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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

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

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Caps in α -Keggin-type $[\text{PM}_2\text{Nb}_{12}\text{O}_{40}]^{9-}$ (M: Nb=O or V=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 Sb_2O_3 or V_2O_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 $\text{V}^{\text{IV,V}}$,¹ Ni^{II} ,² Cu^{II} ,³ Zn^{II} ,⁴ Sb^{III} ,⁵ and La^{III} ,⁶ are known as caps; among these $\text{V}^{\text{IV,V}}$ 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 spintronics⁷ and as supramolecular materials for catalytic applications.^{4,8} For the polyoxoniobates, vanadyl-capped Keggin-type polyoxoniobate ions have been synthesized recently, including $[\text{PV}_2\text{Nb}_{12}\text{O}_{40}]^{9-}$ ion ($\text{PV}_2\text{Nb}_{12}$).⁹ Here we expand the library of capped Keggin polyoxoniobates as TMA (tetramethylammonium) salts; Sb^{III} - or $\text{Nb}^{\text{V}}=\text{O}$ -bicapped α -Keggin polyoxoniobates $\text{TMA}_9[\text{PSb}_2\text{Nb}_{12}\text{O}_{40}] \cdot 28\text{H}_2\text{O}$ ($\text{PSb}_2\text{Nb}_{12}$) and $\text{TMA}_9[\text{PNb}_{14}\text{O}_{42}] \cdot 26\text{H}_2\text{O}$ (PNb_{14}). We also isolated novel $\text{TMA}_{10}\text{H}_5[\text{PNb}_{12}\text{O}_{40}] \cdot 30.5\text{H}_2\text{O}$ (PNb_{12}) via an uncapping reaction starting from PNb_{14} in highly basic condition. The synthesis of discrete PNb_{14} clusters is important because Nb^{V} -bicapped Keggin niobates have been only isolated as chain structures formed by $\text{Nb}-(\mu_2\text{-O})_2\text{-Nb}$ bridges.¹⁰

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 Co^{II} -, V^{IV} -, and Sb^{III} -capped Keggin ion has been reported previously.¹¹ 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, Sb_2O_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 counteranions are found per cluster, so the cluster formula is $[\text{PSb}^{\text{III}}_2\text{Nb}_{12}\text{O}_{42}]^{9-}$. Bond-valence-sum (BVS) values for three

antimony sites are 3.14, 3.07 and 3.26, which agree with the oxidation state of Sb^{III} . Electrospray-ionization mass spectrometry (ESI-MS) of the compound provided spectra consistent with the stoichiometry, and the peaks are finely split due to the natural isotopes of antimony (Fig. S1).

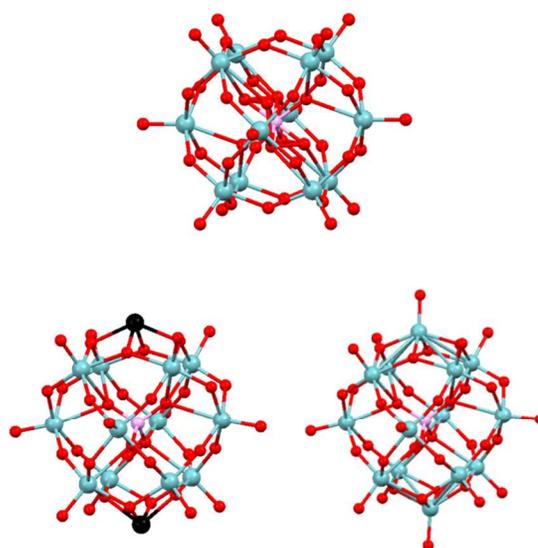


Fig. 1 Ball-and-stick models (pink: P, red: O, light blue: Nb, black: Sb) of PNb_{12} (top), $\text{PSb}_2\text{Nb}_{12}$ (bottom left) and PNb_{14} (bottom right) clusters

A different Keggin-type cluster formed when the hydrothermal reaction was carried out without Sb_2O_3 . The product was generally waxy and we crystallized it in a hot concentrated ethanol solution. The crystal structure shows the cluster of $[\text{PNb}_{14}\text{O}_{42}]^{9-}$, with two bicapping *trans* $\text{Nb}^{\text{V}}=\text{O}$ (Fig. 1). Only seven TMA ions were found in the crystal structure, but elemental analysis and TGA data (Fig. S2) of the compound better agrees with nine TMA, as was the case in $\text{PSb}_2\text{Nb}_{12}$ and $\text{PV}_2\text{Nb}_{12}$. 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 $[\text{PNb}_{13}\text{O}_{41}]^{12-}$ (PNb_{13}) (Figure S1). A Ge^{IV} -centered $[\text{GeNb}_{13}\text{O}_{41}]^{13-}$ as Cs^+ or Rb^+ salt was structurally characterized recently, and this also supports our assignment of the small impurity peaks as the PNb_{13} .¹²

In the structure of PNb_{14} , capping $\text{Nb}^{\text{V}}=\text{O}$ are slightly tilted

from the pseudo- C_4 rotational axis of the Keggin ion (angles of P1-Nb13-O41=173.04° and P1-Nb14-O42=170.24°) (Fig. S3). Thermal ellipsoids of the capping Nb^V=O oxygen atoms are horizontally elongated compared to other terminal oxygen atoms, and the Nb^V=O bond lengths (1.726(13) and 1.735(12) Å) at the capping sites are slightly shorter than other Nb^V=O bonds (1.741(9) to 1.774(9) Å). These might be due to the rare pentacoordinate Nb^V environment in the capping site,¹³ and explain the reactivity of Nb^V=O capping site as described below.

