

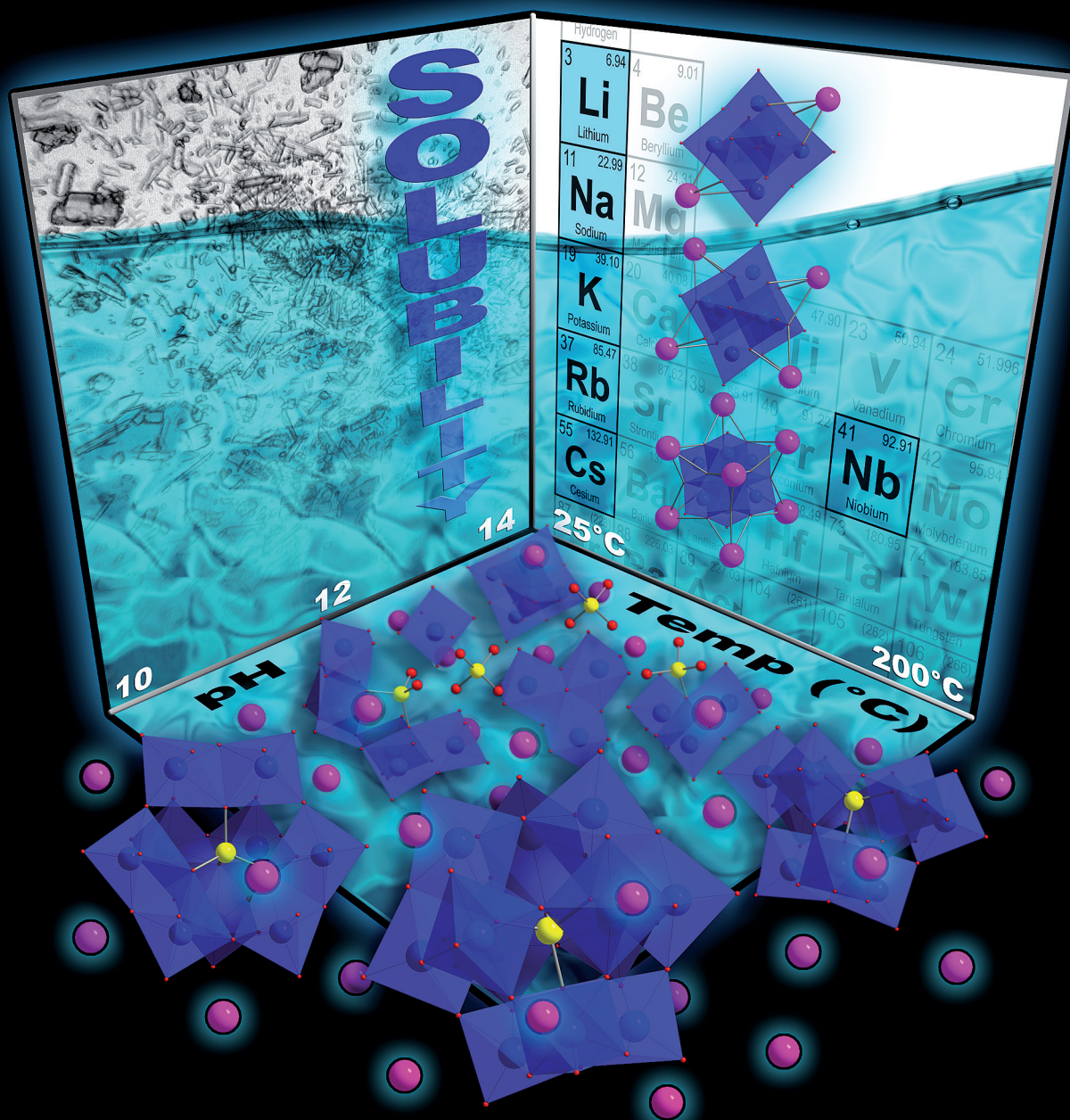
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Polyoxoniobate chemistry in the 21st century

May Nyman*

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Polyoxometalate (POM) chemistry of W, Mo and V is rich and diverse; and new discoveries are frequent and abundant. The prolificacy of this POM chemistry is attributed to rich redox chemistry, an acidic nature that is compatible with addendum metal cations, and most importantly an understanding and ability to control solution behavior. In contrast, the POM chemistry of Nb and Ta (PONb, POTa) is hindered by minimal redox chemistry, alkalinity that is incompatible with the solubility of most metal cations, and a relatively poor understanding of the behavior in aqueous media. Despite these hurdles, considerable advancements in PONb chemistry (and to a much lesser extent POTa chemistry) have been made in the last decade. These include synthesis of the first heteropolyniobate Keggin derivatives, utilization of organic counteranions to obtain unprecedented PONb geometries and compositions, and investigation of PONb solution behavior using advanced techniques such as nuclear magnetic resonance (NMR), electrospray ionization mass spectrometry (ESI MS) and small-angle X-ray scattering (SAXS). This Perspective article summarizes the recent successes, continued shortcomings, and some unique and potentially exploitable features of PONb chemistry. More importantly, this annotated compilation of recent PONb literature has revealed the most logical and promising directions for the continued growth of the most challenging of polyoxometalate chemistries.

1. Introduction

To paraphrase the most common introductory statement in polyoxometalate (POM) literature; POMs are anionic metal-oxo clusters of the Group VI and Group V transition metals, commonly Mo, W, V, Nb and Ta. While it would be more sequentially correct to list the Group V metals (V, Nb and Ta) first, the Group VI metals always receive primary attention due to their relative importance. The chemistries of polyoxoniobates and polyoxotantalates are somewhat disappointing in their current state of advancement; and they take a backseat to the POM chemistry of molybdates, tungstates and even vanadates. The Group VI POMs have surged forward into the 21st century with such surprising developments as the 'giant' polyoxomolybdates^{1,2} and polyoxotungstates,³ self-assembly of POMs into hollow vesicles in solution,^{4,5} and POM inorganic ligands that stabilize transient or unprecedented chemical entities.^{6,7} Polyoxovanadates have their own unique characteristics; very rich redox chemistry,⁸ non-aqueous chemistry⁹ and a tendency to form linked frameworks.¹⁰ These various developments could not have come about without the ability to understand and manipulate the solution behavior of the POMs; including controlled assembly and disassembly of both clusters and cluster assemblies using pH, redox chemistry, counterions, and complex solvent mixtures.

At the end of the 20th century, polyoxoniobate (abbreviated PONb) chemistry consisted mainly of the $[\text{Nb}_6\text{O}_{19}]^{8-}$ Lindqvist ion observed both in solution and solid-state along with some coordination complexes thereof (*i.e.* $\text{Mn}[\text{Nb}_6\text{O}_{19}]_2^{12-}$),¹¹ and a

Sandia National Laboratories, P.O. Box 5800, MS-0754, Albuquerque, NM 87185, USA



May Nyman

May Nyman's educational training is diverse: she received a BSc in Geology, a MSc in Materials Science and Engineering (both from Virginia Tech), and a PhD in Inorganic Chemistry (University of New Mexico). She has been an employee of Sandia National Laboratories in Albuquerque, NM (USA) since 1998, developing functional materials for a variety of environmental and energy applications. These include water-treatment coagu-

lants, sorbents for contaminants and nuclear waste treatment, photocatalysts, ion conductors, and phosphors. However, aqueous synthesis of polyionic clusters is May's passion. In addition to polyoxoniobate chemistry, May is also active in the synthesis and characterization of actinide clusters and ferric and alumina clusters. These together facilitate fundamental studies of ion association and contaminant and colloid transport in aqueous environments.

single structural report of the related decaniobate $[\text{Nb}_{10}\text{O}_{28}]^{6-}$.¹² Polyoxotantalate (POTa) chemistry fared worse, only the $[\text{Ta}_6\text{O}_{19}]^{8-}$ cluster was known in both solution and solid-state. Some Nb-substituted polyoxotungstates of the classic Lindqvist¹³ and Keggin^{14,15} derivatives had been produced, but always adapting the niobate chemistry to the tungstate chemistry rather than *visa versa*.

