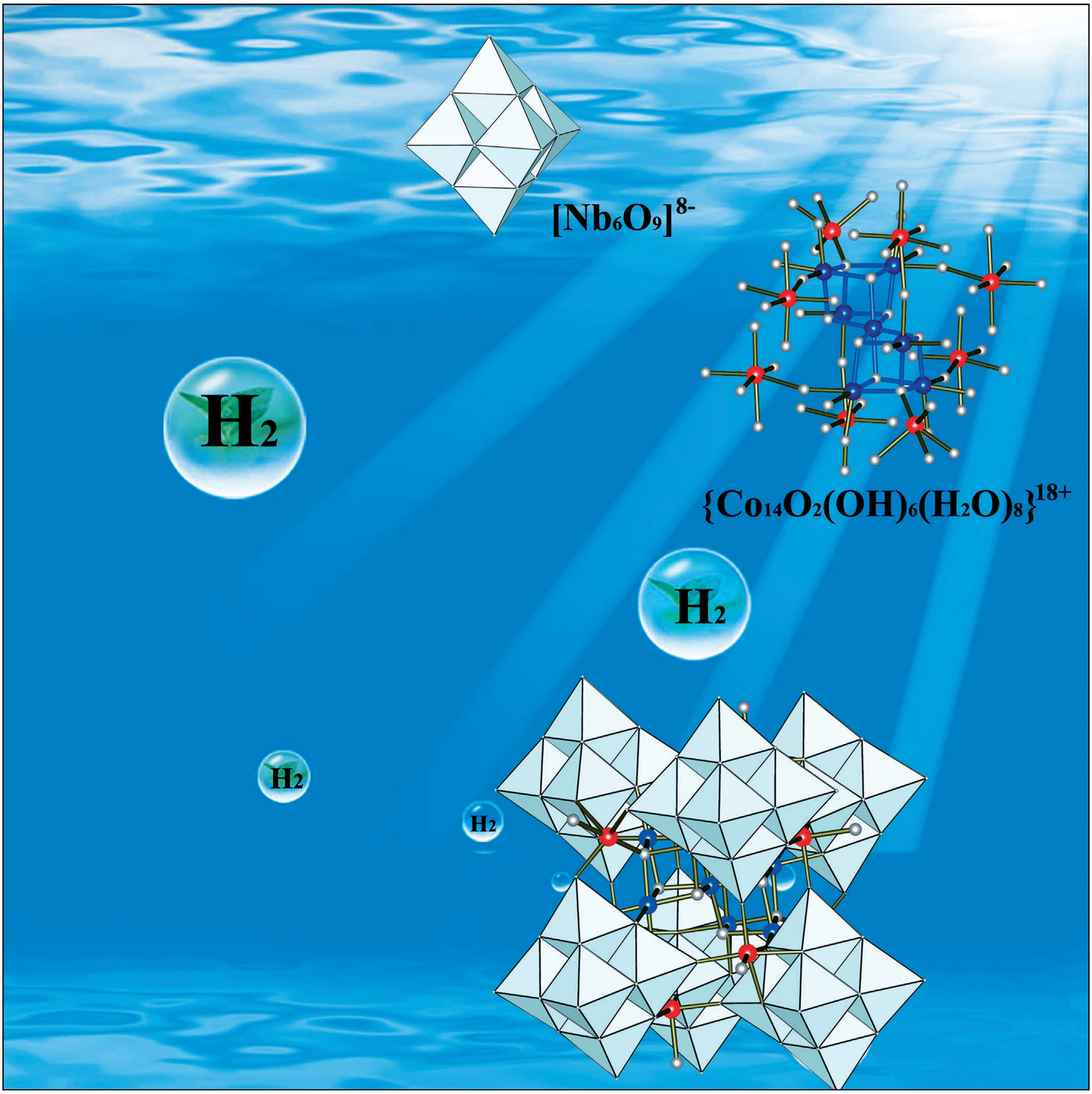

Abstract: A gigantic Co_{14}-containing 36-niobate, $Na_{12}K_8[Co_{14}(OH)_{16}(H_2O)_8Nb_{36}O_{106}]\cdot 71H_2O$ (**1**), has been prepared by the hydrothermal method and structurally characterized. Polyanion $[Co_{14}(OH)_{16}(H_2O)_8Nb_{36}O_{106}]^{20-}$ (**1a**) comprises a central Co_7 core, surrounded by another seven isolated Co^{2+} ions and six Lindqvist-type (Nb_6O_{19}) hexaniobate fragments. This is the first example of a high-nuclear cobalt-cluster-containing polyoxoniobate. The photocatalytic H_2 evolution activity of Pt-loaded **1** was observed in methanol solution under irradiation using a 300 W Xe lamp.

