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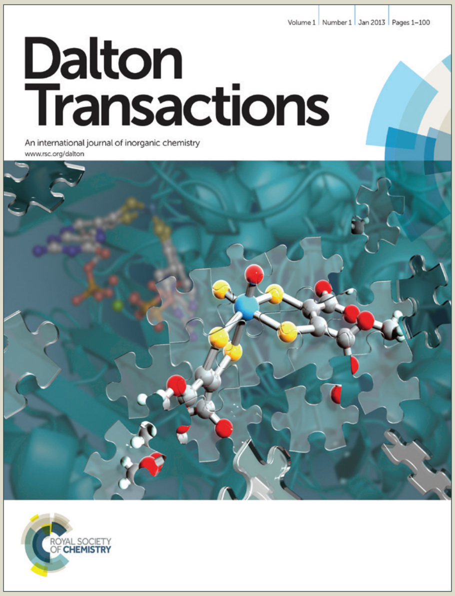

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ARTICLE TYPE

Synthesis, Crystal structure and Photocatalytic Property of an unprecedented arsenic-disubstituted Lindqvist-type peroxopolyoxoniobate ion: $\{As_2Nb_4(O_2)_4O_{14}H_{1.5}\}^{4.5-}$

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An unprecedented arsenic-disubstituted Lindqvist-type peroxopolyoxoniobate $Cs_{2.5}Na_2\{As_2Nb_4(O_2)_4O_{14}H_{1.5}\}\cdot 11H_2O$ has been successfully synthesized and characterized. The photocatalytic activity of the cluster for H_2 evolution from water is investigated by irradiating with a 300 W Xe lamp, which shows a certain photocatalytic water splitting activity.

Polyoxoniobates (PONs) have attracted significant interest not only for the relatively limited structural diversity reported, but also for their significant potential applications in different areas, such as virology, nuclear-waste treatment, and the base-catalyzed decomposition of biocontaminants.[1] Although the synthetic conditions of PONs are more difficult compared with the larger classes of polyoxometalate based on W, Mo or V, the number of substituted niobates known to date still has achieved great progress in the past ten years. Up to now, isopolyoxoniobates including $[Nb_6O_{19}]^{8-}$,[2] $[Nb_{10}O_{28}]^{6-}$,[3] $[Nb_{20}O_{54}]^{8-}$,[4] $[H_9Nb_{24}O_{72}]^{15-}$,[5] $[HNb_{27}O_{76}]^{16-}$,[6a] $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$,[6a] and $[H_{10}Nb_{32}O_{96}]^{4-}$[6b] have been isolated in the literature. On the other hand, a number of transition-metal-substituted heteropolyoxoniobates have been reported, including Ti^{IV}-substituted PONs $[Ti_2Nb_8O_{28}]^{8-}$,[7a] $[TiNb_9O_{28}]^{7-}$,[7b] and $[Ti_{12}Nb_6O_{44}]^{10-}$.[7c] The copper-substituted ion $[CuNb_{11}O_{35}H_4]^{9-}$,[8] the vanadium-substituted ions $[VNb_{12}O_{40}(VO)_2]^{9-}$,[9a] $[H_6V_4Nb_6O_{30}]^{4-}$,[9b] $[Nb_{10}V_4O_{40}(OH)_2]^{12-}$,[9c] and $[V_3Nb_{12}O_{42}]^{9-}$,[9d] the chromium-substituted ion $[Cr_2(OH)_4Nb_{10}O_{30}]^{8-}$,[10] the iron-substituted ion $[H_2Fe^{III}Nb_9O_{28}]^{6-}$ [11] and the nickel-substituted ion $[H_3Ni^{II}Nb_9O_{28}]^{6-}$ [11] were also obtained. Furthermore, inspired by the work of Finke,[12,13] Hill [14] and their co-workers, the peroxopolyoxoniobates synthesized by the $[Nb_6O_{19}]^{8-}$ reaction in H_2O_2 solution are appropriate candidates for studying PONs in acidic solution. Peroxide-ligated PONs have been isolated, including $[Ti_{12}Nb_6O_{38}(O_2)_6]^{10-}$ [15] and $[H_3Nb_6O_{13}(O_2)_6]^{5-}$,[16] and so on. However, heterometal-substituted Lindqvist-type PONs are relatively less explored and the only two examples of ions are the tungsten-rich $[HNb_2W_4O_{19}]^{3-}$ [17] and the tellurium-monosubstituted $[H_2TeNb_5O_{19}]^{5-}$.[18] To date, both peroxide-ligated and heteroatoms-substituted Lindqvist-type PONs have never been reported in the literature.