From the point of view of the PONb chemist, what is most remarkable and enviable about the Group VI POMs is the ability to control the parent cluster geometry through pH. By increasing pH, vacancies in the cluster are formed and these lacunary holes can then be 'filled' with virtually any other metal on the periodic table. This fundamental process gives rise to the so-called sandwich complexes, and furthermore extended networks of POM building blocks can be formed by linking through the addendum metals. These addenda provide numerous functionalities as well, introducing rich redox activity, catalytic behavior, *etc.* Furthermore, with appropriate use of counteranions, these more affluent POMs can be dissolved and precipitated reversibly, and transferred into non-aqueous phases intact. In this manner, POM chemistry seems limitless, as illustrated by the many papers published each year introducing new structural and functional developments.

The Group V POMs have much higher charge : size ratios than the Group VI POMs; the higher-charge clusters are generally stable at higher pH. Given these different features, especially the suitable pH for self-assembly of the aqueous POMs; it is somewhat surprising that Group V and Group VI POMs are broadly considered to be the same class of materials. The only true common features include (1) The MO_6 octahedra building blocks of POMs are distorted with a terminal $\text{M}=\text{O}$ bond ('y' oxygen) *trans* to a long $\text{M}-\text{O}$ bond, and (2) Some identical Group V and Group VI POM geometries are featured in the solid-state.

In the last decade of PONb chemistry, there have been spurious findings that are akin to routinely-mastered chemistries of the Mo, W and V POMs. These include non-aqueous PONb chemistry, Keggin derivatives, 'giant' PONbs, and pH-mediated PONb alteration. The focus of this Perspective article is to summarize these major milestones in PONb chemistry, recognize defining characteristics of PONb chemistry, and attempt to glean some understanding and connection between the seemingly more isolated and random developments. Most importantly, through this annotated (and sometimes anecdotal) account, some clear pathways for deliberate advances in polyoxoniobate (and tantalate) science will provide future inspiration to continue pursuit of this elusive chemistry.

2. Background

This section will begin with a few definitions and guiding figures, particularly for the non-specialist. All the POMs discussed in-depth in this paper are of the Lindqvist¹⁶ or the Keggin¹⁷ geometry, or derivatives thereof. Both these plenary structures derive their names from the individuals who initially reported the solid-state structure, and are shown in Fig. 1. The Lindqvist ion, or hexametalate (*i.e.* hexaniobate, hexatantalate, *etc.*) is best described as a superoctahedron of 6 edge-sharing octahedra, and every octahedral metal is bonded to the central oxygen, with a formula $[\text{M}_6\text{O}_{19}]$. The α -Keggin polymorph contains a central tetrahedral oxoanion (PO_4 , SiO_4 , AlO_4 , *etc.*). Each oxygen of the

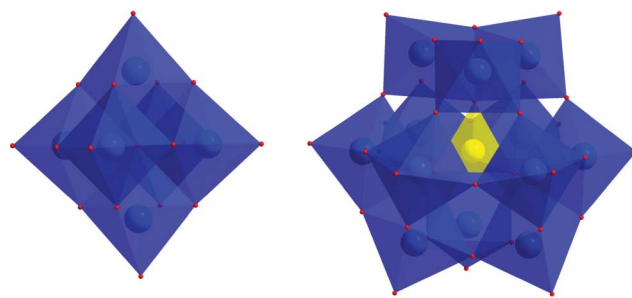


Fig. 1 The two polyoxometalate (POM) geometries from which most polyoxoniobates (PONb), both in solution and solid-state, are derived. Left: the Lindqvist ion, $[\text{Nb}_6\text{O}_{19}]^{8-}$. It is a super-octahedron consisting of six edge-sharing NbO_6 octahedra. With its small size and high charge, this hexaniobate has the highest charge-density of all POMs (0.32, see Table 1). Right: the plenary α -Keggin ion, $[\text{TNb}_{12}\text{O}_{40}]^{16-}$ ($\text{T}=\text{Ge},\text{Si}$). It consists of four sets of three edge-sharing octahedra, Nb_3O_{13} , that are arranged in a tetrahedral fashion around a central oxoanion tetrahedron. This dodecaniobate also has a very high charge density (0.30, see Table 1). The blue polyhedra are NbO_6 and the yellow polyhedron is the central tetrahedron.

central anion is the terminal oxygen for three edge-sharing MO_6 octahedra, and the four MO_6 trimers are corner-sharing, with a formula $[\text{TM}_{12}\text{O}_{40}]$ (T = tetrahedral metal). In different Keggin polymorphs, the trimers are linked together in different ways, but we are only concerned with the α -polymorph in this paper. POMs are sometimes further sub-categorized as isopolyanions and heteropolyanions. An isopolyanion contains no heterometals or addenda metals, and the Lindqvist ion is an example of this. The heteropolyanion does contain heterometals, the Keggin ion being an example.

Group VI POMs (POW and POMo) and polyoxovanadates (POV) are most commonly synthesized by acidification of solutions of the highly soluble tetrahedral oxoanions, $\text{MO}_4^{2/3-}$ ($\text{M} = \text{V},\text{Mo},\text{W}$): the process is hydrolysis and condensation. The pH of the oxoanion solution is initially quite high (>12). The 'plenary' (meaning complete) Keggin ion forms at low pH (-1 – 3). The lacunary (meaning cave, hole or missing part) derivatives are formed from the plenary geometry by removing $\text{M}=\text{O}$ ($\text{M} = \text{Mo},\text{W}$) octahedra at higher pH; the exact pH at which a cluster geometry is best isolated also depends on other variables such as the counterion, temperature and concentration.¹⁸

3. Aqueous synthesis of polyoxoniobates

In contrast to the V, Mo and W POMs, aqueous PONb (and POTa) chemistry is limited to the alkaline end of the pH scale; predominantly above 10.5. Furthermore, no such readily soluble NbO_4^{3-} or TaO_4^{3-} salts exist for the convenience of ambient aqueous synthesis: the Nb/Ta^{5+} ion is too small to remain tetrahedral and monomeric in the aqueous solution. In fact, many early reports of the synthesis of the Lindqvist hexaniobate (and hexatantalate) were essentially solid-state reactions, described as such: melt an alkali hydroxide, carbonate or superoxide with Nb_2O_5 (Ta_2O_5) in a crucible, and dissolve the resulting product in water for crystallization.^{11,16,19} This reaction is messy and not necessarily reproducible - many things can go awry including reaction with the crucible, 'boiling over', reaction with atmospheric CO_2 , *etc.* Reports of the dissolution of hydrous M_2O_5 ($\text{M} = \text{Nb},\text{Ta}$) in

alkali hydroxide solutions were rarer, but also not described quantitatively for possible reproduction.²⁰ We partially owe our inroads into advancing PONb chemistry in the early 21st century to simply having a good Nb-precursor. We obtained an abundant supply of amorphous $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ ($x = 6-7$) as a generous gift from Reference Metals Co., Inc; Bridgeville, PA. Large quantities of this oxide could be dissolved in 1–10 M KOH, RbOH or CsOH solution, and the Lindqvist ion crystallized by either evaporation of the aqueous solution or addition of a less polar solvent (usually alcohol).²¹ In this manner, we can obtain large quantities (10's of grams) of pure material. The less soluble Lindqvist salts of Na or Li (more on this later) were trickier in that the Lindqvist salts would be precipitating at the same time the hydrous niobium oxide was dissolving. Therefore to obtain the Li^{22} or Na^{23} salt in a pure and well-crystallized form, the K, Rb or Cs salt is dissolved in a minimal amount of water and added to 1–2 molar LiOH or NaOH solution, from which the corollary Lindqvist salt precipitates rapidly. We also developed a more reliable solution synthesis for K, Rb and Cs hexatantalate, making use of the peroxotantalate, $\text{Ta}(\text{O}_2)_4$ salts.²³ Again, the less soluble Li and Na hexatantalate salts are obtained by dissolution of the more soluble salts in LiOH or NaOH solution.^{22,23}