Polyoxoniobates are a subfamily of polyoxometalates (POMs) and have attracted increasing attention owing to their unique structural characteristics and potential applications in nuclear waste treatment, antiviral therapy, and photocatalysis.[1] Most reported polyoxoniobates[2,3,4] are heteropolyoxoniobates such as $[XNb_{12}O_{40}]^{n-}$ ($X = Si^{IV}$, Ge^{IV}, $n = 16$; $X = P^{V}$, $n = 15$),[2a–c,e,1h] $[H_2Si_4Nb_{16}O_{56}]^{14-}$,[2a] $[(PO_2)_3PNb_9O_{34}]^{15-}$,[2d] $[SiNb_{18}O_{54}]^{16-}$,[2f] $[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}]^{10-}$,[1h] and $[XNb_{18}O_{54}]^{18-}$ ($X = Al^{III}$, Ga^{III}).[2h] Several isopolyoxoniobates are also known, such as $[Nb_{10}O_{28}]^{6-}$,[3a] $[Nb_{20}O_{54}]^{8-}$,[3b] $[H_9Nb_{24}O_{72}]^{15-}$,[1d] $[HNb_{27}O_{76}]^{16-}$,[1g] $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$,[1g] and $[Nb_{32}O_{96}H_{28}]^{10-}$.[1i] On the other hand, transition-metal-containing polyoxoniobates have been rarely investigated.[1d,4e–f,5,6] Unlike V, Mo, and W, all of which can form POMs in neutral and acidic pH ranges, polyoxoniobates are mainly stable in strongly alkaline media, in which transition metal ions can easily precipitate. This complicates the synthesis of transition-metal-containing polyoxoniobates. To date, only a few such species have been reported, such as $[H_{23}NaO_8Cu_{24}(Nb_7O_{22})_8]^{16-}$,[4e] $[H_9Cu_{25.5}O_8(Nb_7O_{22})_8]^{28-}$,[4e] $[Ti_{12}Nb_6O_{44}]^{10-}$,[1f] $[\{Cu(H_2O)L\}_2\{CuNb_{11}O_{35}H_4\}]^{5-}$ (L = phen (phenanthroline), 2,2′-bipy (bipyridine)),[4f] $[\{Cu(en)_2\}_{3.5}\{Cu(en)_2(H_2O)\}\{[VNb_{12}O_{40}(VO)_2][Cu(en)_2]\}]\cdot 17H_2O$ (en = ethylenediamine),[2g] $[\{Cu_6(phen)_6(H_2O)_3\}\{Nb_{10}V_4O_{40}(OH)_2\}_2]$,[4g] and $[V_4Nb_6O_{30}]^{10-}$.[4h] It is expected that other 3d metals can also be incorporated into polyoxoniobate backbones, and so we systematically explored the reaction of cobalt ions with hexaniobate.

Herein, we report the tetradecacobalt(II)-containing 36-niobate cluster, $[Co_{14}(OH)_{16}(H_2O)_8Nb_{36}O_{106}]^{20-}$ (**1a**), which was isolated as a hydrated, mixed sodium–potassium salt, $Na_{12}K_8[Co_{14}(OH)_{16}(H_2O)_8Nb_{36}O_{106}]\cdot 71H_2O$ (**1**). Although some pioneering work on cobalt-containing POMs has been performed for polyoxotungstates,[7] and -molybdates,[8] with cobalt nuclearities ranging from 2 to 36,[9] almost no cobalt-containing polyoxoniobates have been reported to date, except for some simple cobalt-cation-bridged species.[6] In addition, the photocatalytic H_2 evolution activity of Pt-loaded **1** was investigated in methanol solution under irradiation using a 300 W Xe lamp. The result suggests that **1** can, to some extent, photocatalyze H_2 evolution.

