Reversible capping/uncapping of phosphorous-centered Keggin-type polyoxoniobate clusters†

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Caps in α-Keggin-type polyoxometalates \([\text{PM}_2 \text{Nb}_{12} \text{O}_{40}]^{9−} (\text{M} = \text{Nb} = \text{O} \text{ or } \text{V} = \text{O})\) can be removed in basic condition to produce uncapped \([\text{PNb}_{12} \text{O}_{40}]^{15−}\). Transmetalation or capping occurs from the reaction of \([\text{PNb}_{14} \text{O}_{42}]^{9−}\) or \([\text{PNb}_{12} \text{O}_{40}]^{15−}\) with either \(\text{Sb}_2 \text{O}_3\) or \(\text{V}_2 \text{O}_5\) to form \([\text{PSb}_2 \text{Nb}_{12} \text{O}_{40}]^{9−}\) or \([\text{PV}_2 \text{Nb}_{12} \text{O}_{42}]^{9−}\), respectively.

One interesting mode of heterometal addition to the Keggin-type polyoxometalate clusters is capping, whereby a capping metal reduces the overall charge of the cluster. Several heterometals, such as \(\text{V}^{IV}, \text{V}^{V}, \text{Cu}^{II}, \text{Zn}^{II}, \text{Sb}^{III}, \text{and La}^{III}\), are known as caps; among these \(\text{V}^{IV}, \text{V}^{V}\) caps are the most common. The number of capping site can vary from 1 to 6. The capped Mo-, V- or W-based Keggin-type clusters have proven to be useful for spintronics and as supramolecular materials for catalytic applications. For the polyoxoniobates, vanadyl-capped Keggin-type polyoxoniobate ions have been synthesized recently, including \([\text{PV}_2 \text{Nb}_{12} \text{O}_{42}]^{9−}\) ion (PV\(_2\)Nb\(_{12}\))\(^9\). Here we expand the library of capped Keggin polyoxoniobates as TMA (tetramethylammonium) salts; \(\text{Sb}^{III}\) or \(\text{Nb}^{V} = \text{O}\)-bicapped α-Keggin polyoxoniobates \(\text{TMA}_n[\text{PSb}^{III}_2 \text{Nb}_{12} \text{O}_{40}]^{9−}\) and \(\text{TMA}_n[\text{PNb}_{14} \text{O}_{42}]^{9−}\). We also isolated novel \(\text{TMA}_n[\text{PNb}_{12} \text{O}_{40}]^{9−}\) via an uncapping reaction starting from \(\text{PNb}_{14}\) in highly basic condition. The synthesis of discrete \(\text{PNb}_{14}\) clusters is important because \(\text{Nb}^{V}\)-bicapped Keggin niobates have only been characterized as chain structures formed by \(\text{Nb}−(\mu_2-\text{O})_2−\text{Nb}\) bridges.

Here we show that capping/uncapping reaction can be reversed for vanadyl capping group. Although many kinds of capped-Keggin clusters are known, reversibility is not commonly shown, nor well understood. We believe that reaction studies at the capping site in the Keggin ion can be particularly useful for polymerization studies that exploit reactions at the caps. We note that a controlled capping reaction of \([\text{PMo}_{12} \text{O}_{40}]^{3−}\) by using electrochemical reduction to produce \(\text{Co}^{II}, \text{V}^{IV}, \text{and Sb}^{III}\)-capped Keggin ion has been reported previously.

The \(\text{PSb}_2 \text{Nb}_{12}\) cluster (Fig. 1) was synthesized by hydrothermal reaction of the mixture of stoichiometric amounts of hydrous niobium oxide, \(\text{Sb}_2 \text{O}_3\), TMAOH and phosphoric acid. In the crystal structure, two distinct \(\text{PSb}_2 \text{Nb}_{12}\) clusters are present in the crystallographic lattice; one of them has a pseudo-Keggin structure, which features central Po\(_8\) with half-occupied oxygen atoms due to rotational disorder. Nearly nine TMA counterions are found per cluster, so the cluster formula is \([\text{PSb}^{III}_2 \text{Nb}_{12} \text{O}_{40}]^{9−}\). Bond-valence-sum (BVS) values for three antimony sites are 3.14, 3.07 and 3.26, which agree with the oxidation state of \(\text{Sb}^{III}\). Electrospray-ionization mass spectrometry (ESI-MS) of the compound provided spectra consistent with the stoichiometry, and

![Fig. 1 Ball-and-stick models (pink: P, red: O, light blue: Nb, black: Sb) of \(\text{PNb}_{12}\) (top), \(\text{PSb}_2 \text{Nb}_{12}\) (bottom left) and \(\text{PNb}_{14}\) (bottom right) clusters.](image-url)
the peaks are finely split due to the natural isotopes of antimony (Fig. S1, ESI†).