Dissolution of the hydrous Nb_2O_5 at ambient aqueous conditions - *i.e.* less than 100 °C in an open beaker, akin to standard POM synthesis procedures - will only produce the Lindqvist ion since high hydroxide solutions are required. In addition to the hydrous metal oxide, other available precursors for Nb and Ta include chlorides, peroxides and alkoxides. However, these are immediately or gradually converted to hydrous oxides upon introduction to an aqueous environment, so the end result is the same. Thus other methods are necessary to broaden PONb chemistry beyond the Lindqvist ion.

3.1 The heteropolyoniobate Keggin phases

In 2001, we fortuitously discovered the unprecedented dodecaniobate Keggin ion $[\text{SiNb}_{12}\text{O}_{40}]$, and with further exploration we were able to report²⁴ a general synthetic procedure that produced a variety of new polyniobate geometries, most being Keggin ion derivatives. Ironically, this first dodecaniobate Keggin ion was an unidentified impurity in an industry-prepared sorbent designed for removing radioactive Cs from alkaline nuclear wastes. This unidentified impurity was problematic in that during waste treatment in an ion-exchange column, it dissolved and precipitated as an amorphous, Nb-rich oxide that would clog the column. Following a study to unearth the cause and provide a fix,²⁵ we discovered that this problematic impurity was in fact a valuable scientific find! The synthetic guidelines to obtain heteropolyoniobate Keggin-derivatives include: (1) lower AOH:Nb ratios (*i.e.* 1:1–3:1), lower pH (*i.e.* 10.5–12) and lower AOH concentrations (~0.3–0.8 M) than conditions in which the Lindqvist ion is dominant (A = alkali); and (2) hydrothermal treatment, hot for short time (150–220 °C, less than 24 h). Higher hydroxide/pH produced the Lindqvist ion, and longer heating times produced simple oxides such as perovskite NaNbO_3 . Variations on this procedure provided an assortment of Keggin-ion or Keggin-derivative phases, including $\text{K}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}]\cdot 16\text{H}_2\text{O}$ (1),²⁴ $\text{Na}_{14}[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]\cdot 45.5\text{H}_2\text{O}$ (2),²⁴ $\text{Na}_{16}[\text{TNb}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (T = Si, Ge) (3),²⁶ $\text{Na}_{12}[\text{Ti}_2\text{O}_2][\text{TNb}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ and $\text{Na}_{10}[\text{Nb}_2\text{O}_2][\text{TNb}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ (T = Si, Ge) (4),²⁷ $\text{Na}_{15}[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]\cdot 22\text{H}_2\text{O}$ (5),²⁸ $\text{K}_{10}[\text{Nb}_2\text{O}_2][\text{GeNb}_{12}\text{O}_{40}]\cdot 11\text{H}_2\text{O}$ (6),²⁹ and $\text{Li}_{13}\text{K}[\text{SiNb}_{12}(\text{OH})_2\text{O}_{38}]\cdot 17\text{H}_2\text{O}$ (7). From this synthetic method, we also obtained a di-titanium substituted derivative of the decaniobate, $\text{Na}_8[\text{Nb}_8\text{Ti}_2\text{O}_{28}]\cdot 34\text{H}_2\text{O}$ (8).³⁰

The dodecaniobate Keggin ion carries an extraordinarily high charge, $[\text{SiNb}_{12}\text{O}_{40}]^{16-}$ for instance, compared to the related silicotungstate, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$; and its solid-state and solution behavior differs greatly, likely as a result of the vast difference in charge since the cluster geometries are virtually identical. The silicotungstate is a classic, well-behaved soluble polyanion. It is readily dissolved as an acid, precipitated with just about any inorganic or organic counteraction, and transferable to organic media with the appropriate counteractions. The siliconiobate on the other hand, due to its high charge, undergoes strong cation association which controls its behavior. The plenary α -Keggin ion has been isolated as a Na-salt (3) and a Li-salt (7), and we have not yet been able to redissolve these and confirm their state in solution; either through recrystallization or some sort of spectroscopic characterization in solution (*i.e.* ²⁹Si NMR). Furthermore they are very sparingly soluble in both pure water and miscellaneous electrolyte solutions. While the crystal lattice of (3) has 16 Na^+ per cluster, it has only four molecules of water, which means the sodium is directly bonded to the cluster (Fig. 2a); 30–38 Na^+ cations are directly bonded to each Keggin ion.²⁶ Viewing this lattice, it is very easy to understand why this compound cannot readily be dissolved: it is essentially a solid-state lattice of cations and anions with very few intervening water molecules. While the dodecaniobate $[\text{SiNb}_{12}\text{O}_{40}]$ Na-salt (3) was synthesized hydrothermally from NaOH and $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, a similar hydrothermal reaction using

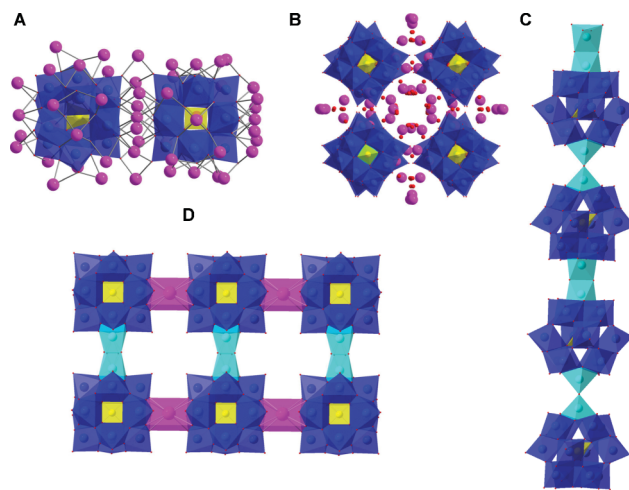


Fig. 2 Various linkages of the $[\text{TNb}_{12}\text{O}_{40}]$ (T = Si, Ge) plenary Keggin ion in the solid-state. (a) View of $\text{Na}_{16}[\text{TNb}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (3) showing two Keggin ions and the close association of the Na-cations in the solid-state lattice. (b) View looking down the axis of the Keggin chains of $\text{K}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}]\cdot 16\text{H}_2\text{O}$ (1). (c) Side view of the Keggin chains of both $\text{K}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}]\cdot 16\text{H}_2\text{O}$ (1), $\text{Na}_{12}[\text{Ti}_2\text{O}_2][\text{TNb}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ and $\text{Na}_{10}[\text{Nb}_2\text{O}_2][\text{TNb}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ (4). (d) View of the Keggin ion layers of $\text{K}_{10}[\text{Nb}_2\text{O}_2][\text{GeNb}_{12}\text{O}_{40}]\cdot 11\text{H}_2\text{O}$ (6) linked in one direction by edge-sharing NbO_6 , and K^+ in the second direction. The blue polyhedra are NbO_6 , the yellow polyhedra are SiO_4 or GeO_4 , the turquoise polyhedra are TiO_6 , or NbO_6 that link the Keggin ions and the pink spheres or polyhedra are the alkalis, Na^+ or K^+ .