Dark green crystals of **1** were obtained by the hydrothermal reaction of $K_7[HNb_6O_{19}]\cdot 13H_2O$ with $Co(NO_3)_2\cdot 6H_2O$, 2,2′-bipy, and 4,4′-bipy in water at pH 11.7 and at 120 °C. Notably, 2,2′-bipy and 4,4′-bipy are essential for the formation of **1**, although they do not appear in the structure. Such observations have also been made by Wang et al.[10] Single-crystal X-ray diffraction studies reveal that **1** crystallizes in the monoclinic space group *C*2/*m*. Polyanion **1a** exhibits idealized D_{3d} point group symmetry (Figure 1a and b, and Figures S1, S2 in the Supporting Information). Bond valence sum (BVS) calculations of **1** indicate that the oxidation state for all Co atoms is +2 (Table S1 in the Supporting Information),[11a] which is further confirmed by XPS spectra (Figure S3 in the Supporting Information). The Co $2p_{3/2}$ and Co $2p_{1/2}$ binding energies of 779.2 and 795.2 eV for **1** are in agreement with earlier results,[11b] indicating that the oxidation state for all Co centers is +2. The BVS values for O1C1, O13C, O7T, O3T, and O10T in **1a** are 1.24, 1.26, 1.37, 1.43, and 1.48, suggesting that they are monoprotonated, whereas the BVS values for O1C4, O1C5, and O1C6 are 0.28, 0.28, and 0.68, indicating that they are diprotonated (Figure S4 in the Supporting Information). Hence, we have a total of 16 hydroxyl groups and 8 aqua ligands associated with **1a** (Figure S5, Tables S2, S3 in the Supporting Information).

The gigantic polyanion **1a** has dimensions of about 16 × 17 Å² and contains the novel $\{Co_{14}O_2(OH)_6(H_2O)_8\}^{18+}$ cluster core (Figure 1c) encapsulated by six Lindqvist-type $[Nb_6O_{19}]^{8-}$ units, leading to an overall trigonal-antiprismatic assembly. The central $\{Co_{14}O_2(OH)_6(H_2O)_8\}^{18+}$ cluster is composed of an inner, corner-shared double-cubane core, $\{Co_7O_2(OH)_6\}^{4+}$ (Co1, Co2, Co3, Co2A, Co3A, Co3B, Co3C), and seven external Co^{II} ions (Co4, Co4A, Co4B, Co4C, Co5, Co5A, Co6, Co6A). It should be noted that Co6 and Co6A occupy special positions with an occupancy factor of 0.5 for each. The Co1 ion is located in the center of **1a** and is shared by six μ_3-OH groups, and Co2, Co3, and Co3B (as well as the symmetry equivalents Co2A, Co3A, and Co3C) are linked by three μ_3-OH groups and one μ_4-O atom, forming the central double-cubane core, $\{Co_7O_2(OH)_6\}^{4+}$. Such a connectivity mode has already been encountered in cobalt clusters.[9d,12] The Co4, Co4A, Co4B, Co4C, Co5, and Co5A ions are all linked to the central double-cubane unit, $\{Co_7O_2(OH)_6\}^{4+}$, by a bridging oxygen atom from each of the $[Nb_6O_{19}]^{8-}$ units, whereas the Co6 and Co6A ions are each connected with the central $\{Co_7O_2(OH)_6\}^{4+}$ core by one μ_4-O atom of the latter (Figure 1c and d, and Figure S6 in the Supporting Information). The six independent cobalt(II) ions (Co1, Co2, Co3, Co4, Co5, and Co6) in **1a** display two types of coordination geometries: Co6 exhibits a five-coordinate mode with a trigonal-bipyramidal geometry, which is rather rare in coordination chemistry,[13] whereas the remaining cobalt ions adopt

