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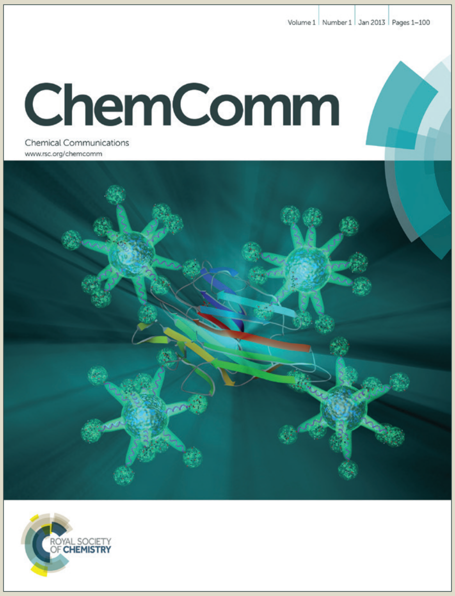

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Antimony-dependent Expansion for the Keggin Heteropolyniobate Family

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Nine new Sb-bicapped α-Keggin-type heteropolyoxoniobates (HPNb) were synthesized under hydrothermal conditions. Among them, the As-centered HPNb is firstly reported, 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.[1] This area is attracting increasingly interest for their significant applications in such as catalysis,[2] magnetism[3] and nanotechnology.[4] As is known, the POM chemistry has been dominated by polyoxo-tungstates, -molybdates and -vanadates. In other hand, substituted POMs are also a significant branch. In the Nb-substituted POMs, typical examples are the Keggin-type polyoxotungstates, α/β-$XW_9Nb_3O_{40}^{n-}$ (X = Si, P, Ge or As).[5]

However, a rapid development of Nb-based POM chemistry only occurs in recent decades, because polyoxoniobates (PONbs) are found to be difficultly obtained by usual acidifications at ambient conditions, like the case for the classical POMs mentioned above. Pioneer investigations, by Nyman, Casey and others, have successfully harvested various isopolyoxoniobates (IPNbs) under basic conditions, including $\{Nb_6\}$,[6] $\{Nb_7\}$,[7] $\{Nb_{10}\}$,[8] $\{Nb_{20}\}$,[9] $\{Nb_{24}\}$,[10] $\{Nb_{27}\}$,[11] $\{Nb_{31}\}$[11] and $\{Nb_{32}\}$.[12] Relatively, heteropolyniobate (HPNb) chemistry is explored slowly, 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, $[Ti_2O_2][SiNb_{12}O_{40}]\}^{12-}$ and $[H_2Si_4Nb_{16}O_{56}]^{14-}$,[13] a dozen of the Keggin-type HPNbs and analogues have been reported, namely, $[XNb_{18}O_{54}]^{n-}$ (X = Si, Ga or Al),[14] $[XNb_{12}O_{40}]^{16-}$ (X = Si or Ge),[15] $[XNb_{12}O_{40}(VO)_2]^{n-}$ (X = Si, Ge, P or V),[16] $[(PO_2)_3PNb_9O_{34}]^{15-}$,[17] $[Nb_2O_2][TNb_{12}O_{40}]^{10-}$,[18] $[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}]^{10-}$,[19] $[X_2(XOH)_2Nb_{16}O_{54}]^{14-}$ (X = Si or Ge),[20] $[XNb_8V_4O_{40}(VO)_4]^{15-}$ (X = P or V) and $[PNb_{12}O_{40}(VO)_6]^{3-}$.[21] Among these HPNbs, most possess of the capped Keggin-type structures, with $\{TiO_n\}$,[13] $\{VO\}$[16,21] and $\{NbO_n\}$[18,19] as the capping groups, to neutralize high negative charges of Keggin cores. Inspired by the foregoing work, we try to introduce Sb into the HPNb system, as Sb^{3+} 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 $\{PMo_{12}O_{40}Sb_2\}$ cores were reported by Xu's group,[22] and $[PNb_{12}Sb_2O_{40}]^{n-}$ was reported by Casey's group quite recently.[23] Herein we report a series of Sb-bicapped HPNb compounds, $[Cu(en)_2(H_2O)_2]_4[\alpha\text{-}H_nTNb_{12}O_{40}Sb_2]\cdot 18H_2O$ (**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**)]; $[Cu(en)_2]_3[Cu(en)_2(H_2O)]_4\{[Cu(en)_2]_2[\alpha\text{-}HTNb_{12}O_{40}Sb_2]_2\}\cdot 18H_2O$ (**2**) [T: Si (**2-Si**); Ge (**2-Ge**)]; $[Cu(en)_2]\{[Cu(en)_2]_3[\alpha\text{-}TNb_{12}O_{39}Sb_2]\}\cdot 11H_2O$ (**3**) [T: Si (**3-Si**); Ge (**3-Ge**)] (en = ethanediamine). All these compounds are consisted of new Sb-bicapped $[TNb_{12}O_{40}Sb_2]^{n-}$ polyanions. Especially, the As-centered Keggin-type HPNb cluster is firstly reported. **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 reveals that five compounds of **1** are isostructural, thus the structure of **1-Si** is described in details. The cell unit of **1-Si** consists of a quarter of a crystallographically independent Sb-bicapped Keggin-type polyanion $[\alpha\text{-}H_2SiNb_{12}O_{40}Sb_2]^{8-}$ (as shown in Fig. 1a) and one crystallographically independent $[Cu(en)_2(H_2O)]^{2+}$ cation. Two Sb atoms, in a distorted square pyramidal coordination geometry, oppositely cap on two $\{Nb_4O_4\}$ (O6, O7, O6#, O7#) windows of the $\{\alpha\text{-}SiNb_{12}\}$ core (Fig. S1, ESI†). Sb-O bond lengths and O-Sb-O bond angles are 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 is lowered from T_d to D_{2d}, and the negative charge of the Keggin HPNb anion is neutralized from -14 in an uncapped one to -8 in the capped one. $[Cu(en)_2(H_2O)]^{2+}$ is a free cation in which Cu^{2+} is 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 Table S3, S4 and S6 (ESI†).