Herein, based on the previous work, we report the synthesis and structural characterization of an unprecedented arsenic-disubstituted Lindqvist-type peroxopolyoxoniobate $Cs_{2.5}H_{1.5}Na_2\{As_2Nb_4(O_2)_4O_{14}\}\cdot 11H_2O$ (**1**). To our knowledge, this compound represents the first example of integrating arsenic atoms into the peroxopolyoxoniobate.

Compound **1** was prepared by the reaction of $K_7H[Nb_6O_{19}]\cdot 13H_2O$[19,20], H_2O_2, $Na_3AsO_4\cdot 12H_2O$, HCl and NaOH at 80℃ for 3 h. In the synthesis of compound **1**, parallel experiments show that several factors such as reactants, temperature, pH value and the concentration of reaction system can influence the structure and extend structural fashions of the products. It is worth noting that crystals only can be obtained by the diffusion method and the best mixed solvent volume ratio of CH_3CH_2OH/H_2O is 1:2.

The phase purity of **1** was characterized by the powder X-ray diffraction (PXRD) pattern of the bulk product. The PXRD pattern is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction (Fig. S1), which confirms that the phase is pure. The difference in intensity may be due to the preferred orientation of the powder samples. Single-crystal X-ray structural analysis shows that the structure of compound **1** possesses the cluster of $\{As_2Nb_4(O_2)_4O_{14}H_{1.5}\}^{4.5-}$ along with 1.5 protons, 2.5 Cs^+ cations and eleven water molecules with orthorhombic molecular symmetry, Pnma space group. In the novel cluster of $\{As_2Nb_4(O_2)_4O_{14}H_{1.5}\}^{4.5-}$, four Nb and two As atoms connect each other through bridging oxygen atoms (Figure 1). Compared with the archetype Lindqvist-type structure of $[Nb_6O_{19}]^{8-}$ ion, the cluster of **1** can be seen as two Nb atoms being replaced by the two As atoms. The angles of Nb-O_b-Nb, Nb-$O\mu_4$-Nb are between 109.3(3)-113.5(3)°, 96.4(4)-98.3(4)°, and the band lengths of Nb-O_b, Nb-μ_4-O are in the range of 1.875-2.095 Å and 2.106-2.273 Å, respectively. Notably, in the polyanion of **1**, all four terminal oxygen atoms of Nb atoms are replaced by η^2-$O^{(I)}{}_2{}^{2-}$ and the band lengths of Nb-$O^{(I)}{}_2{}^{2-}$ are between 1.951(7)-1.979(9) Å which are longer than the Nb-Ot (1.75-1.80 Å).[21] And the average band length of the four peroxo-containing bands is 1.47 Å which is comparable to that observed in the crystal structure of hydrogen peroxo (1.49Å)[22] and also similar to those in the peroxo groups in other reported POMs.[14a-c,23,24] Interestingly, these atoms including Nb(2), Nb(3), As(1), As(2), O(7) are coplanar and can form a symmetry plane of the whole structure. The X-ray diffraction analyses also show that the Nb atoms here adopt a pseudo-octahedral configuration which is similar to that of the reported ion $[H_3Nb_6O_{13}(O_2)_6]^{5-}$,[16] and the substituted arsenic atoms here adopt a tetrahedral geometry. The central As-O bond lengths range from 1.655(9) to 1.699(9) Å and the O-As-O angles are in the range of 106.6(5)-115.1(4)°. The band valence sum (BVS) calculations[25] confirm that all the Nb and As atoms are in the +5 oxidation state [Scheme. S1]. Furthermore, the BVS calculations give the values of 1.35, 1.36 for O_{14}, O_{15}, respectively, which are relatively lower than those of other oxygen atoms in the framework (1.65-2.10) and further indicate the most possible sites for protonation. [the details are depicted in Fig. S2 and Scheme. S2, S3].

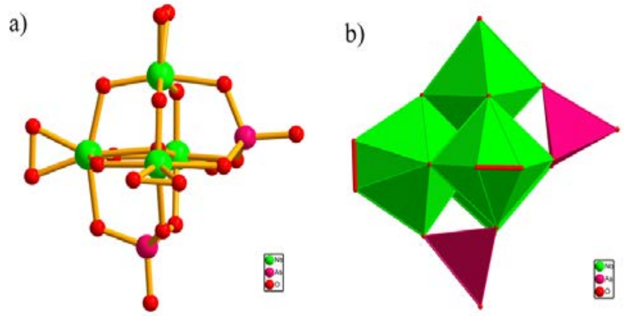

Figure 1. (a) ball-and-stick representation of $\{As_2Nb_4(O_2)_4O_{14}\}^{6-}$ unit. (b) Polyhedral view of the $\{As_2Nb_4(O_2)_4O_{14}\}^{6-}$ cluster. The discrete Cs^+, Na^+ cations and lattice water molecules are omitted for clarity.