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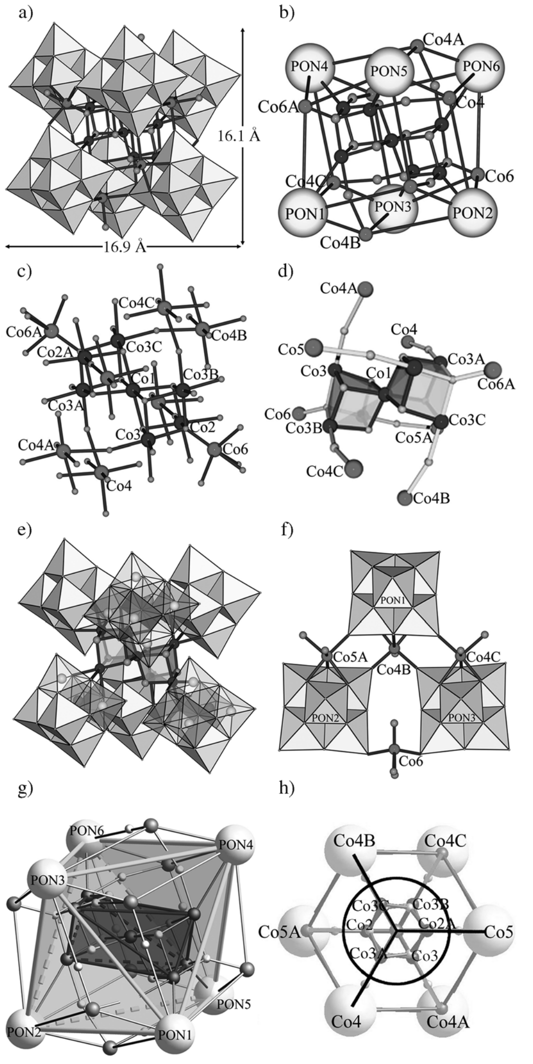

Figure 1. Different views of **1 a** or fragments thereof: a) combined polyhedral/ball-and-stick representation of **1 a**; b) schematic illustration of **1 a** (PON = polyoxoniobate); c) ball-and-stick representation of the $\{Co_{14}O_2(OH)_6(H_2O)_8\}^{18+}$ unit in **1 a**, containing the central, double-cubane $\{Co_7O_2(OH)_6\}^{4+}$ core; d) simplified view of the $\{Co_{14}O_2(OH)_6(H_2O)_8\}^{18+}$ core; e) the $\{Co_7O_2(OH)_6\}^{4+}$ core and six $[Nb_6O_{19}]^{8-}$ units; f) three adjacent $[Nb_6O_{19}]^{8-}$ units linked by cobalt bridges; g) schematic view of **1 a** displaying the trigonal-antiprisms of Co_6 and $\{Nb_6O_{19}\}_6$; h) Newman-style projection of the Co_{14}-core, indicating the two types of cobalt ions, and a staggered configuration. All hydrogens, sodium ions, and lattice water molecules are omitted for clarity. Symmetry codes: A: −*x*, *y*, 2−*z*; B: *x*, −*y*, *z*; C: −*x*, −*y*, 2−*z*.

six-coordinate modes with octahedral geometry. Except for Co1, which is corner-sharing in the central $\{Co_7O_2(OH)_6\}^{4+}$ double-cubane core, the six cobalt(II) ions in this $\{Co_7\}$ core are connected to each $[Nb_6O_{19}]^{8-}$ unit by three bridging oxygen atoms (Figure S7 in the Supporting Information), resulting in the formation of the main skeleton of **1 a** (Figure 1 e). The stability of **1 a** is enhanced by Co4, Co4A, Co4B, Co4C, Co5, Co5A, Co6, and Co6A linking six $[Nb_6O_{19}]^{8-}$ units. Co4 (and the symmetry equivalents Co4A, Co4B, Co4C) and Co5 (and the symmetry-related Co5A) are each coordinated by two Nb–O$_t$ and three Nb–O$_b$ atoms of neighboring $[Nb_6O_{19}]^{8-}$ units and one terminal water molecule, whereas Co6 is bound to three terminal oxygen atoms of three different $[Nb_6O_{19}]^{8-}$ units, to one oxygen atom of the $\{Co_7O_2(OH)_6\}^{4+}$ core, and to one terminal water molecule. Figure 1 d reveals that the central $\{Co_7O_2(OH)_6\}^{4+}$ double-cubane unit in **1 a**, containing six μ_3-OH ions and two μ_4-O ions, acts as a template and induces the structural motif for Co4, Co5, Co4B, Co6A, and Co4A, Co4C, Co5A, Co6. So far, the $\{Co_7O_2(OH)_6\}^{4+}$ double-cubane core has been unobserved in polyoxoniobate chemistry. In **1 a**, three adjacent $[Nb_6O_{19}]^{8-}$ units are bridged by four cobalt ions (Figure 1 f). It is noteworthy that the central groups of Co2, Co3, and Co3B and Co2A, Co3A, and Co3C exhibit trigonal-antiprismatic geometry. As the six $[Nb_6O_{19}]^{8-}$ units are also arranged in a trigonal-antiprismatic geometry, **1 a** consists of two trigonal-antiprisms (Figures 1 g and 2). A tungstophosphate containing three tetrahedra has been reported previously;[14] however, **1 a** is a polyoxoniobate comprising two trigonal-antiprismatic fragments. The structure of **1 a** allows for an analogy with organic molecules, namely substituted ethane derivatives, and so-called Newman projections. The staggered Newman configuration of the central Co2, Co3, Co3B and Co2A, Co3A, Co3C in the $\{Co_7O_2(OH)_6\}^{4+}$ core induces staggered Newman configurations of Co4, Co4B, Co5 and Co4A, Co4C, Co5A, as well as polyoxoniobate (PON) units 1, 4, 5 and 2, 3, 6 (Figures 1 h and 3, Figure S8 in the Supporting Information). To the best of our knowledge, **1 a** is the first high-nuclear cobalt-cluster-containing polyoxoniobate. Examples of other high nuclearity Co-containing species include Kortz's Co_{16}-containing 36-tungsto-8-phosphate, $[\{Co_4(OH)_3PO_4\}_4(PW_9O_{34})_4]^{28-}$,[12d] and Winpenny's Co_{14}-containing phosphonates, $[(Co_{14}(OH)_2(X)_2(chp)_{20}(O_3PR)_2(H_2O)_2]$ (X = F or OH and R = Benzyl, Me, Et, *n*-octyl, chp=6-chloro-2-hydroxypyridine) and $[(Co_{14}(chp)_{20}(Hchp)_2(HPO_3)_2(OH)_2F_2(H_2O)_2]$.[15] Finally, the orderly alignment of individual polyanions, **1 a**, in the solid-state lattice of **1** generates rhombic channels with dimensions of roughly 5 × 14 Å^2 (Figure S9 in the Supporting Information).

