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

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Caps in α-Keggin-type polyoxometalates $[PM_2Nb_{12}O_{40}]^{9-}$ (M: Nb═O or V═O) can be removed in basic condition to produce uncapped $[PNb_{12}O_{40}]^{15-}$. Transmetalation or capping occurs from the reaction of $[PNb_{14}O_{42}]^{9-}$ or $[PNb_{12}O_{40}]^{15-}$ with either Sb_2O_3 or V_2O_5 to form $[PSb_2Nb_{12}O_{40}]^{9-}$ or $[PV_2Nb_{12}O_{42}]^{9-}$, 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 $V^{IV,V}$,[1] Ni^{II},[2] Cu^{II},[3] Zn^{II},[4] Sb^{III},[5] and La^{III},[6] are known as caps; among these $V^{IV,V}$ 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 spintronics[7] and as supramolecular materials for catalytic applications.[4,8] For the polyoxoniobates, vanadyl-capped Keggin-type polyoxoniobate ions have been synthesized recently, including $[PV_2Nb_{12}O_{42}]^{9-}$ ion (PV_2Nb_{12}).[9] Here we expand the library of capped Keggin polyoxoniobates as TMA (tetramethylammonium) salts; Sb^{III}- or Nb^V═O-bicapped α-Keggin polyoxoniobates $TMA_9[PSb_2Nb_{12}O_{40}]\cdot 28H_2O$ (PSb_2Nb_{12}) and $TMA_9[PNb_{14}O_{42}]\cdot 26H_2O$ (PNb_{14}). We also isolated novel $TMA_{10}H_5[PNb_{12}O_{40}]\cdot 30.5H_2O$ (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 only been characterized as chain structures formed by Nb–(μ_2-O)$_2$–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 $[PMo_{12}O_{40}]^{3-}$ by using electrochemical reduction to produce Co^{II}-, V^{IV}-, and Sb^{III}-capped Keggin ion has been reported previously.[11]

The PSb_2Nb_{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 PSb_2Nb_{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 countercations are found per cluster, so the cluster formula is $[PSb^{III}{}_2Nb_{12}O_{40}]^{9-}$. Bond-valence-sum (BVS) values for three antimony sites are 3.14, 3.07 and 3.26, which agree with the oxidation state of Sb^{III}. Electrospray-ionization mass spectrometry (ESI-MS) of the compound provided spectra consistent with the stoichiometry, and

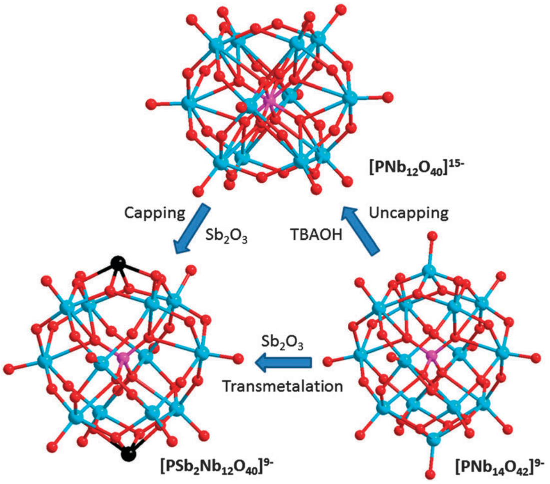

Fig. 1 Ball-and-stick models (pink: P, red: O, light blue: Nb, black: Sb) of PNb_{12} (top), PSb_2Nb_{12} (bottom left) and PNb_{14} (bottom right) clusters.

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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 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 $[PNb_{14}O_{42}]^{9-}$, with two bicapping *trans* $Nb^V{=}O$ (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 PSb_2Nb_{12} and PV_2Nb_{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 $[PNb_{13}O_{41}]^{12-}$ (PNb_{13}) (Fig. S1, ESI†). A Ge^{IV}-centered $[GeNb_{13}O_{41}]^{13-}$ 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 $Nb^V{=}O$ 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. 1 and Fig. S3, ESI†). 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 PNb_{14} can be uncapped under strongly basic conditions. When PNb_{14} was mixed with TBAOH solution in an open vial and kept at 85 °C in a dry oven overnight, crystalline materials of PNb_{12} formed at the bottom of the vial. ESI-MS peaks of the newly formed PNb_{12} appear in lower *m/z* region relative to spectra for the PNb_{14} and match well with the composition of PNb_{12} 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 $H_{14}[PNb_{11}O_{39}](H_2O)^{4-}$ ion, which could have formed by fragmentation in ESI-MS.

The PNb_{12} cluster in the crystal structure exhibits a pseudo-Keggin structure, similar to one of the clusters in PSb_2Nb_{12} structure (Fig. 1). The O···O distances between the square-like window for capping (2.65–2.70 Å) in PNb_{12} are less contracted than those in the Sb^{III}-capped window of same pseudo-Keggin unit in PSb_2Nb_{12} (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 $PNb_{12} > PNb_{14} > PSb_2Nb_{12} > PV_2Nb_{12}$ (Fig. S4 and S5, ESI†). Although PNb_{12} 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 PNb_{12} 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 PNb_{12} Keggin structure has not been reported as a soluble form so far.