the Na-Lindqvist salt²⁰ produced (4),²⁷ a phase with the Keggin ions linked into chains *via* $[\text{Nb}_2\text{O}_2]^{6+}$ bridges, charge-balanced by hydrated Na^+ between chains. It is tempting to assume it is the Na:Nb ratio that controls the crystallization of the two phases: 3.25:1 for $\text{Na}_{16}[\text{SiNb}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ and 1.15:1 for $\text{Na}_{10}[\text{Nb}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$, but the formation pathway of the dodecaniobate Keggin ion is yet to be investigated. The linked dodecaniobate Keggin ion chains were also formed with $[\text{Ti}_2\text{O}_2]^{4+}$ bridges with K^+ (1) (Fig. 2b and 2c) or Na^+ (4) as the counterions, and all compositional variations of (4) are excellent ion-exchange materials, but do not possess good chemical stability.³¹ In one case, $\text{K}_{10}[\text{Nb}_2\text{O}_2][\text{GeNb}_{12}\text{O}_{40}]\cdot 11\text{H}_2\text{O}$ (6), the Keggin ions are linked into layers - by the $[\text{Nb}_2\text{O}_2]^{6+}$ bridges in one direction and K^+ -cations in the second direction (Fig. 2d).²⁹ Along with (3), this is yet another example in PONb chemistry where the alkali metals behave more like structure-directing, framework metals than hydrated counterions.

Two examples of lacunary niobate Keggin ion derivatives have also been made by hydrothermal synthesis, $\text{Na}_{14}[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]\cdot 45.5\text{H}_2\text{O}$ (2) and $\text{Na}_{15}[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]\cdot 22\text{H}_2\text{O}$ (5), Fig. 3a and 3b. Unfortunately, we cannot correlate the experimental conditions to the formation of a plenary *vs.* lacunary Keggin-ion phase. All are very similar in terms of temperature, T:Nb ratio (T = tetrahedral metal), Na^+ concentration, Na:Nb ratio and pH (10.5–12): the optimal conditions for formations of all niobate Keggin ion phases reviewed here were determined by systematic variations. This is in contrast to the POW chemistry where lacunary derivatives are isolated at higher pH, as discussed prior. The $[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]^{15-}$ cluster of (5) is described as an A-type trivalent lacunary α -Keggin ion decorated with three PO_4 tetrahedra, or PO_2^+ groups.²⁸ Like the plenary niobate Keggin ion phases described above, this Na-salt is absolutely insoluble: the Na^+ -counterions bridge the clusters in a layered-framework, no solution characterization of this cluster is possible. $[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]^{14-}$ (2) is more akin to the Wells-Dawson (and related) POM geometries from POW chemistry: a linkage of two lacunary Keggin-ion fragments with two TO_4 anions inside.²⁴ However, the specific geometry of (2) has not been observed in POW chemistry. (2) is the only one of the niobate Keggin derivatives that can be dissolved, characterized in solution (by ^{29}Si NMR)²⁴ and recrystallized intact. A reasonable hypothesis as

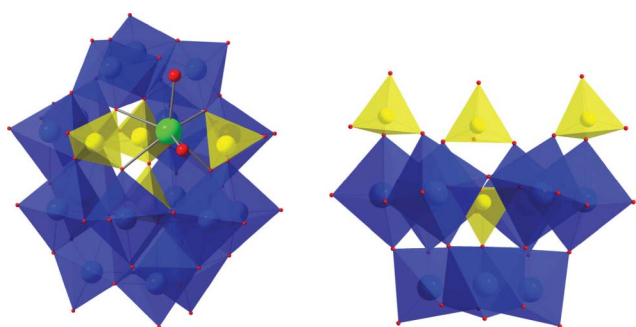


Fig. 3 Two lacunary PONb Keggin derivatives. Left: $[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]^{14-}$ (2) and right: $[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]^{15-}$ (5). The blue polyhedra are NbO_6 and the yellow polyhedra are SiO_4 (2) and PO_4 (5). (2) features a central Si_2O_7 and two decorating SiO_4H . A Na^+ -cation resides in the pocket (green sphere). (5) has both central PO_4 and three decorating PO_4 on the rim of the lacunary cavity.

Table 1 Charge-density^a of niobate POMs and tungstate POMs

POM	Anionic charge	# of non-hydrogen atoms	Charge density (charge per atom)
$[\text{Nb}_6\text{O}_{19}]$	8	25	0.32
$[\text{Ti}_2\text{Nb}_8\text{O}_{28}]$ (8)	8	38	0.21
$[\text{Nb}_{10}\text{O}_{28}]$	6	38	0.16
$[\text{SiNb}_{12}\text{O}_{40}]$ (3)	16	53	0.30
$[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]$ (5)	15	53	0.28
$[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]$ (2)	14	76	0.18
$[\text{W}_6\text{O}_{19}]$	2	25	0.080
$[\text{SiW}_{12}\text{O}_{40}]$	4	53	0.075
$[\text{SiW}_{11}\text{O}_{39}]$	8	51	0.16
$[\text{PW}_9\text{O}_{34}]$	9	44	0.20

^a Charge-density (charge/atom) = (anionic charge of the POM)/(number of non-hydrogen atoms of the POM).

to why this cluster behaves more like a typical heteropolyanion is that it has lower “charge-density”, expressed as:

$$\text{Charge-density (charge/atom)} =$$

$$(\text{anionic charge of the POM})/(\text{number of non-hydrogen atoms of the POM})$$

Summarized in Table 1 is the charge density of a sampling of niobate POMs and tungstate POMs for comparison.

Here we see the charge density of (2) is indeed considerably lower than that of the other heteropolyaniobate geometries ((4) & (5)), and intermediate between the lacunary POW Keggin ions, $[\text{SiW}_{11}\text{O}_{39}]$ and $[\text{PW}_9\text{O}_{34}]$.

One POM area that the inception of the Nb-heteropolyanions was anticipated to impact was medicinal and other microbiological applications. POMs have known antiviral, antitumoral, and anticancer activity.³² The stability of the POM in biological media (pH~7.4) is a key characteristic of the most effective POMs, and Nb-substituted POWs had received particular attention for these applications.^{15,33} (2) was tested for anti-HIV activity with anticipation, but was determined to be ineffective. In 2005, a study by Prusiner and Long³⁴ unveiled another potential microbiological application of POMs; the selective precipitation of prions from normal proteins, with selectivity increasing with the charge of the tungstate Keggin ion. Again, (2) was tested and did not show considerable efficacy. Of course these results were disappointing (and never published for obvious reasons), but they did provide insight into the ion-association of polyniobates. We concluded that the poor performance was related to too much charge-density, which simply meant that excessive non-specific ion association (and precipitation as a result) of the polyniobate occurs in biological media that contains significant amounts of Na^+ . The non-specific ion association of the POM with Na^+ means the charge is not accessible by oppositely-charged macromolecules such as prions; and the resultant precipitation, of course, renders the POM inaccessible.