The magnetic susceptibility for **1** was measured at 2–300 K under an external magnetic field of 1000 Oe (Figure 4). The value of χ_M slowly increases with decreasing temperature, from 0.11 emu mol^{-1} at 300 K to 0.75 emu mol^{-1} at 16 K, and then exponentially, reaching a maximum of 4.85 emu mol^{-1} at 2 K. At 300 K, the $\chi_M T$ value of 32.63 emu K mol^{-1} is significantly higher than the spin-only value of 26.25 emu K mol^{-1} expected for 14 non-interacting high-spin Co^{II} ions ($S = 3/2$), which is supported by the X-band EPR spectrum ($g = 2.54$) of **1** at room temperature (Figure S10 in the Supporting Information). This magnetic behavior indicates the presence of a large orbital contribution arising from the ground state triplet $^4T_1$ of each Co^{II} ion, a contribution that is known to be significant in an octahedral or trigonal bipyramidal ligand field.[12b,16] Upon cooling, the $\chi_M T$ value of **1** gradually decreases with decreasing temperature and reaches a minimum of 9.09 emu K mol^{-1} at 2 K. The $\chi_M T$ versus *T* behavior indicates antiferromagnetic exchange coupling between the cobalt ions, a process that is further confirmed by the negative Weiss constant $\theta = -44.06$ K derived from fitting the Curie–Weiss law to the magnetic data between 30 and 300 K (Figure S11 in the Supporting Informa-

