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A new Keggin-like niobium-phosphate cluster that reacts reversibly with hydrogen peroxide[†]

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Polyoxoniobate clusters that are stable in acidic solutions are rare and particularly useful in industrial processes. Here we report a new pentaphosphate niobate polyoxometalate cluster (TMA)₉H₃Nb₉P₅O₄₁·28H₂O (Nb₉P₅) that is stable over a wide pH range and that can be converted reversibly into the peroxo form.

The layered niobium-phosphate hydrate (NbOPO₄·xH₂O) is a useful catalyst for biomass conversion, such as the conversion of sugars to 5-hydroxymethylfurfural (HMF) and other dehydration reactions.¹ Its structure consists of corner-shared NbO₆ and PO₄ units² and the coexistence of both basic and acidic sites in NbOPO₄·xH₂O is responsible for its catalytic activity.³ Although niobium phosphate is widely used as a catalyst, its solution chemistry is rarely studied. Among the previous Keggin-type polyoxoniobates,⁴ Nyman et al. reported phosphate-decorated lacunary Keggin-type polyoxoniobate as an insoluble sodium salt, Na₁₅[(PO₂)₃PNb₉O₃₄]·22H₂O (Nb₉P₄), which was characterized by crystallography and MAS NMR.⁵ Recently we synthesized sets of peroxoniobophosphate clusters as water-soluble precursors for electron-beam-patterned niobium-phosphate films.⁶ Among them, the $[HNb_4P_2O_{14}(O_2)_4]^{5-}$ cluster (peroxo-Nb₄P₂) is stable over a wide pH range, spanning into acidic conditions, which is remarkable in itself because polyoxoniobates are generally only stable and soluble in neutral to basic solutions. We here report the synthesis, structure and characterization of a Keggin-like mixed niobium-phosphate cluster as a highly soluble tetramethylammonium (TMA) salt, (TMA)₉H₃Nb₉P₅O₄₁·28H₂O (Nb₉P₅). The new cluster Nb₉P₅ features a central phosphate and four additional phosphates in the outer layers.

The Nb_9P_5 cluster was synthesized by hydrothermal reaction of hydrous niobium oxide, TMAOH and phosphoric acid.



Fig. 1 Polyhedral (left) and ball-and-stick (right) drawing of Nb_9P_5 cluster (Nb: gray, P: blue, O: red).

The solution pH is a key factor for the formation of Nb₉P₅. In the given synthesis condition (see ESI[†]), Nb₉P₅ forms exclusively and the solution pH = 9 after reaction. When a larger amount of TMAOH was used to make pH = 10 after reaction, a mixture of Nb₉P₅ and Keggin-type [PNb₁₄O₄₂]⁹⁻ cluster (PNb₁₄) formed,⁷ as we determined by electrospray-ionization mass spectrometry (ESI-MS). The PNb₁₄ dominated when the pH of the reaction solution was higher than 11.

The shape of Nb₉P₅ is similar to the Keggin-type cluster, but it possesses no symmetry [Fig. 1]. There are some irregularly shaped polyoxoniobate clusters reported previously.8 Symmetry is lost in Nb₉P₅ because of the multiple substitutions of PO₄ groups for the different NbO₆ sites in the normal Keggin structure. The structure of Nb₉P₅ is significantly different from Nb_9P_4 , which possesses pseudo- C_3 symmetry.⁵ The previous Nb_9P_4 structure has three neighboring phosphate groups bound to the lacunary-Keggin PNb₉ unit and there are two coordinating Na⁺ ions between the phosphate groups. Examples of similar mixed-addenda polyoxometalates with group 15 elements include an arsenate-containing polyoxovanadate.9 In the structure of Nb9P5, there are four metal-oxo triads bonded to the central phosphate. The basal plane of the Nb₉P₅ cluster in Fig. 1 (farthest from the viewer) is a regular Nb₃O₁₃ triad, which is a common building unit in Keggin ions. The other three triads are Nb₂PO₁₂ moieties. The two Nb₂PO₁₂ triads are in a similar orientation, with P3 and P4 coordinating the basal Nb3O13 triad, while the other Nb2PO12 triad that contains P2 is rotated about 120° counterclockwise relative to

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the others. These three Nb_2PO_{12} triads are connected by an additional phosphate (P1) at the top of the Nb_9P_5 cluster (closest from viewer). In the crystal structure, nine TMA countercations are found and this number of TMA agrees with elemental analysis result. Thus three charge-balancing protons should be bound on the cluster to make the formula as $[H_3Nb_9P_5O_{41}]^{9-}$. The positions of the protons could not be determined, by either crystallography nor by bond-valence sum calculation of the oxygen atoms.

