Antimony-dependent expansion for the Keggin heteropolyaniobate family†

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Nine new Sb-bicapped α-Keggin-type heteropolyaniobiates (HPNb) were synthesized under hydrothermal conditions. Among them, the As-centered HPNb was never reported before, and the two dimer compounds are the biggest isolated HPNbs at present.

Polyoxometalates (POMs), as a large and multifunctional class of discrete nano-sized transition metal oxide clusters, exhibit variety of chemical properties. This area is attracting increasing interest for their significant applications in catalysis, magnetism and nanotechnology. As is known, the POM chemistry has been dominated by polyoxotungstates, molybdates and vanadates. On the other hand, substituted POMs are also a significant branch. In the Nb-substituted POMs, typical examples are the Keggin-type polyoxotungstates, αβ-XW₆Nb₂O₄₆⁽⁻⁾ (X = Si, P, Ge or As).6

However, a rapid development of Nb-based POM chemistry only occurred in recent decades, because polyoxoniobates (PONbs) were difficult to obtain through the usual acidic conditions at ambient conditions, as in the case of the classical POMs mentioned above. Pioneer investigations by Nyman, Casey and others, have successfully harvested various isopolyoxoniobates (IPONbs) under basic conditions, including {Nb₂O₆}, {Nb₅}, {Nb₁₀}, {Nb₂₀}, {Nb₃₁}, {Nd₂₇}, {Nb₃₃} and {Nd₃₂}.11 Relatively, heteropolyaniobate (HPNb) chemistry is explored rarely, perhaps due to severe reaction conditions, such as higher temperatures and narrow pH windows (10.5–12.5). Since Nyman and coworkers reported the first HPNbs, [Ti₂O₃][SiNb₂O₄₀]¹₂⁻ and [H₂Si₂Nb₁₄O₅₆]¹⁴⁻, a dozen of the Keggin-type HPNbs and analogues have been reported, namely, [XNb₁₂O₄₀]¹⁺ (X = Si, Ga or Al), [XNb₁₂O₄₀]¹⁻ (X = Si or Ge) [XNb₁₂O₄₀(VO)₆]²⁻ (X = Si, Ge, P or V), [PO₃]₂PNb₂O₄₃ [PO₃]₂PNb₂O₄₃ [Nb₂O₃][TiNb₁₂O₄₀]¹₀⁻, [Nb₂O₃(H₂O)] [SiNb₁₂O₄₀]¹₀⁻, [X₁(XOH)₂Nb₁₆O₅₄]¹⁺ (X = Si or Ge), [XNb₁₈O₅₄(VO)₆]¹⁻ (X = P or V) and [PNb₁₂O₄₀(VO)₆]¹⁻. Among these HPNbs, most possess the capped Keggin-type structures, with {TiO₆}, {VO₆} and {NbO₆} as the capping groups, to neutralize high negative charges of Keggin cores. Inspired by the foregoing work, we tried to introduce Sb into the HPNb system, as Sb³⁻ ion with high positive charge, may play a capping role anchoring on the HPNb clusters to neutralize the Keggin cores. Till now, only Sb-bicapped Keggin-type {PMO₁₂O₄₀Sb₂} cores were reported by Xu’s group,22 and {PND₁₂Sb₂O₃₆}¹⁻ was reported by Casey’s group quite recently.23 Herein, we report a series of Sb-bicapped HPNb compounds, [Cu(en)]₃[H₂O] [x-H₂TNb₁₂O₄₀Sb₂] · 18H₂O (1: T: Si, n = 2 (1-Si); Ge, n = 2 (1-Ge); P, n = 1 (1-P); As, n = 1 (1-As); V, n = 1 (1-V)); [Cu(en)₃][Cu(en)₃[H₂O] [x-HNTNb₁₂O₄₀Sb₂] · 18H₂O (2: T: Si (2-Si); Ge (2-Ge)); [Cu(en)₃][Cu(en)₃][x-TNb₁₂O₉Sb₂] · 11H₂O (3: T: Si (3-Si); Ge (3-Ge) (en = ethanediamine). All these compounds consist of new Sb-bicapped [TNb₁₂O₄₀Sb₂]²⁻ polyaniobanes. Especially, the As-centered Keggin-type HPNb cluster was never reported before. 3 is the first example of dimer fused by two Keggin-type HPNb clusters, which are the biggest isolated clusters based on the Keggin-HPNb at present.

The single-crystal X-ray diffraction analysis revealed that five compounds of 1 were isostructural, thus the structure of 1-Si is described in details. The cell unit of 1-Si consisted a quarter of a crystallographically independent Sb-bicapped Keggin-type polyanion [x-HTNb₁₂O₄₀Sb₂]²⁻ (as shown in Fig. 1a) and one crystallographically independent [Cu(en)]₂[H₂O]²⁺ cation. Two Sb atoms, in a distorted square pyramidal coordination geometry oppositely capped on two {NbO₆} [O₆, O7, O6#, O7#] windows of the [x-Nb₁₂Sb₂] core (Fig. S1, ESI†). Sb-O bond lengths and O-Sb-O bond angles were in the ranges of 1.992(6)–2.152(6) Å and 76.3(2)–135.8(3)°, respectively. Thus, the symmetry of the α-Keggin-type cluster was lowered from Tₐ to D₉d and the negative charge of the Keggin HPNb anion was neutralized from −14 in an uncapped one to −8 in the capped one.