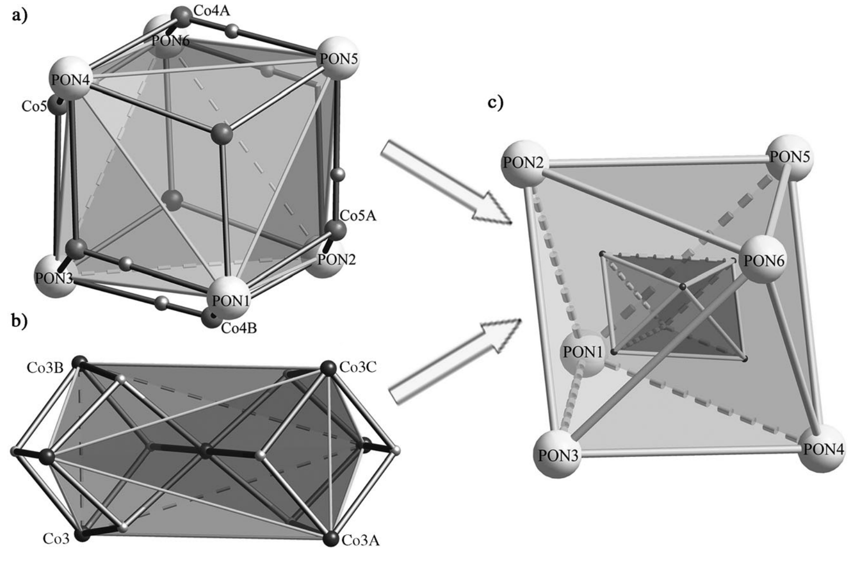

Figure 2. Simplified views of **1 a** showing two trigonal-antiprisms. Symmetry codes: A: −*x*, *y*, 2−*z*; B: *x*, −*y*, *z*; C: −*x*, −*y*, 2−*z*.

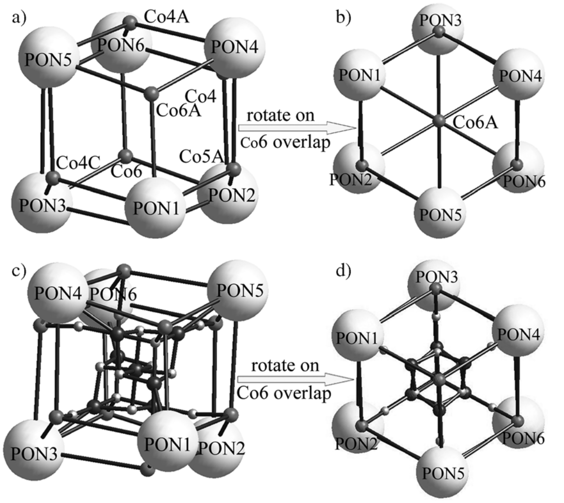

Figure 3. a) A simplified view of **1 a**; b) the trigonal-antiprismatic arrangement of the six $[Nb_6O_{19}]^{8-}$ units can be described as a staggered Newman configuration; c) schematic illustration of **1 a**; d) **1 a** can be demonstrated as two staggered Newman configurations. Symmetry codes: A: −*x*, *y*, 2−*z*; B: *x*, −*y*, *z*; C: −*x*, −*y*, 2−*z*.

tion). Such antiferromagnetic coupling has been previously observed for some cobalt-containing POMs.[17]

We also investigated the catalytic properties of **1**. To explore the photocatalytic H_2 evolution activity of polyanion **1 a**, 100 mg of 0.5 % Pt-loaded **1** was suspended in 100 mL of a 20 % methanol solution in a quartz cell. The catalyst suspension was irradiated under a 300 W Xe lamp. As shown in Figure 5 (top), the H_2 evolution rate in three runs was 456, 566, and 557 $\mu mol\,g^{-1}\,h^{-1}$. The total H_2 evolved over 7.5 h was 394 μmol, corresponding to a turnover number of 32. In contrast, in the absence of **1**, the H_2 evolution rate was 44 $\mu mol\,g^{-1}\,h^{-1}$ (Figure 5 (bottom)). This result suggests that **1** can to some extent photocatalyze H_2 evolution.

In conclusion, we have synthesized a gigantic Co_{14}-containing polyoxo-36-niobate, **1 a**, by hydrothermal synthesis. To date, **1 a** represents the largest cobalt-oxo-cluster-containing polyoxoniobate and hence provides an important reference point in polyoxoniobate chemistry. The photocatalytic H_2 evolution activity of **1** has also been investigated. From the viewpoint of synthetic chemistry, it could be interesting to explore the replacement of cobalt(II) in **1 a** by nickel(II), manganese(II), iron(III), or iron(II), which would lead to novel transition-metal-substituted polyoxoniobate aggregates. Moreover, by the hydrothermal technique, we expect that lanthanide cations can be introduced to this system and it would be possible to construct lanthanide-incorporated polyoxoniobate clusters. From the standpoint of application prospects, by varying the components of desired polyoxoniobates, discovering novel photocatalytic and molecule-based polyoxoniobate materials is very possible. For example, if the single-molecule magnetic $\{Mn_{12}\}$ cluster can be combined with polyoxoniobate fragments, unique $\{Mn_{12}\}$-anchored polyoxoniobate-based single-molecule magnetic materials may be fabricated. In addition, in our previous research, the antitumor activities of $[\{Cu(H_2O)L\}_2\{CuNb_{11}O_{35}H_4\}]^{5-}$ (L = phen, 2,2′-bipy) have been evaluated.[4f] Therefore, medical activities of polyoxoniobates may be also an interesting field in time. In summary, the successful synthesis of **1 a** not only opens the door for cobalt-containing polyoxoniobate chemistry and for preparing other d or f (and maybe even mixed d/f) metal derivatives, but perhaps offers us new expectations and possibilities about diverse application potentials of polyoxoniobate chemistry. Currently we are exploring such possibilities.