A different Keggin-type cluster formed when the hydrothermal reaction was carried out without Sb₂O₅. The product was generally waxy and we crystallized it in a hot concentrated ethanol solution. The crystal structure shows the cluster of [PNb₁₄O₄²⁻], with two bicapping trans Nb⁵⁺=O (Fig. 1). Seven TMA ions were found in the crystal structure, but elemental analysis and TGA data (Fig. S2, ESI†) of the compound better agrees with nine TMA, as was the case in Psb₂Nb₁₂ and PV₂Nb₁₂. We thus conclude that two TMA are disordered in the solvent region and thus could not be found during the structure refinement. In the ESI-MS spectra, the products always showed small peaks with lower m/z number and we tentatively assign this impurity as the mono-capped [PNb₁₂O₄]¹²⁻ [PNb₁₃] (Fig. S1, ESI†). A Ge⁺V centered [GeNb₁₂O₄]¹³⁻ as Cs⁺ or Rb⁺ salt was structurally characterized recently, and this also supports our assignment of the small impurity peaks as the PNb₁₃.¹²

In the structure of PNb₁₄, capping Nb⁵⁺=O are slightly tilted from the pseudo-C₂ rotational axis of the Keggin ion (angles of P₁–Nb₁₃–O₄₁ = 173.04° and P₁–Nb₁₄–O₄₂ = 170.24°) (Fig. 1 and Fig. S3, ESI†). Thermal ellipsoids of the capping Nb⁵⁺=O oxygen atoms are horizontally elongated compared to other terminal oxygen atoms, and the Nb⁵⁺=O bond lengths (1.726(13) and 1.735(12) Å) at the capping sites are slightly shorter than other Nb⁵⁺=O bonds (1.741(9) to 1.774(9) Å). These might be due to the rare pentacoordinate Nb⁵⁺ environment in the capping site,¹³ and explain the reactivity of Nb⁵⁺=O capping site as described below.

We found that bicapping Nb⁵⁺=O units in PNb₁₄ can be uncapcaged under strongly basic conditions. When PNb₁₄ was mixed with TBAOH solution in an open vial and kept at 85 °C in a dry oven overnight, crystalline materials of PNb₁₂ formed at the bottom of the vial. ESI-MS peaks of the newly formed PNb₁₂ appear in lower m/z region relative to spectra for the PNb₁₄ and match well with the composition of PNb₁₂ identified in the crystal structure (Fig. S1, ESI†). We see an additional peak at m/z = 426.6 and tentatively assign it to a lacunary H₄[PNb₆O₃]H₂O⁴⁺ ion, which could have been formed by fragmentation in ESI-MS.

The PNb₁₂ cluster in the crystal structure exhibits a pseudo-Keggin structure, similar to one of the clusters in Psb₂Nb₁₂ structure (Fig. 1). The O···O distances between the square-like window for capping (2.65–2.70 Å) in PNb₁₂ are less contracted than those in the Sb⁵⁺-capped window of some pseudo-Keggin unit in Psb₂Nb₁₂ (2.50–2.51 Å), due to the absence of capping metal. Generally, the O···O distances in the capping site are in the order of PNb₁₂ > PNb₁₄ > Psb₂Nb₁₂ > PV₂Nb₁₂ (Fig. S4 and S5, ESI†). Although PNb₁₂ should possess a −15 charge, only 10 TMA ions are found in the crystal structure, and this number agrees with elemental analyses and TGA data (Fig. S2, ESI†). We propose that five protons are disordered on the PNb₁₂ cluster surface, but we are unable to assign the protonation sites by BVS values (1.57 to 1.86) of the surface µ₅-oxygens. We note that uncapped PNb₁₂ Keggin structure has not been reported as a soluble form so far.