3.2 The Lindqvist-ion

As noted above, the hexaniobate $[\text{Nb}_6\text{O}_{19}]^{8-}$ Lindqvist ion was the first PONb to be studied in both the solid-state and solution; and due to its easy accessibility and handle-ability, it continues to be studied and utilized to form new solid-state phases featuring hexaniobate,^{35–39} to investigate aqueous behavior,^{40–42} and

to synthesize niobate materials *via* soft-chemical methods.^{43–45} Furthermore, $[\text{Nb}_6\text{O}_{19}]^{8-}$ can be crystallized as any alkali salt, and even as a tetramethylammonium salt,⁴⁶ which further extends its range of utility in these studies. The $[\text{Nb}_6\text{O}_{19}]^{8-}$ Lindqvist ion has the highest charge-density of all known POMs (see Table 1); and this feature provides interesting opportunity and challenges. The alkali- $[\text{Nb}_6\text{O}_{19}]^{8-}$ bonding in the solid-state is a classic example of increased ion-association down the periodic group, where the bigger, less hydrated ions exhibit more contact ion-association, not intermediated by water;^{21,22} see Fig. 4. Considering just the bonding mode in which the alkali sits on the face of the $[\text{Nb}_6\text{O}_{19}]^{8-}$ superoctahedron with three bonds to cluster oxygens: we observe that two Li/Na^+ cations are face-bonded to $[\text{Nb}_6\text{O}_{19}]^{8-}$, four K^+ cations are associated to the faces of $[\text{Nb}_6\text{O}_{19}]^{8-}$, and finally all eight faces of $[\text{Nb}_6\text{O}_{19}]^{8-}$ bind Rb/Cs^+ in this manner. While this is a well-known trend,⁴⁷ what is truly remarkable and unusual for the $[\text{Nb}_6\text{O}_{19}]^{8-}$ alkali salts is that the solubility increases from $\text{Li} < \text{Na} < \text{K} < \text{Rb}/\text{Cs}$. Generally, Cs-salts of large anions such as POMs are notoriously insoluble and Li-salts are soluble. This is indeed a logical trend in that the larger Cs-cations that do not have a tightly bound water shell more readily bind to and bridge anions, initiating local charge-neutralization and thus precipitation from water. While this unusual reverse of the trend with hexaniobate is not understood, it served us well to investigate ion-association in solution *via* Small Angle X-ray Scattering (SAXS).⁴¹ The heavier alkalis, Cs and Rb are better X-ray scatterers, in addition to providing optimum ion-association and solubility. This study did indeed show that the completely neutralized hexaniobate, $\text{A}_8[\text{Nb}_6\text{O}_{19}]$ ($\text{A} = \text{Rb}, \text{Cs}$), shown in Fig. 4 is the dominant species in AOH solution, while the ‘nude’ anion $[\text{Nb}_6\text{O}_{19}]^{8-}$ dominates in TMAOH (TMA = tetramethylammonium) solutions. The results of this SAXS study, confirming the predominance of neutral $\text{A}_8[\text{Nb}_6\text{O}_{19}]$ in aqueous solution, renders its high solubility even more profound: why is an essentially neutral entity so highly stable in aqueous solution where hydration is the normal mode of dissolution of ionic salts? It is worth mentioning here that the hexatantalate $[\text{Ta}_6\text{O}_{19}]^{8-}$ ²³ also has similar solubility trends, but exhibiting lower solubility than the equivalent hexaniobate salts; another curious phenomenon we are currently studying *via* SAXS.

Another feature of hexaniobate owed to its high charge-density is protonation both in the solid-state and solution. When hexaniobate is dissolved in pure water, the pH rises to ~ 12 , indicative of proton-binding. For instance, in buffered K^+ -salt

systems, triprotonated $[\text{H}_3\text{Nb}_6\text{O}_{19}]^{5-}$ diprotonated $[\text{H}_2\text{Nb}_6\text{O}_{19}]^{6-}$ monoprotonated $[\text{HNb}_6\text{O}_{19}]^{7-}$ and $[\text{Nb}_6\text{O}_{19}]^{8-}$ are the dominant species at pH $\sim 8, 10, 12$ and 14 , respectively.⁴⁸ For comparison, the protonated states of hexatantalate are all observed at lower pH values.⁴⁹ However, while the hexaniobate has been characterized in its various protonation states in the solid-state, the protonated hexatantalate has rarely been observed. A single very recent and fascinating exception to this is a tetrabutylammonium (TBA) salt of the di-protonated hexatantalate.⁵⁰ As we might expect, the non-aqueous conditions in which this phase has formed provided an opportunity for increased anion-proton pairing that seems more favorable in less polar solvents.

4. The role of transition metals in PONb chemistry

Transition-metal or rare-earth substituted POMs is a very active role of research, particularly for the POMs of tungstate, molybdate and vanadate. As described in the introduction, these are often formed from the lacunary POMs, by filling vacancies in the cluster with the metal, and these addenda metals can then link clusters into larger and extended assemblies. Furthermore, they offer functionality such as redox behavior, catalysis, magnetism, *etc.* The equivalent chemistry of PONbs is challenging, due to the basic nature of these POMs in aqueous media. As stated in the prior section, self-buffering pH's of dissolved PONbs such as the hexaniobate are generally above 12, a state in which most metals simply precipitate as hydroxides. Thus the metals must be either (1) the rare alkaline-soluble or amphoteric metal, yet still reactive enough to undergo hydrolysis and condensation reactions, or (2) complexed by a protective ligand, yet still accessible to bind to the ‘inorganic ligand’ POMs. These strategies have been tried: the most successful example of the former is Ti^{4+} , and the most successful example of the latter is $\text{Cu}(\text{II})$ amine complexes.

Ti is a good base-soluble metal, and the titanium alkoxide precursor can be utilized in alkaline hydrothermal reactions. As mentioned prior, the $[\text{Ti}_2\text{O}_2]^{4+}$ -linked dodecaniobate Keggin ions have been synthesized hydrothermally, as has the Na-salt of the $[\text{Ti}_2\text{Nb}_8\text{O}_{28}]^{8-}$ (**8**) derivative of the decametallate cluster. In the latter cluster, as in Ti-substituted polytungstates, Ti occupies cluster sites, which do not have terminal ν l oxygens, in that the $\text{Ti}=\text{O}$ is not a stable and known moiety. With use of organic counterions, TMA⁺ in particular, the Casey group was able to expand the titanoniobate POMs to include $[\text{TiNb}_9\text{O}_{28}]^{7-}$

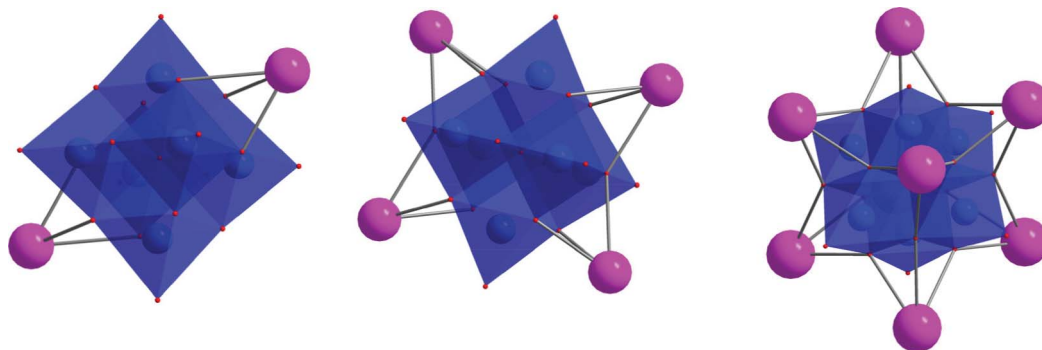


Fig. 4 Alkali-cation bonding to the $[\text{Nb}_6\text{O}_{19}]^{8-}$ Lindqvist ion; illustrating increased bonding with increased alkali radius (see text). Left: $\text{A}_2[\text{Nb}_6\text{O}_{19}]^{6-}$ ($\text{A} = \text{Li}, \text{Na}$), middle $\text{A}_4[\text{Nb}_6\text{O}_{19}]^{4-}$ ($\text{A} = \text{K}$), and right: $\text{A}_8[\text{Nb}_6\text{O}_{19}]$ ($\text{A} = \text{Rb}, \text{Cs}$).

and $[\text{Ti}_{12}\text{Nb}_6\text{O}_{44}]^{10-}$.⁵¹⁻⁵³ The latter cluster is a remarkable giant octahedral shaped cluster with Ti in all the sites with no γ oxygens, and Nb at the apices of the octahedron; these clusters will be discussed more later in the realm of use of organic counter-cations.