The ^{31}P 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 PSb_2Nb_{12}, PNb_{14} and PNb_{12}, respectively. The downfield ^{31}P peak shift of PSb_2Nb_{12} and PNb_{14} compared to PNb_{12} can be attributed to the existence of capping atoms (Sb^{III} or Nb^V), and more downfield shift in PSb_2Nb_{12} is attributed to higher electronegativity of antimony compared to niobium. The spectra of PNb_{14} features additional small peak at 1.04 ppm. We propose that the small peak arises from PNb_{13}, as indicated by ESI-MS (Fig. S1, ESI†). The ^{31}P-NMR peak of PNb_{12} 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 PNb_{12} range 1.500(10)–1.628(11) Å, while the P–O bonds in PSb_2Nb_{12} and PNb_{14} have more regular P–O bonds (1.529(7)–1.594(7) Å and 1.544(9)–1.559(8) Å, respectively).

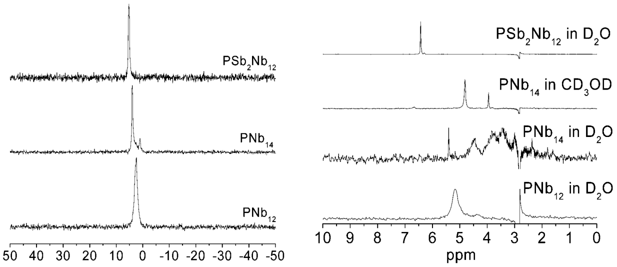

Fig. 2 ^{31}P MAS NMR (left) and ^{31}P solution NMR (right) spectra. The apparent peaks at 2.8 ppm (right) are instrumental artifacts.

Stability of the clusters in solution was checked by using ^{31}P NMR (Fig. 2). When the compounds were dissolved in D_2O, PSb_2Nb_{12}, PNb_{14} and PNb_{12} showed peaks at 6.4, 5.4 and 5.2 ppm, respectively, and the peak from PNb_{12} was broad, similarly to MAS NMR. The PNb_{14} showed large amount of unassignable broad peaks upfield, suggesting polymerization of PNb_{14} in water. In methanol, PNb_{14} shows two peaks at 4.8 and 3.9 ppm with integral ratio 1 : 0.3, which might correspond to PNb_{14} and PNb_{13}. The sharp peaks in methanol suggest that the series of broad peaks of PNb_{14} in D_2O 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 PV_2Nb_{12}, 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 PNb_{12} 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†). PSb_2Nb_{12} was seen to be stable between $4 < pH < 12$, similar to the stability range of PV_2Nb_{12}. The PNb_{12} 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 PNb_{12} formed precipitate when pH was reduced to below pH = 6, consistent with charge neutralization. In contrast, The PNb_{14} cluster exhibited a narrower pH stability range ($8 < pH < 12$), and the cluster was unstable when titrated with acid.

Both PNb_{14} and PNb_{12} can directly react with Sb_2O_3 or V_2O_5 to form PSb_2Nb_{12} or PV_2Nb_{12} by simple solution reaction at

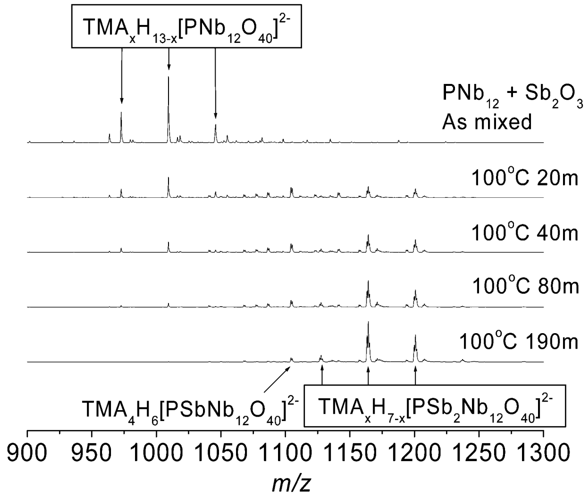

Fig. 3 ESI-MS monitored during the reaction of 50 mg of PNb$_{12}$ and 5 mg of Sb$_2$O$_3$ in 2 mL of water.

high yields. By using ESI-MS, we monitored the reaction in a capped vial at 100 °C and 70 °C for antimony and vanadium capping, respectively (Fig. S10 and S11, ESI†). The complete formation of PSb$_2$Nb$_{12}$ was slower (~2 h) than PV$_2$Nb$_{12}$ (<1 h). When starting from PNb$_{14}$, the formation of hetero-capped Keggin ions such as [PSbNb$_{13}$O$_{41}$]$^{9-}$ or [PVNb$_{13}$O$_{42}$]$^{9-}$ as intermediates was detected by using ESI-MS. The capping reaction of PNb$_{12}$ was also monitored similarly, and the reaction proceeds with intermediates such as mono-capped [PVNb$_{12}$O$_{41}$]$^{12-}$ or [PSbNb$_{12}$O$_{40}$]$^{12-}$ (Fig. 3 and Fig. S11, ESI†). Thus the reaction apparently occurs *via* stepwise substitution from PNb$_{14}$, or addition of capping sites to PNb$_{12}$, respectively. These reactions can be completed even at room temperature after stirring the mixture for a few days. Because the conversion of PNb$_{14}$ to PSb$_2$Nb$_{12}$ or PV$_2$Nb$_{12}$ 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 PNb$_{14}$ to form PNb$_{12}$, PV$_2$Nb$_{12}$ can also be uncapped to form PNb$_{12}$ in a same condition, thus uncapping/capping reaction of V^{V}=O is reversible (see experimental section in ESI†). The PSb$_2$Nb$_{12}$ could not be uncapped even with larger amount of base added during attempted reaction.

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 can be used as a precursor for rational synthesis of oligomeric chains of Keggin ions in materials science.

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