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

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Caps in α-Keggin-type [PM
5−2O
12−40] (M: Nb=O or V=O) can be removed in basic condition to produce uncapped [PNb
12−9O
42−12] 5−. Transmetalation or capping occurs from the reaction of [Pb
12−9O
42−12] 5− or [PNb
12−9O
42−12] 5− with either Sb=O or V=O to form [PSb
12−9O
42−12] 5− or [PVb
12−9O
42−12] 5−, 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=V, Ni=II, Cu=II, Zn=II, Sb=III, and La=II, are known as caps; among these 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 been useful for spintronics 2 and as supramolecular materials for catalytic applications.3−8 For the polyoxoniobiates, vanadyl-capped Keggin-type polyoxoniobate ions have been synthesized recently, including [PVb
12−9O
42−12] 5− ion (PVb=O) 9 Here we expand the library of capped Keggin polyoxoniobiates as TMA (tetramethylammonium) salts; Sb=O or Nb=O-bicapped α-Keggin polyoxoniobiates TMA,[PSb
12−9O
42−12]·28H2O (PSb=O) 10 and TMA,[PNb
12−9O
42−12]·26H2O (PNb=O). We also isolated novel TMA2H,[PNb
12−9O
42−12]·30H2O (PNb=O) via an uncapping reaction starting from PNb=O in highly basic condition. The synthesis of discrete PNb14 clusters is important because Nb=O-bicapped Keggin niobiates have been only isolated as chain structures formed by Nb-(η2=O2)-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 cations at the caps. We note that a controlled capping reaction of [PM
5−2O
12−40] 5− by using electrochemical reduction to produce Co=O, V=O−, and Nb=O− capped Keggin ion has been reported previously.11

The PSb=O cluster (Fig. 1) was synthesized by hydrothermal reaction of the mixture of stoichiometric amounts of hydrous niobium oxide, Sb2O5, TMAOH and phosphoric acid. In the crystal structure, two distinct PSb=O clusters are present in the crystallographic lattice; one of them has a pseudo-Keggin structure, which features central PO4 with half-occupied oxygen atoms due to rotational disorder. Nearly nine TMA counterions are found per cluster, so the cluster formula is [PSb=O2] 5−. 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=O. 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).

A different Keggin-type cluster formed when the hydrothermal reaction was carried out without Sb2O3. The product was generally waxy and we crystallized it in a hot concentrated ethanol solution. The crystal structure shows the cluster of [PNb=O] 5−, with two bicapping trans Nb=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 PSb=O and PVb=O. 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=O] 5− (PNb=O) (Figure S1). A Ge=O-centered [GeNb=O] 13− as Cs+ or Rb+ salt was structurally characterized recently, and this also supports our assignment of the small impurity peaks as the PNb=O 13−.

In the structure of PNb,14 capping Nb=O are slightly tilted...
from the pseudo-\(C_2\) rotational axis of the Keggin ion (angles of \(\text{P1-Nb13-O41}=173.04^\circ\) and \(\text{P1-Nb14-O42}=170.24^\circ\) (Fig. S3). Thermal ellipsoids of the capping \(\text{Nb}^\text{V}=\text{O}\) oxygen atoms are horizontally elongated compared to other terminal oxygen atoms, and the \(\text{Nb}^\text{V}=\text{O}\) bond lengths (1.726(13) and 1.735(12) Å) at the capping sites are slightly shorter than other \(\text{Nb}^\text{V}=\text{O}\) bonds (1.741(9) to 1.774(9) Å). These might be due to the rare pentacoordinate \(\text{Nb}^\text{V}\) environment in the capping site,\(^{13}\) and explain the reactivity of \(\text{Nb}^\text{V}=\text{O}\) compared to other compounds.  