Copper amine complexes, which are cationic (*i.e.* $\text{Cu}(\text{en})_2^{2+}$; en = ethylenediamine) are soluble in alkaline solutions, and a number of Cu-amine decorated hexaniobate phases have been synthesized.^{35,37,38,54,55} Furthermore, the unprecedented heptaniobate^{36,56} and pentaniobate⁵⁷ were isolated by use of charge-balancing and decorating Cu-amine cations; but this will be discussed further below. There are numerous other examples where various metals have been combined with the hexaniobate in solution, usually with the metal protected by chelating ligands, and a crystalline product results where the metal is either directly bonded to or acting as a charge-balancing cation to the hexaniobate. Oftentimes, the metal exhibits the same face-bonding as the alkalis, Cs and Rb in particular. Specific examples include Mn^{4+} sandwiched between two Lindqvist ions,¹¹ Mn/Retriscarbonyl decorating two opposing faces of both hexaniobate and hexatantalate,⁵⁸ ligated Ni coordinated to hexaniobate,^{59,60} and hydrated Al and Eu loosely associated with hexaniobate through hydrogen bonding.⁶¹

We have also attempted to form TM-PONb complexes with amine-protected Cu and Co and the lacunary-type heteropolyoniobates. In the first example, $[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]^{14-}$ (**2**) was combined with $\text{Cu}(\text{II})(\text{en})_2$, and a dimer sandwich-type compound crystallized,⁶² see Fig. 5a. However, the ‘filling’ of the sandwich is only Na^+ that links the two monomers; the central point of linkage is a Na^+ -cation that sits in the lacunary hole that is also present in the monomer (**2**). Dissolution of the monomer in a K^+ -electrolyte solution provided a material of (**2**) linked by K^+ cations into a zig-zag chain (Fig. 5b). Again, the Na^+ cation remains in the lacunary pocket. Furthermore, the octahedral Cu cations, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, are not bonded to the PONb at all. In other words, the roles of the alkali counterions and transition metal are switched, relative to what we have come to expect from heteropolytungstate chemistry. More recently however, POW sandwich compounds where alkalis bind and stabilize the equator of the dimer, similar to our PONb dimer of (**2**), have been recognized.^{63,64}

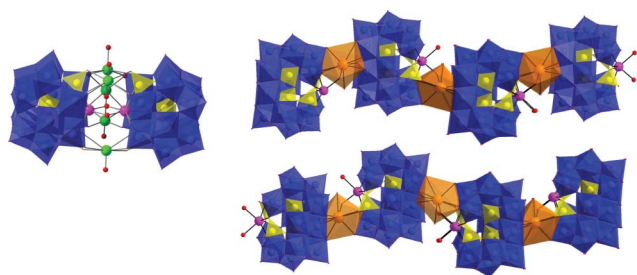


Fig. 5 $[\text{H}_2\text{Si}_4\text{Nb}_{16}\text{O}_{56}]^{14-}$ (**2**) as it assembles in the solid-state when combined with $\text{Cu}(\text{en})_2$ (en = ethylenediamine) in solution (see text). Left: sodium ‘pseudo-sandwich’ crystallized from a $\text{Cu}(\text{en})_2$ solution. Right: the sodium ‘pseudo-sandwich’ recrystallized from a potassium electrolyte solution. The NbO_6 octahedra are blue, SiO_4 tetrahedra are yellow, the pink spheres are Na^+ in the pocket of the monomer cluster, green is also Na^+ and orange polyhedra are K^+ .

The second example was never published due to poor crystal quality, but serves the purpose of illustration here. While the prior mentioned experiments were carried out by manipulation of the PONb in ambient conditions, the following was done hydrothermally. The hydrothermal synthesis of $\text{Na}_{15}[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]\cdot 22\text{H}_2\text{O}$ (**5**) was modified with the addition of $\text{Co}(\text{II})$ -ammonia complex, and resulted in the crystallization of layers of the $[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]^{15-}$ cluster, linked by hydrated Co^{2+} . The other difference between the Co-linked clusters (denoted **Co-5**) and those with only Na^+ as a counterion/linker, is what sits inside the trivacant lacunary cavity that is rimmed with decorating PO_4 tetrahedra. While (**5**) has two Na^+ -cations nested inside, **Co-5** has three. Furthermore, in **Co-5**, the orientation of the PO_4 plus Na^+ cations is such that they close the cluster with a ‘cap’. In essence, the Na-cations in the lacunary opening become an integral part of the heteropolyanion (Fig. 6).

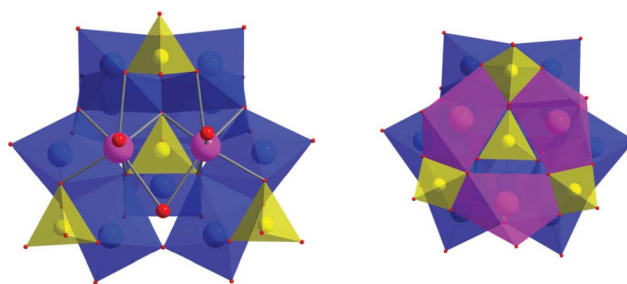


Fig. 6 Left: $[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]^{15-}$ (**5**) showing two Na^+ -cations (pink spheres) bonded inside the lacunary pocket. Right: cluster of (**5**) when linked together in the solid-state with $\text{Co}(\text{II})$. For the Co-linked (**5**), the PO_4 tetrahedra (yellow tetrahedra) plus three Na^+ -cations (pink polyhedra) essentially form a cap that closes the lacunary hole (see text).

The examples described in this section illustrate that the incorporation of transition metals (or lanthanides) into PONb chemistry in the manner that they serve POW chemistry still remains a challenge. The challenge of course is being able to control the solubility of these metals in alkaline conditions without completely rendering them unreactive through chelation: we recognized this issue at the onset of these studies. A secondary challenge appears to be removing these strongly associated alkalis from potential binding sites for other types of addenda metals, as the latter two examples above illustrate. While it has long been recognized that the encapsulation of alkalis can be important in templating POMs, there have also been means of replacing these alkalis.⁶⁵⁻⁶⁷ Our attempts thus far at finding strategies to replace these alkalis have actually resulted in closer association and more extensive bonding between the alkalis and PONbs, while the transition metals remain chelated and/or bonded peripherally. This represents another challenge for PONb chemists for the future.