The ESI-MS of the Nb₉P₅ cluster [Fig. S1, ESI[†]] exhibit a relatively complex multi-peak pattern when compared to simpler spectra of other substituted polyoxoniobate clusters that we have synthesized.^{6,7,10} There are multiple side peaks near the assigned peaks, which could be due to loss or addition of water from the Nb₉P₅ cluster during the ionization or drying steps in the ESI-MS analysis. Multiple side peaks in ESI-MS were also observed for $[H_2Mn^{IV}Nb_{10}O_{32}]^{8-}$ cluster.¹¹ There are also some unassigned peaks between 800 < m/z < 950, which must be due to fragmentation of Nb₉P₅.

The ³¹P NMR spectrum of an aqueous Nb₉P₅ solution shows four phosphate peaks assignable to the cluster [Fig. 2]. The integrated peak areas, from left to right, are approximately 1:2:1:1, which agree with five different phosphate groups in the cluster stoichiometry. We hypothesized that the average P-O lengths within PO₄ groups [Fig. S2, ESI[†]] and ³¹P chemical shifts are related. Assuming that the chemical shift depends on the average P-O lengths to the nucleus, we assign the peak at -1.2 ppm as the central phosphate (P5), the peak at -3.8 ppm as P1 and P4. These P1 and P4 have similar average P-O lengths, so the merged peak in the NMR spectra is understandable if the chemical shieldings were also similar. Accordingly, we assign the peak at -6.4 as P2, and the most upfield peak at -11.3 ppm as P3. The peak assignment is also in agreement with the peak widths. The P3 has the widest range of P-O lengths in the X-ray structure, and also the broadest peak in the NMR spectra, and the central P5 has the most regular P-O lengths and correspondingly the sharpest peak. The correlation suggests that asymmetry of the ³¹P nuclei are reflected in the spectra. The ³¹P MAS NMR spectra shows three overlapping peaks (-1.6, -2.4, and -3.2 ppm) in the more downfield region and a broader upfield peak at -10.1 ppm [Fig. 2]. Deconvolution and integration of the peaks gives approximate ratios of 1:2:2 for (-1.6 ppm and -2.4 ppm): -3.2 ppm: -10.1 ppm peaks. The peaks at -1.6 and -2.4 ppm are assigned to the central P5.



Fig. 2 ^{31}P MAS-NMR (top) and ^{31}P solution NMR (bottom, 30 mM in D2O) spectra of Nb9P5.

Similarly to the solution ³¹P NMR peak assignment, the -3.2 ppm peak is assigned to P1 and P4, and the peak at -10.1 ppm is assigned to P2 and P3. In the ³¹P MAS NMR study of Nb₉P₄, two broad peaks were observed at 6.1 and 1.4 ppm, and these are assigned to outer phosphate and central phosphate groups, respectively.⁵ We speculate that the considerable downfield shift of the outer phosphate group in Nb₉P₄ compared to Nb₉P₅ can be due to the coordination of Na⁺.

The Nb₉P₅ was also characterized *via* FT-IR and Raman spectroscopy [Fig. S3, ESI†]. The FT-IR spectra show multiple P–O bands in the range of 1000–1200 cm⁻¹, which arise from different PO₄ groups. The Nb \equiv O band is located at 900 cm⁻¹ and weaker M–O–M bands are observed below 800 cm⁻¹. In the Raman spectra, multiple overlapping Nb \equiv O bands near 900 cm⁻¹ are observed, possibly due to the asymmetric structure of Nb₉P₅. We assign the weak bands in 950–1100 cm⁻¹ to different PO₄ groups.

The stability of the Nb₉P₅ cluster in different pH conditions was examined by using ESI-MS [Fig. S4, ESI[†]]. The pH of the 6 mM solution of Nb₉P₅ was 7.3, and the cluster was apparently kinetically stable in solution for many months. The Nb₉P₅ cluster was stable until pH 12 when titrated with TMAOH. The cluster was also kinetically stable when titrated with HCl until pH 3. The solution at pH < 3, however, became a transparent hydrogel after a few days, which indicates a slow proton-induced charge neutralization, rearrangement and condensation.