We found that bicapping \(\text{Nb}^\text{V}=\text{O}\) units in \(\text{PNb}_{14}\) can be uncapped under strongly basic conditions. When \(\text{PNb}_{14}\) was mixed with TBAOH solution in an open vial and kept at 85°C in a dry oven overnight, crystalline materials of \(\text{PNb}_{12}\) formed at the bottom of the vial. ESI-MS peaks of the newly formed \(\text{PNb}_{12}\) appear in lower \(m/z\) region relative to spectra for the \(\text{PNb}_{14}\) and match well with the composition of \(\text{PNb}_{12}\) identified in the crystal structure (Fig. S1). We see an additional peak at \(m/z=426.6\) and tentatively assign it to a lacunary \(\text{H}_3\text{[PNb}_{11}\text{O}_{36}\text{]}\text{(H}_2\text{O)}^+\) ion, which could have formed by fragmentation in ESI-MS.\(^{14}\)  

The \(\text{PNb}_{12}\) cluster in the crystal structure exhibits a pseudo-Keggin structure, similar to one of the clusters in \(\text{PSb}_{12}\text{Nb}_{12}\) structure (Fig. 1). The \(O-O\) distances between the square-like window for capping (2.65-2.70 Å) in \(\text{PNb}_{12}\) are less contracted than those in the \(\text{Sb}^\text{VII}\)-capped window of same pseudo-Keggin unit in \(\text{PSb}_{12}\text{Nb}_{12}\) (2.50-2.51 Å), due to the absence of capping metal. Generally, the \(O-O\) distances in the capping sites are in the order of \(\text{PNb}_{12}>\text{PSb}_{12}\text{Nb}_{12}>\text{PV}_{2}\text{Nb}_{12}\) (Fig. S4 and S5). Although \(\text{PNb}_{12}\) should possess a -1 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 \(\text{PNb}_{12}\) cluster surface, but we are unable to assign the protonation sites by BVS values (1.57 to 1.86) of the surface \(\mu_5\)-oxygen. We note that uncapped \(\text{PNb}_{12}\) Keggin structure has not been reported as a soluble form so far.\(^{20}\)  

The \(^{31}\text{P}\) 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 \(\text{PSb}_{12}\text{Nb}_{12}\), \(\text{PNb}_{14}\) and \(\text{PNb}_{12}\), respectively. The downfield \(^{31}\text{P}\) peak shift of \(\text{PSb}_{12}\text{Nb}_{12}\) and \(\text{PNb}_{14}\) compared to \(\text{PNb}_{12}\) can be attributed to the existence of capping atoms (\(\text{Sb}^\text{VII}\) or \(\text{Nb}^\text{V}\)), and more downfield shift in \(\text{PSb}_{12}\text{Nb}_{12}\) is attributed to higher electronegativity of antimony compared to niobium. The spectra of \(\text{PNb}_{14}\) features additional small peak at 1.04 ppm. We propose that the small peak arises from \(\text{PNb}_{13}\), as indicated by ESI-MS (Fig. S1). The \(^{31}\text{P}\)-NMR peak of \(\text{PNb}_{12}\) 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 \(\text{PNb}_{12}\) range 1.500(10)-1.628(11) Å, while the P-O bonds in \(\text{PSb}_{12}\text{Nb}_{12}\) and \(\text{PNb}_{14}\) 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 \(^{31}\text{P}\) NMR (Fig. 2). When the compounds were dissolved in \(\text{D}_2\text{O}\), \(\text{PSb}_{12}\text{Nb}_{12}\), \(\text{PNb}_{14}\) and \(\text{PNb}_{12}\) showed peaks at 6.4, 5.4 and 5.2 ppm, respectively, and the peak from \(\text{PNb}_{12}\) was broad, similarly to MAS NMR. The \(\text{PNb}_{14}\) showed large amount of unassignable broad peaks upfield, suggesting polymerization of \(\text{PNb}_{14}\) in water. In methanol, \(\text{PNb}_{14}\) shows two peaks at 4.8 and 3.9 ppm with integral ratio 1:0.3, which might correspond to \(\text{PNb}_{14}\) and \(\text{PNb}_{13}\). The sharp peaks in methanol confirm that the series of broad peaks of \(\text{PNb}_{14}\) in \(\text{D}_2\text{O}\) 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 \(\text{PV}_{2}\text{Nb}_{12}\), featuring P-O band around 1025 cm\(^{-1}\), \(\text{Nb}^\text{V}=\text{O}\) band around 880 cm\(^{-1}\) and some \(\text{Nb}^\text{V}=\text{O}-\text{Nb}\) bands between 850-600 cm\(^{-1}\).\(^{11}\) We note that the FT-IR spectrum of \(\text{PNb}_{12}\) generally shows broader bands than other compounds, possibly due to its less compact structure due to the absence of capping ions.
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.

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$_{13}$ ion would be used as a precursor for rational synthesis of oligomeric chains of Keggin ions in materials science.

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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/