We found that bicapping Nb^V=O units in PNB₁₄ can be uncapped 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). We see an additional peak at $m/z=426.6$ and tentatively assign it to a lacunary H₁₄[PNb₁₁O₃₉](H₂O)⁴⁻ ion, which could have 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 Sb^{III}-capped window of same 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). 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). 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 μ_2 -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 (Sb^{III} or Nb^V), and more downfield shift in PSb₂Nb₁₂ is attributed to higher electronegativity of antimony compared to niobium. The spectra of PNB₁₄ features additional small peak at 1.04 ppm. We propose that the small peak arises from PNB₁₃, as indicated by ESI-MS (Fig. S1). 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 via 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 confirm that the series of broad peaks of PNB₁₄ in D₂O are due to polymerization of the molecules in water. FT-IR spectra (Fig. S6) 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 due to the absence of capping ions.

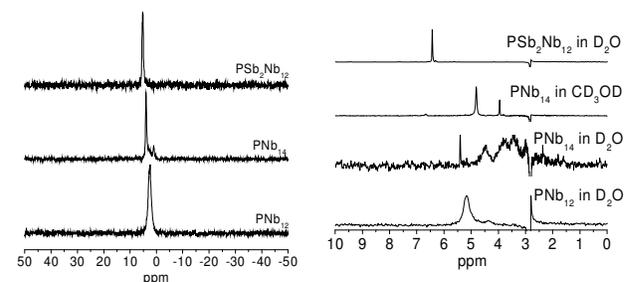


Fig. 2 ³¹P MAS NMR (left) and ³¹P solution NMR (right) spectra. The apparent peaks at 2.8 ppm (right) is an instrumental artifact.

The stabilities of these clusters were monitored by ESI-MS as a function of pH (Fig. S7 to S9). 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 Sb₂O₃ or V₂O₅ to form PSb₂Nb₁₂ or PV₂Nb₁₂ by simple hydrothermal treatment at nearly quantitative yields. By using ESI-MS, we were able to monitor the reaction in a capped vial at 100°C and 70°C for antimony and vanadium capping, respectively (Fig. S10 and S11). The complete formation of PSb₂Nb₁₂ was slower (~2h) than PV₂Nb₁₂ (<1h). When starting from PNB₁₄, the formation of hetero-capped Keggin ions such as [PSbNb₁₃O₄₁]⁹⁻ or [PVNb₁₃O₄₂]⁹⁻ as intermediates was detected by using ESI-MS. The capping reaction of PNB₁₂ was also monitored similarly, and the reaction proceeds with intermediates such as mono-capped [PVNb₁₂O₄₁]¹²⁻ or [PSbNb₁₂O₄₀]¹²⁻ (Fig. 3, Fig. S11). Thus the reaction apparently occurs via stepwise substitution from PNB₁₄, or addition of capping sites to PNB₁₂, respectively. The reaction can be completed even at room temperature after stirring the mixture for a few days. Because the conversion of PNB₁₄ to PSb₂Nb₁₂ or PV₂Nb₁₂ apparently involves direct substitution of the capping unit from Nb^V=O to Sb^{III} or V^V=O, this reaction can be regarded as transmetalation. Transmetalation is a well-known synthetic strategy in organometallic chemistry, but rare in polyoxometalates to our knowledge.¹⁵ Similarly to the uncapping reaction of PNB₁₄ to form PNB₁₂, PV₂Nb₁₂ can also be uncapped to form PNB₁₂ in a same condition, thus uncapping/capping reaction of V^V=O is reversible. PSb₂Nb₁₂ could not be uncapped even with larger amount of base added during attempted reaction.

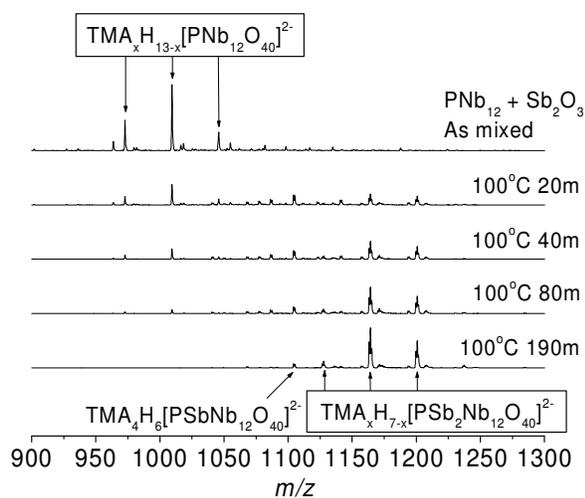


Fig. 3 ESI-MS monitored during the reaction of 50 mg of PNb_{12} and 5 mg of Sb_2O_3 in 2 mL of water.

Conclusions

We demonstrate that P-centered Keggin polyoxoniobate can be capped or uncapped at certain reaction conditions, and the reaction depends on the stability of the capped niobate. Such a capping or transmetalation reaction, starting from PNb_{12} or PNb_{14} , is an attractive route for selective capping by various types of transition metals and allows unprecedented control. This control over capping/uncapping can be particularly useful for polymerizing Keggin ions by exploiting the heterogeneity of opposed apical bicaps. The newly isolated and discrete PNb_{14} ion would be used as a precursor for rational synthesis of oligomeric chains of Keggin ions in materials science.

Acknowledgement

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

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[†] Electronic Supplementary Information (ESI) available: Experimental details, crystallographic table, TGA, FT-IR, ESI-MS spectra and pH dependent ESI-MS spectra of the compounds, ESI-MS while monitoring the reactions. See DOI: 10.1039/b000000x/

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