5. Alkali-free polyoxoniobate chemistry

One way to rid polyoniobates of tightly associated alkalis is to eliminate them from the synthesis altogether and instead utilize organic counterions. Organic counterions, alkylammoniums in particular, have always played a very important role in POM chemistry; to facilitate non-aqueous chemistry in particular. While this too has been a challenge for PONb chemistry, there are

now enough examples to start to understand some trends and certainly to recognize that organic counterions are crucial in the further development of this chemistry. The first example was the tetramethylammonium (TMA) salt of decaniobate $[\text{Nb}_{10}\text{O}_{28}]^{6-}$, mentioned prior.^{12,68,69} Casey's group went on to produce TMA salts of $[\text{Nb}_6\text{O}_{19}]^{8-}$, $[\text{Ti}_2\text{Nb}_8\text{O}_{28}]^{8-}$, $[\text{TiNb}_9\text{O}_{28}]^{7-}$ and $[\text{Ti}_{12}\text{Nb}_6\text{O}_{44}]^{10-}$, as well as $[\text{Nb}_6\text{O}_{13}(\text{O}_2)]^{8-}$ where the terminal oxygen ligands are replaced with peroxide ligands.^{46,52,70,51,71} Finally, a decaniobate dimer $[\text{Nb}_{20}\text{O}_{54}]^{8-}$ was isolated with the use of tetrabutylammonium (TBA) counterions.⁷² These niobates and titanoniobates are illustrated in Fig. 7.

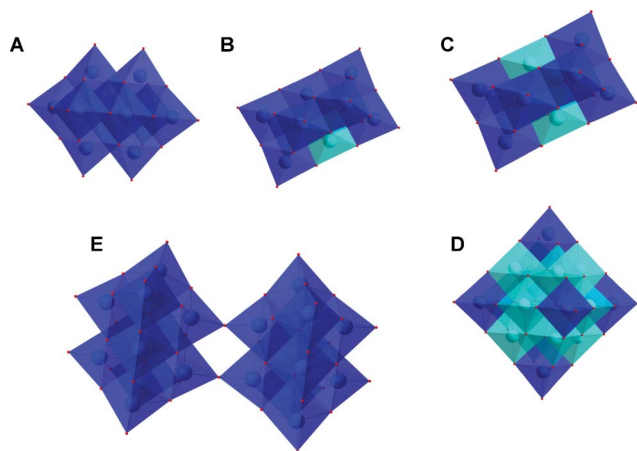


Fig. 7 Decaniobate and titanoniobate derivatives. (a) decaniobate, $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ (b) monotitanoniobate $[\text{TiNb}_9\text{O}_{28}]^{7-}$, (c) ditanoniobate $[\text{Ti}_2\text{Nb}_8\text{O}_{28}]^{8-}$, (d) 'super-Lindqvist' $[\text{Ti}_{12}\text{Nb}_6\text{O}_{44}]^{10-}$, and (e) icosaniobate $[\text{Nb}_{20}\text{O}_{54}]^{8-}$. The blue octahedra are NbO_6 and turquoise octahedra are TiO_6 . Note: Ti always adopts the POM sites that have no terminal oxygens.

Although the decaniobate structure was first reported in 1977,¹² the methanolic synthesis was irreproducible until Marek⁶⁹ discovered that it readily crystallized out of ethanol, whereas it remained in solution in methanol. Ohlin *et al.*⁴⁶ modified the synthesis of TMA-decaniobate, and found that TMA-hexaniobate could be obtained from a similar synthesis, but with higher base concentration and different crystallization conditions (pure ethanol for the former; ethanol-acetone mix for the latter). This work suggested that there exists a relationship between these two entities in solution, which is detailed in the next section.

All the TMA salts of titanoniobate were produced from hydrothermal processing of titanium alkoxide, hydrous Nb_2O_5 , and TMAOH in aqueous solution. The water was then evaporated and the TMA salts crystallized from alcohol, usually methanol. The clusters with different Nb : Ti ratios were obtained from proportionally different ratios in the precursor mixture. As mentioned prior, the Ti always adopts the sites with no terminal oxygens. The evolution from the decametallates to the $[\text{Ti}_{12}\text{Nb}_6\text{O}_{44}]^{10-}$ cluster is a beautiful illustration of how one might systematically build larger and larger clusters related to the hexametallate *via* Nb : Ti ratio. Recognizing this when we originally synthesized the Na-salt of $[\text{Ti}_2\text{Nb}_8\text{O}_{28}]^{8-}$,³⁰ we too attempted to obtain clusters of different Nb : Ti ratios, but only with alkali hydroxides as the base. We did not succeed. This suggests the TMA⁺ counterion, with its lower charge-density and larger size, stabilizes clusters with similarly lower charge-densities and/or larger size. These

TMA-titanoniobates all required crystallization from appropriate solvents, which is another synthetically tricky detail of working with alkylammonium counterions: and oftentimes crystallization is the limiting process in identifying new cluster geometries. However, there is increasing recognition of the power of electrospray ionization mass spectrometry (ESI MS) as a tool to identify clusters in solution without the benefit of crystallization. An exemplary use of ESI-MS in polyniobate chemistry is detailed in the next section.

6. pH-controlled evolution of polyniobate geometries

By synthetic strategies, as well as similarity in geometry, there is an apparent relationship between the hexaniobate and decaniobate. In a ¹⁷O NMR study, Villa *et al.*⁶⁸ observed the conversion of the decaniobate to hexaniobate at pH~12.5. This is not surprising for two reasons: (1) Clusters with lower charge-density are less stable in more alkaline conditions (decaniobate = 0.16; hexaniobate = 0.32; see Table 1) and (2) the decaniobate is likely to be only metastable in aqueous conditions in general, in that it is synthesized readily only in alcohol. By ESI-MS, a heptaniobate ion, $[\text{Nb}_7\text{O}_{22}]^{9-}$ was observed as an intermediate in the conversion from decaniobate to hexaniobate.⁶⁸ This heptaniobate unit was identified two years prior in solid-state structures,^{36,56} confirming its viability. This collection of studies represents a rare example in polyniobate chemistry of identifying the link between cluster geometries, altered by pH control.

The question then arises as to what synthetic conditions are optimal for isolating the intermediate heptaniobate (and by inference, other potentially metastable fragments); and more importantly, how can we utilize this knowledge to further expand polyoxoniobate chemistry? The heptaniobate (Fig. 8a) can be considered a hexaniobate with an additional NbO_6 octahedron sharing one face of the superoctahedral hexaniobate, much in the fashion that the alkalis bond as described prior. The heptaniobate has almost identical charge density as hexaniobate (0.31 *vs.* 0.32). However, what probably makes it less stable and thus rarer is this additional NbO_6 octahedron has three terminal oxygen ligands, which is why it condenses as a portion of a larger cluster in both the solid-state structures reported. Both from our laboratory³⁶ and the group of Niu,⁵⁶ $[\text{Nb}_{24}\text{O}_{72}\text{H}_9]^{15-}$ was structurally characterized (Fig. 8b). Briefly, it features three heptaniobate clusters linked in a ring by three additional (NbO_6H) polyhedra, where these three