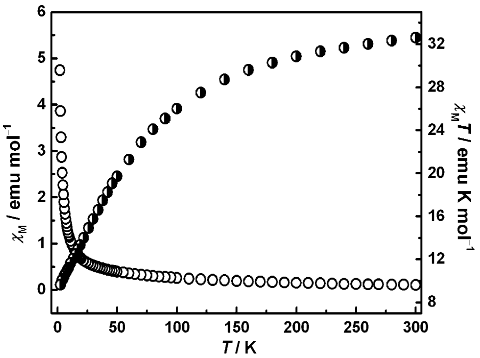

Figure 4. Temperature dependence of the molar magnetic susceptibility χ_M and the product $\chi_M T$ for **1** between 2 and 300 K.

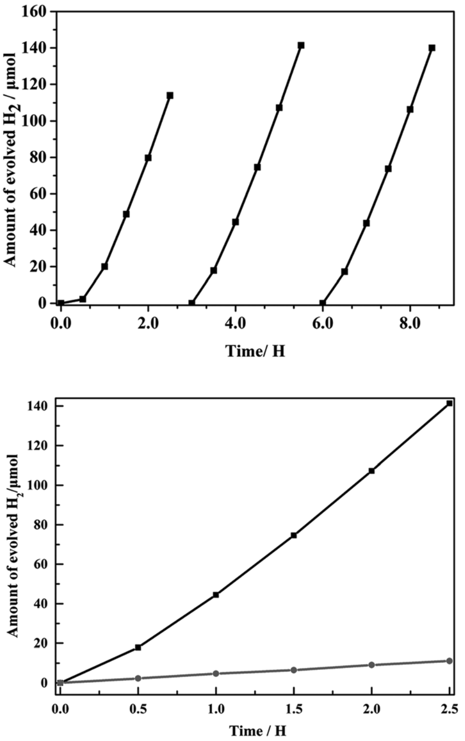

Figure 5. Top: Time course of 0.5 % Pt-loaded photocatalyst **1** under UV irradiation (300 W Xe lamp) in 20 % methanol aqueous solution. Bottom: Time profile of photocatalytic H_2 evolution with **1** as photocatalyst (squares) and in the absence of **1** (circles). The experiments were performed in 100 mL of solution containing 20 mL CH_3OH, 80 mL 0.5 M HCl, 0.05 mg H_2PtCl_6, and 100 mg 0.5 % Pt-loaded photocatalyst.

Experimental Section

Preparation of 1

$K_7[HNb_6O_{19}]\cdot 13H_2O$ (0.750 g, 0.550 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.582 g, 2.000 mmol), 2,2′-bipy (0.062 g, 0.400 mmol) and 4,4′-bipy (0.129 g, 0.067 mmol) were dissolved in water (20 mL). The pH value was adjusted to 11.7 by using NaOH solution, and the resulting suspension was transferred to a 30 mL Teflon-lined autoclave and kept in an oven at 120 °C for 6 days, and then cooled to room temperature. The pH value after the synthesis was about 9.3. Dark green, block-shaped crystals of $Na_{12}K_8[Co_{14}(OH)_{16}(H_2O)_8Nb_{36}O_{106}]\cdot 71H_2O$ (**1**) were obtained by filtration and dried in air. Yield: 0.10 g, 14 % (based on $K_7[HNb_6\ O_{19}]\cdot 13H_2O$). Elemental analysis (%) calcd for $Co_{14}H_{174}\ K_8Na_{12}Nb_{36}O_{201}$: H 2.15, Co 10.12, K 3.84, Na 3.39, Nb 41.04; found: H 2.44, Co 10.40, K 2.69, Na 3.39, Nb 40.85. IR (KBr): ν= 871(s), 680(s), 547(s) cm^{-1} (Figure S12 in the Supporting Information).

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Keywords: H_2 evolution · high-nuclear cobalt cluster · photocatalysis · polyoxometalate · polyoxoniobate

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