The ³¹P MAS-NMR data of the synthesized Keggin compounds are shown in Fig. 2. The chemical shifts of each Keggin structure are slightly different, with 5.2, 4.0 and 2.4 ppm for Psb₂Nb₁₂, PNb₁₄ and PNb₁₂, respectively. The downfield ³¹P peak shift of Psb₂Nb₁₂ and PNb₁₄ compared to PNb₁₂ can be attributed to the existence of capping atoms (Sb⁵⁺ or Nb⁵⁺), and more downfield shift in Psb₂Nb₁₂ is attributed to higher electronegativity of antimony compared to niobium. The spectra of PNb₁₃ features additional small peak at 1.04 ppm. We propose that the small peak arises from PNb₁₃ as indicated by ESI-MS (Fig. S1, ESI†). The ³¹P-NMR peak of PNb₁₂ is broader than the peaks of bicapped Keggin compounds, due to less symmetric P···O bonds at the center of the structure. The P···O bonds in PNb₁₂ range 1.500(10)–1.628(11) Å, while the P···O bonds in PSb₂Nb₁₂ and PNb₁₄ have more regular P···O bonds (1.529(7)–1.594(7) Å and 1.544(9)–1.559(8) Å, respectively).

Stability of the clusters in solution was checked by using ³¹P NMR (Fig. 2). When the compounds were dissolved in D₂O, Psb₂Nb₁₂, PNb₁₄ and PNb₁₂ showed peaks at 6.4, 5.4 and 5.2 ppm, respectively, and the peak from PNb₁₂ was broad, similarly to MAS NMR. The PNb₁₄ showed large amount of unassignable broad peaks upfield, suggesting polymerization of PNb₁₄ in water. In methanol, PNb₁₄ shows two peaks at 4.8 and 3.9 ppm with integral ratio 1:0.3, which might correspond to PNb₁₄ and PNb₁₃. The sharp peaks in methanol suggest that the series of broad peaks of PNb₁₄ in D₂O are due to polymerization of the molecules in water. FT-IR spectra (Fig. S6, ESI†) of the three compounds are all similar to that of previously reported PV₂Nb₁₂, featuring P···O band around 1025 cm⁻¹, Nb=O band around 880 cm⁻¹ and some Nb–O–Nb bands between 850–600 cm⁻¹.¹⁴ We note that the FT-IR spectrum of PNb₁₂ generally shows broader bands than other compounds, possibly due to its less compact structure from the absence of capping ions.

The stabilities of these clusters were monitored by ESI-MS as a function of pH (Fig. S7 to S9, ESI†). Psb₂Nb₁₂ was seen to be stable between 4 < pH < 12, similar to the stability range of PV₂Nb₁₂. The PNb₁₂ was stable in the higher pH region (6 < pH < 12), which is consistent with its formation condition at high pH and its high molecular charge. A solution of PNb₁₂ formed precipitate when pH was reduced to below pH = 6, consistent with charge neutralization. In contrast, The PNb₁₄ cluster exhibited a narrower pH stability range (8 < pH < 12), and the cluster was unstable when titrated with acid.

Both PNb₁₄ and PNb₁₂ can directly react with Sb₂O₅ or V₂O₅ to form Psb₂Nb₁₂ or PV₂Nb₁₂ by simple solution reaction at
When starting from PNb\textsubscript{14}, the formation of hetero-capped capping, respectively (Fig. S10 and S11, ESI†). The capping reaction of V\textsubscript{2}Nb\textsubscript{12} or PV\textsubscript{2}Nb\textsubscript{12} apparently involves direct substitution of the capping unit from Nb\textsuperscript{V} or V\textsuperscript{V} as intermediates was detected by using ESI-MS. The capping reaction proceeds with intermediates such as mono-capped [PVNb\textsubscript{12}O\textsubscript{41}]	extsuperscript{12−} or [PVNb\textsubscript{13}O\textsubscript{42}]	extsuperscript{9−} or [PSbNb\textsubscript{13}O\textsubscript{41}]	extsuperscript{9−}. Keggin ions such as [PSbNb\textsubscript{13}O\textsubscript{41}]	extsuperscript{9−} or [PVNb\textsubscript{13}O\textsubscript{42}]	extsuperscript{9−} or [PVNb\textsubscript{13}O\textsubscript{42}]	extsuperscript{9−} or [PSbNb\textsubscript{13}O\textsubscript{41}]	extsuperscript{9−}.}

Fig. 3 ESI–MS monitored during the reaction of 50 mg of PNb\textsubscript{12} and 5 mg of Sb\textsubscript{2}O\textsubscript{3} in 2 mL of water.

This work was supported by an NSF CCI grant through the Center for Sustainable Materials Chemistry, number CHE-1102637. Additional support to JHS was via NSF-CHE-1310368 to WHC. The authors thank Dr Ping Yu, Corey Pilgrim and Gerry Ochoa for help collecting the NMR spectra. We also thank Dana Reusser and Prof. Alex Navrotsky for TGA data.

Notes and references