The two compounds of **2** are isostructural, comprised of one crystallographically independent $[HTNb_{12}O_{40}Sb_2]^{9-}$, two crystallographically independent $[Cu(en)_2(H_2O)]^{2+}$ (Cu1 and Cu4) and 2.5 crystallographically independent $[Cu(en)_2]^{2+}$ (Cu2, Cu3 and Cu5) (Fig. S2, ESI†). The bond parameters for **2** are listed in Table S5, S8 and S9 (ESI†).

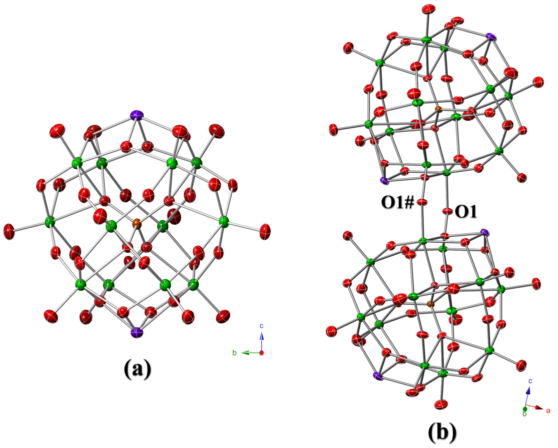


Fig. 1 Thermal ellipsoid representation of (a) $\{\alpha\text{-}H_nTNb_{12}O_{38}Sb_2\}$ in **1** (occupancy 0.25) and (b) $[(TNb_{12}O_{38}Sb_2)_2(\mu_2\text{-}O)_2]^{16-}$ in **3**. (Color code: orange, Si; green, Nb; purple, Sb; red, O) (50% probability for the ellipsoids).

The two compounds of **3** are isostructural. Each one consists of an unusual dimer $[(TNb_{12}O_{38}Sb_2)_2(\mu_2\text{-}O)_2]^{16-}$ anion formed by two Keggin-type $\{\alpha\text{-}TNb_{12}Sb_2\}$ clusters *via* two μ_2-O (O1 and O1#) (Fig. 1b). The Nb-μ_2-O bond lengths and Nb-μ_2-O-Nb bond angles for **3** are as shown in Fig. S3 (ESI†). The dimer has a C_{2h} *anti* symmetry with a symmetric center coinciding the center of O1···O1#, a symmetric axis passing through O1···O1#, and a mirror plane of Sb1, Sb2, Sb1# and Sb2#. The C_{2h} *anti* symmetry, firstly found in the structures of the Keggin-type HPNbs, is different from the C_{2v} *syn* symmetry of the $[(SiW_9Nb_3O_{38})_2(\mu_2\text{-}O)_2]^{10-}$ core reported by Hill (Fig. 2).[5b] In the unit cell, three $[Cu(en)_2]^{2+}$ fragments decorate a $\{TNb_{12}O_{39}Sb_2\}$ cluster *via* weak coordination interactions between Cu and O_t (O_t, terminal oxygen) of a HPNb core to form a tri-supporting HPNb cluster (Fig. S4, ESI†). The Cu-O bond lengths for **3-Si** are 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** are 2.381(6) Å, 2.302(6) Å and 2.500 Å, respectively. The bond parameters of **3** are listed in Table S7, S10 and S11 (ESI†).