The IR spectrum of compound **1** [Fig. S3] is recorded between 400 and 4000 cm^{-1} with a KBr pellet, which is very useful for identification of characteristic vibration bands in products. In the IR spectrum of compound **1**, the characteristic bands located at around 856 cm^{-1} and 853 cm^{-1} are assigned to the ν(As-O) and peroxo group ν(O-O) vibrations,[26] respectively, while the characteristic peaks in the ranges of 400-800 cm^{-1} are attributed to the ν(Nb-O_b-Nb) vibrations.[27]

The UV spectrum of compound **1** in aqueous solution displays two absorption bands centered at 200 nm and 280 nm, respectively. The higher energy band (200 nm) can be assigned to the O_t→Nb charge transfer transition, whereas the lower one (280 nm) can be attributed to the charge transfer transition of O_b→Nb, suggesting the presence of the polyoxoanion. In order to investigate the stability of **1** in the aqueous solution, the in-situ UV spectroscopic measurements were performed, and the systematic results revealed that **1** could stably exist at least 24 h in the aqueous solution at ambient temperature [Fig. S4].

It is well known that the PONs are commonly sensitive to the pH values of the media. Therefore, in order to investigate the influences of the pH values on the stability of **1** in aqueous solution, the compound **1** has also been elaborately probed by the means of UV spectra. Diluted HCl solution and NaOH solution were used to adjust the pH values in the acidic direction and in the alkaline direction, respectively. The UV spectrum of compound **1** in aqueous solution displays two absorption bands at 200 and 280 nm, respectively, and the original pH value of it in water (5×10^{-5} mol/L) was 7.5 [Fig. S5]. When the pH value gradually decreases to 2.0, the absorbance band at 280 nm occurs red-shift and disappears finally. While the other absorbance band at 200 nm shows a little blue-shift and the peak changes pointy. The reason for the red-shift of the O_t→Nb band may be related to the protonation of the terminal oxygen atoms of the polyoxoanion.[28, 29] In contrast, when the pH value of **1** gradually increases to 10.0, the absorption band at 280 nm shows a little blue-shift and becomes weaker and weaker until it vanishes. While the absorption band at 200 nm only becomes a little weaker than initial state. All these changes suggest the decomposition of the **1** skeleton, and the results indicate that the skeleton of **1** can remain stable in the pH range of 4.0~8.0.

For the sake of studying the conductivity of **1**, the UV−vis diffuse reflectance spectrum of its powder sample was measured to achieve its band gaps (Eg), which was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka-Munk function F against E. As is shown in Fig. S6, the corresponding well-defined optical absorption associated with Eg can be assessed at 3.5 eV which is smaller than the Eg of $K_7H[Nb_6O_{19}]\cdot13H_2O$ [Fig. S7], revealing the presence of an optical band gap and the nature of semiconductivity with a wide band gap.

Thermal gravimetric analysis (TGA) was performed under N_2 atmosphere from 25 to 800 ºC [Fig. S8]. The TG curve of **1** exhibits one slow step of weight loss, giving a total loss of 18.98 % (calcd. 18.97%) in the range of 25−800 ºC. The total weight loss can be assigned to the removal of eleven crystal water molecules, the dehydration of 1.5 protons and the loss of one oxygen atom in each peroxo group.

To explore the photocatalytic H_2 evolution activity of **1**, the experiments were performed in a quartz cell with 50 mL solution which containing 50.0 mg sample of **1**, 10 mL CH_3OH, 40 mL 0.5 M HCl, 1.0 mL H_2PtCl_6 solution (1.50 mg Pt)[18, 26b]. The catalyst solution was irradiated under UV and visible light from a 300 W Xe lamp. Methanol was used as a sacrificial electrondonor and H_2 was monitored by gas chromatography. The photocatalytic water splitting activity of $K_7H[Nb_6O_{19}]\cdot13H_2O$ was also measured. As is shown in Figure 2, the total evolved H_2 of **1** and $K_7H[Nb_6O_{19}]\cdot13H_2O$ during 10 h were 98.8 and 145.7 μmol, and the H_2 evolution rate of them were 197.6, 291.4 μmol g^{-1} h^{-1}, respectively. As a result, the effectivity of H_2 evolution activity from water of **1** was worse than the $K_7H[Nb_6O_{19}]\cdot13H_2O$, which suggests that Nb atoms play the mainly role in the process of photocatalytic H_2 evolution activity. After photocatalytic experiments, the PXRD pattern of **1** unable to be obtained because the smaller amount of the flocculent precipitate and the presence of Pt cocatalyst. However, the FT-IR and UV-Vis spectras before and after the photocatalytic reactions have been given in Supporting Information to testify the stability of **1**. The results showed the cluster of **1** has changed after the photocatalytic reactions, which means the catalyst can not be recycling used [Fig. S9, S10].