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[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+} \text{ was a free cation in which } \text{Cu}^{2+} \text{ was chelated by two en molecules and coordinated by one water molecule in a tetragonal pyramid coordination geometry. The bond parameters for 1 are listed in Tables S3, S4 and S6 (ESI†).}

The two compounds of 2 were isostructural, comprised of one crystallographically independent \([\text{HTNb}_{12}\text{O}_{38}\text{Sb}_{2}]^{6−}\), two crystallographically independent \([\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^2+\) (Cu1 and Cu4) and 2.5 crystallographically independent \([\text{Cu}(\text{en})_2]^2+\) (Cu2, Cu3 and Cu5) (Fig. S2, ESI†). The bond parameters for 2 are listed in Tables S5, S8 and S9 (ESI†).

The two compounds of 3 were isostructural. Each one consists of an unusual dimer \([\text{TNb}_{12}\text{O}_{38}\text{Sb}_{2}]^{6−}\) anion formed by two Keggin-type \(\{\text{SiW}_{9}\text{Nb}_{3}\text{O}_{38}\}\) clusters via two \(\mu_2-O\) (O1 and O1#) (Fig. 1b). The Nb–\(\mu_2-O\) bond lengths and Nb–\(\mu_2-O\)-Nb bond angles for 3 are as shown in Fig. S3 (ESI†). The dimer has a \(C_{2v}\) anti symmetry with a symmetric center coinciding with the center of O1–O1#, a symmetric axis passing through O1–O1#, and a mirror plane of Sb1, Sb2, Sb1# and Sb2#. The \(C_{2v}\) anti symmetry, first found in the structures of the Keggin-type HPNbs, was different from the \(C_{2v}\) sym symmetry of the \([\text{SiW}_{9}\text{Nb}_{3}\text{O}_{38}]^{3−}\) core reported by Hill (Fig. 2).\textsuperscript{50} In the unit cell, three \([\text{Cu}(\text{en})_2]^2+\) fragments decorated a \(\{\text{TNb}_{12}\text{O}_{38}\text{Sb}_{2}\}\) cluster via weak coordination interactions between Cu and O\(_8\) (O\(_8\), terminal oxygen) of a HPNb core to form a tri-supporting HPNb cluster (Fig. S4, ESI†). The Cu–O bond lengths for 3-Si were 2.346(6) Å (Cu1–O3), 2.269(6) Å (Cu2–O12) and 2.378(6) Å (Cu3–O7), and the corresponding Cu–O bond lengths for 3-Ge were 2.381(6) Å, 2.302(6) Å and 2.500 Å, respectively. The bond parameters of 3 are listed in Tables S7, S10 and S11 (ESI†).

All the compounds were obtained under hydrothermal conditions. Scheme 1 shows the synthetic process, and the experimental details are described in ESL†. Reaction time, temperature and proportion of starting materials are important factors. When double amount of Cu(CH\(_3\)COO)\(_2\) and en were added, compounds of 2 were obtained with a little amount of 1. In addition, when 2 were recrystallized, corresponding compounds of 1 were obtained. Interestingly, crystals of 1 were able to be isolated not merely through the usual “one-pot hydrothermal synthesis procedure”, but also through a two-step route, that was, the starting materials without Cu and en firstly suffered a hydrothermal reaction, later Cu\(^{2+}\) and en were added into the hydrothermal-reacted solution. It means that the generation of \(\{\text{TNb}_{12}\text{O}_{38}\text{Sb}_{2}\}\) clusters was independent of Cu\(^{2+}\) and en, and \([\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^2+\) just plays a counterion role. Compounds of 3 were isolated at 165 °C, a temperature that is 45 °C higher than that for 1, and we therefore deduced that a higher temperature was favorable for the dimerization of \(\{\text{TNb}_{12}\text{O}_{38}\text{Sb}_{2}\}\) clusters. What’s more important is that Sb(III) plays a key role to stabilize the Keggin core by neutralizing its excess negative charge.

In summary, nine new HPNb compounds were synthesized in the presence of Sb(III) by different routes, and the HPNb
family obtained an expansion. All the compounds were based on the Sb-bicapped Keggin clusters. Especially, \(\text{1-As}\) was the first As-centered Keggin-type HPNb compound. Temperature is a key factor for the dimerization of \(\{\text{TNb}_{12}\text{O}_{38}\text{Sb}_{2}\}\) to form the \(\{\text{TNb}_{12}\text{O}_{38}\text{Sb}_{2}\}\) dimer. The dimer presents three significant features: (1) its \(C_{2v}\), \(anti\) symmetry is firstly found in the structures of the Keggin-type HPNbs; (2) it is the first example of a dimer fused by the Keggin-type HPNbs; (3) it possesses the highest nuclearity in the isolated HPNb clusters at present. In the following work, we will explore more capping-groups to extend the HPNb family.

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Notes and references