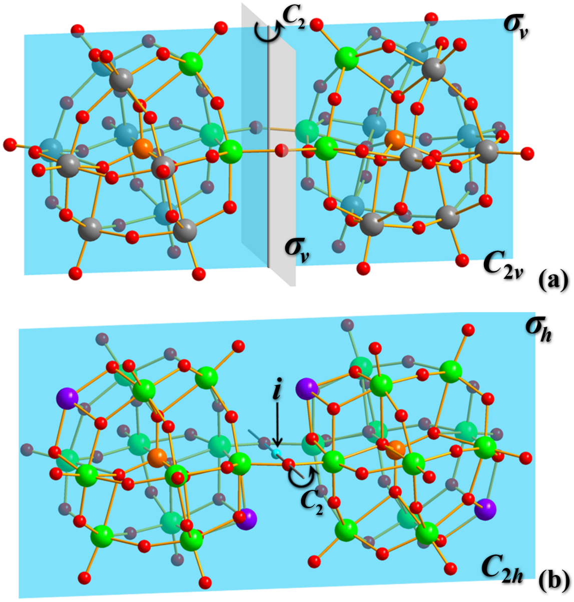
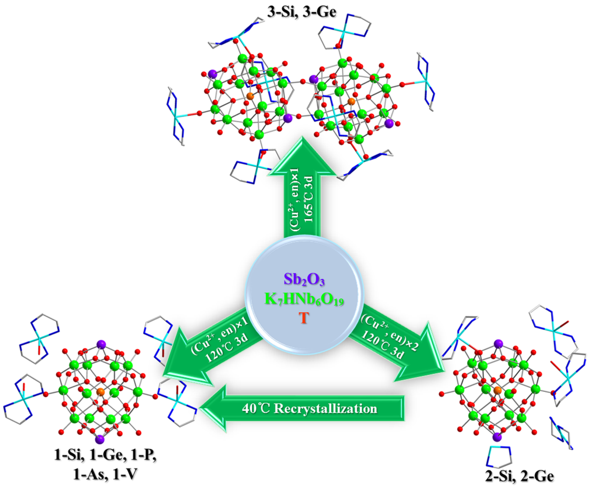


Fig. 2 Symmetric representations of the dimer polyanions: (a) $[(SiW_9Nb_3O_{38})_2(\mu_2\text{-}O)_2]^{10-}$ with C_{2v} symmetry; (b) $[(TNb_{12}O_{38}Sb_2)_2(\mu_2\text{-}O)_2]^{16-}$ with C_{2h} symmetry. (Color code: orange, Si; green, Nb; purple, Sb; red, O; gray, W)

All the compounds were obtained under hydrothermal conditions. Scheme 1 shows the synthetic process, and the experimental details are described in ESI†. Reaction time, temperature and proportion of starting materials are important factors. When double amount of $Cu(CH_3COO)_2$ and en was 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 is, the starting materials without Cu and en firstly suffered a hydrothermal reaction, later Cu^{2+} and en are added into the hydrothermal-reacted solution. It means that the generation of $\{TNb_{12}O_{40}Sb_2\}$ clusters is independence of Cu^{2+} and en, and $[Cu(en)_2(H_2O)]^{2+}$ just plays a counterion role. Compounds of **3** were isolated at 165 °C, a temperature as 45 °C higher than that for **1**, and we therefore deduced that a higher temperature was favorable for dimerization of the $\{TNb_{12}O_{40}Sb_2\}$ clusters. What's more important is that Sb(III) plays a key role to stabilize the Keggin core by neutralizing its excess negative charge.



Scheme 1 Schematic synthetic process of the titled compounds. (Color code: orange, T; green, Nb; purple, Sb; red, O; light blue, Cu; blue, N; gray, C) (T = the starting materials of hetero atoms, Na_2SiO_3, GeO_2, NaH_2PO_4, Na_2HAsO_4 and V_2O_5).

In summary, nine new HPNb compounds were synthesized in the presence of Sb(III) by different routes, and the HPNb family obtains an expansion. All the compounds are based on the Sb-bicapped Keggin clusters. Especially, **1-As** is the first As-centered Keggin-type HPNb compound. Temperature is a key factor for dimerization of $\{TNb_{12}O_{40}Sb_2\}$ to form the $\{(TNb_{12}O_{38}Sb_2)_2(\mu_2\text{-}O)_2\}$ dimer. The dimmer presents three significant features: (1) Its C_{2h} *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

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† Electronic Supplementary Information (ESI) available: Synthesis, details of crystallographic data, structural figures, tables of selected bond lengths and bond angles, BVS calculation results of V and Sb atoms, TGA, XRPD, IR, UV-vis and EDX. See DOI: 10.1039/c000000x/

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