In addition, we also explore the photocatalytic H_2 evolution activity with sample **1** as the UV light photosensitizer and catalysts, $Co^{III}(dmgH)_2pyCl$ complex as cocatalyst, and TEA as the sacrificial electron donor.[6b,30] The experiments were performed in a quartz cell containing 50 mg (0.034 mM) sample, 50 mg (0.125 mmol) cobaloximes and 5 mL TEA in 45ml of water (1/9 v/v). The catalyst solution was irradiated under UV and visible light from a 300 W Xe lamp. As shown in Figure 2a, the total evolved H_2 during 10 h were 51.16 μmol and the H_2 evolution rate of compound **1** was 102.3, if using μmol g^{-1} h^{-1} as unit. Obviously, the photocatalytic H_2 evolution activity of compound **1** in the presence of Pt cocatalyst was much better than in the system of cobaloxime as a cocatalyst.

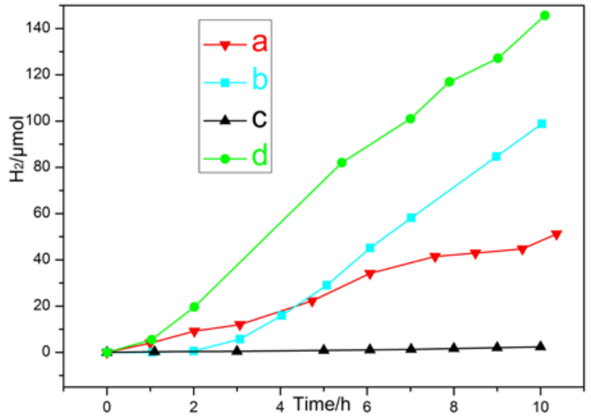

Figure 2. Dependence of H_2 production on irradiation time with the use of compound **1** as photocatalyst: (a) compound **1** in the presence of cobaloxime; (b) compound **1** in the solution of H_2PtCl_6; (c) the absence of compound **1** or $K_7H[Nb_6O_{19}]\cdot 13H_2O$; (d) $K_7H[Nb_6O_{19}]\cdot 13H_2O$ in the solution of H_2PtCl_6.

Conclusions

In conclusion, an unprecedented arsenic-disubstituted Lindqvist-type peroxopolyoxoniobate based on the cluster of $\{As_2Nb_4(O_2)_4O_{14}H_{1.5}\}^{4.5-}$ has been successfully synthesized and characterized, and the photocatalytic H_2 evolution activity of it was also explored. The successful preparation of compound **1** not only provides us a possible strategy to develop unexpectedly PONs derivatives by using the diffusion method, but also enriches the structural diversity of heteroatoms-substituted Lindqvist-type peroxopolyoxoniobates. Currently, we are planning to systematically investigate the influence of the synthetic variables of the experiment procedure on the final products, as well as the photocatalytic H_2 evolution activity of their properties.

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Notes and references

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Electronic Supplementary Information (ESI) available: The experiment sections of **1**, XRPD spectra, bond valence sum calculations, IR spectra, UV spectra, the diffuse reflectance UV-vis-NIR spectra of K-M function vs energy and TG analyses. For crystallographic data in CIF or other electronic format see DOI:10.1039/b000000x/

Crystal data for **1**: CSD 427505. Mr =1452, Orthorhombic, space group $Pnma$, a =17.680(5) Å, b =13.346(4) Å, c = 26.399(8)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$ V = 6229.3(13) Å^3, $Z = 4$, μ = 6.566 mm^{-1}, $F(000)$ = 5528, $GOOF$ = 1.073. Of 30869 total reflections collected, 5707 reflections are unique ($R_{\rm int}$ = 0.0487). R_1 = 0.0513, wR_2 = 0.1610 for 457 parameters and 5707 reflections [$I > 2\sigma(I)$].

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