The key point is that this Nb₉P₅ cluster provides another example of an aqueous niobate cluster that can be processed in acidic solutions. This stability in acidic region was also observed for the peroxoniobophosphates,⁶ but most of other polyoxoniobate clusters tend to precipitate as hydrous niobium oxide below pH \leq 4–5.

We found that the Nb₉P₅ cluster could be reversibly converted to the peroxo-Nb₄P₂ cluster [Scheme 1] when H₂O₂ is added. The conversion process was monitored *via* ESI-MS and ³¹P NMR after addition of the stoichiometric amount of H₂O₂. In the ESI-MS, we observed a set of new complex peaks with lower intensity in the *m/z* regions near those of the Nb₉P₅ [Fig. 3]. These new peaks persist for many hours after adding H₂O₂. This persistence suggests that peroxo-Nb₉P₅ or similar peroxo-Keggin-like species form. We failed to isolate these transient species for crystallization. Other new peaks centered at *m/z* = 288.8 grew and diminished in an hour after adding H₂O₂. We assign this putative new species as [H₃Nb₅PO₁₃(O₂)₅]³⁻, based on *m/z* value [Fig. 3]. The evolution of ESI-MS peaks show that the peroxo-Nb₄P₂ forms exclusively with time. To further understand the





Fig. 3 Time-dependent ESI-MS spectra of Nb₉P₅ solution after adding 2 equivalents of H_2O_2 . The inset shows more detailed peak assignments. The peaks marked with asterisks correspond to peroxo-Nb₄P₂.

reaction, ³¹P NMR spectra were collected after adding H_2O_2 [Fig. 4]. The ³¹P NMR peaks of Nb₉P₅ shift and split after addition of hydrogen peroxide, which indicates that a range of different peroxo-Nb₉P₅ or similar compounds form as transient intermediates. Chemical shifts of the transient species are not much different from Nb₉P₅, which suggests to us that the structures of the transient species can be similar to Nb₉P₅, but perhaps decorated differently with peroxo groups that affect the ³¹P chemical shifts. This observation is consistent with the ESI-MS results that the transient ³¹P NMR peaks show partial dissociation and rearrangement of the molecule, but not wholesale destruction. The sharp transient peak at -1 ppm is tentatively assigned to $[H_3Nb_5PO_{13}(O_2)_5]^{3-}$, which was suggested by ESI-MS.

We note that well resolved ³¹P NMR peaks are observable only when a stoichiometric amount of H_2O_2 is added; only a few broad peaks are observed during the reaction when more H_2O_2



Fig. 4 Change of ³¹P NMR spectra of Nb₉P₅ (30 mM) as a function of time after the addition of one equivalent of H_2O_2 . The spectra are slightly offset to *x*-axis to show the peak changes more clearly. The spectra were taken every 3 minutes after addition of H_2O_2 for 1 hour and the last spectrum was taken 50 hours later.

is added, possibly due to fast speciation changes and disorder upon peroxidation. The reaction is complete after one day when slight excess H_2O_2 is added, but the reaction is faster when a larger excess of H_2O_2 is added. The growing peak of peroxo-Nb₄P₂ shifts upfield to -1 ppm during the reaction, which might be due to an increasing concentration of peroxo-Nb₄P₂. When the reaction is complete, only the peak of peroxo-Nb₄P₂ and a small phosphate peak near 1 ppm are observed [Fig. 4].

The reverse reaction, converting peroxo-Nb₄P₂ to Nb₉P₅, can be achieved by hydrothermal treatment of a solution of peroxo-Nb₄P₂ at 120 °C overnight. It is not surprising that heat destroys the peroxide moieties, but the Nb₉P₅ forms readily because both clusters have a similar Nb : P ratio and because Nb₉P₅ is stable at near-neutral conditions (pH \sim 7). The sensitivity of the peroxide moieties to heat suggests a strategy for laser-patterning of films.

In summary, a new niobium-phosphate cluster is described that is stable over a wide range of solution pH. This cluster thus adds to the small library of polyoxoniobate compounds that can be processed in acidic solutions. Most interestingly, the cluster can reversibly interconvert to and from the peroxo-Nb₄P₂, which suggests an easy means of patterning. This new cluster may be viewed as a molecular form of the solid niobium-phosphate catalyst that is so useful in industrial applications.

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