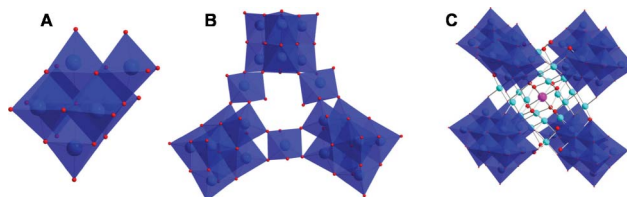


Fig. 8 (a) $[\text{Nb}_7\text{O}_{22}]^{9-}$ heptaniobate. This PONb can be viewed as a hexaniobate Lindqvist ion with a NbO_6 octahedron bonded to one face of the superoctahedron (*via* three bonds, sharing three edges). (b) $[\text{Nb}_{24}\text{O}_{72}\text{H}_9]^{15-}$ consisting of three heptaniobate anions linked by three additional NbO_6H octahedra. (c) Eight heptaniobate anions arranged on the corners of a cube, supporting a central Cu-O cluster with a single K^+ (pink sphere) in the center. The blue octahedra are NbO_6 , turquoise spheres are Cu, and red spheres are O.

plus the three niobate octahedra outside the hexaniobate units comprise the 6-member ring. In both structures, the Nb_{24} units are dimerized through Cu(II) ethylenediamine (en) complexes, and the anionic dimer is further charge-balanced with Cu(II) -en complexes. Neither structure contains any alkalis, although they were synthesized from Rb^{36} and Na or K^{56} hexaniobate salts. In two additional structures by Niu, eight heptaniobate anions arranged on the corners of a cube support a central Cu-O cluster; and for these K^+ and Na^+ provide charge-balance outside of the cluster assembly (Fig. 8c). The commonality between all of these phases is they were obtained between around $\text{pH}\sim 9\text{--}11$ in aqueous solutions containing Cu(en)_2^{2+} . All were obtained by slow evaporation of the solution in ambient conditions. The pH is lower than that at which hexaniobate is extremely stable, thus providing the opportunity to obtain other niobate clusters. Breakdown of the hexaniobate to provide monomers and subsequent association into the heptaniobate is a likely pathway. Similarly in Casey's experiments, breakdown of decaniobate to hexaniobate, also releasing monomers to further combine with hexaniobate, was the supposed mechanism.⁶⁸ Additionally, the monovacant Lindqvist ion, $[\text{Nb}_5\text{O}_{18}]^{11-}$ fragment has also been isolated as part of a complex composed of the plenary Lindqvist ion, and copper-diamine coordination complexes.⁵⁶ The isolation of this specie was similar to the heptaniobate phases: from a $\text{pH}\sim 9\text{--}11$ mixture of the alkali hexaniobate and copper amine at ambient conditions. One might conclude that the Cu -amine complexes are ideal counterions that not only serve to charge-balance but also stabilize *via* bonding to these larger cluster assemblies, which form by partial breakdown of hexaniobate in the appropriate pH range.

The isolation of a TBA salt of a decaniobate dimer, $[\text{Nb}_{20}\text{O}_{54}]^{8-}$ (icosaniobate; Fig. 7e)⁷² can also be related to Casey's decaniobate solution studies. Casey's group noted that the terminal oxygen sites at which the two decaniobate units are joined in the dimer were the most basic, and underwent the most rapid proton-induced ligand exchange,⁶⁸ which obviously provides an opportunity for the dimerization reaction to occur. Although the original synthesis of icosaniobate was presumably from hexaniobate, a more recent study revealed that the decaniobate could be reversibly dimerized to form the icosaniobate.⁷³ Furthermore, new structures of the decaniobate⁷³ revealed H-bonding of water to these basic Nb-O_{yl} sites, also corroborating with solution reactivity data. These combined results, solid-state and solution, reiterate the importance of solution studies for providing information to further broaden this relatively underdeveloped chemistry.

7. The role of hydrothermal synthesis in polyniobate chemistry

Many of the polyniobate salts and framework complexes described in this article could not have been realized without hydrothermal processing. Although hydrothermal synthesis was mentioned prior, particularly in section 3.1 in reference to obtaining the niobate Keggin-derivatives, a brief separate discussion is therefore warranted. Simply put, hydrothermal processing provides solubility for niobium oxide where it is necessary to avoid the alternative; high alkalinity. The combination of high heat and a pH range of $\sim 10\text{--}12.5$ serves to both destabilize (dissociate) the ubiquitous Lindqvist ion while retaining the solubility of the dissociation

products. Thus, alternative polyniobate geometries may assemble from these dissociated fragments. Similarly, the Ti -substituted Lindqvist derivatives described in section 5 were all obtained by hydrothermal synthesis; again, to solubilize titanium oxide and niobium oxide without necessarily using extreme alkalinity; conditions under which the Lindqvist ion is stable. Finally, large polyniobate clusters described in the following section were also obtained by hydrothermal synthesis. Since hydrothermal processing is somewhat of a 'blackbox' technique - the reaction is invisible to *in situ* human observation - we can only guess exactly what occurs over the course of the reaction. For instance, do the PONb salts or framework compounds crystallize before cooling the reactor? Do Lindqvist ions and other cluster geometries co-exist in solution? Does the Lindqvist ion form as an intermediate to other cluster geometries? *In situ* monitoring of the hydrothermal reaction pathways by X-ray diffraction (precipitated solids) or UV-vis spectroscopy (solution) is certainly not unprecedented, and might provide answers to some of these questions.

8. Two miscellaneous examples of polyoxoniobate chemistry

Although some developments of PONb chemistry defy characterization within the realm of this paper because they are isolated examples, they are certainly worthy of mention because they may point the way to future developments. The first example is the $[\text{H}_{10}\text{Nb}_{31}\text{O}_{93}(\text{CO}_3)]^{23-}$ and $[\text{HNb}_{27}\text{O}_{76}]^{16-}$ (Nb_{31} and Nb_{27} , respectively) clusters reported recently by Cronin⁷⁴ (Fig. 9). These clusters are mixed Na/K salts, and were synthesized hydrothermally: although crystallization involved either slow evaporation of the solvent from the mother-liquor, or diffusion of alcohol into the mother liquor. They are more similar to the Keggin ion than the Lindqvist ion in that they have corner-linked polyhedra in addition to edge-sharing polyhedra. These cluster geometries are unprecedented in any POM chemistry and are the largest isopolyniobates reported to date. Furthermore, both feature pentagonal bipyramid and square pyramid Nb -geometries, unprecedented in PONb chemistry. The carbonate ligand of Nb_{31}

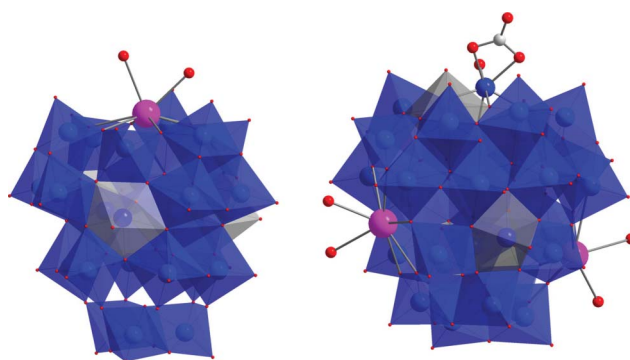


Fig. 9 Left: $[\text{HNb}_{27}\text{O}_{76}]^{16-}$ and right: $[\text{H}_{10}\text{Nb}_{31}\text{O}_{93}(\text{CO}_3)]^{23-}$ (Nb_{27} and Nb_{31} , respectively). These are the largest Keggin-like polyoxoniobates that have been produced to date. Both feature the unusual pentagonal bipyramid NbO_7 geometry and square pyramid NbO_5 . Both also have K^+ in a pocket, and Nb_{31} features a single niobium with a carbonate ligand replacing the terminal oxygen ligand. The niobium octahedra and square pyramids are blue, the pentagonal bipyramids are highlighted in gray and K^+ is pink spheres.

was presumably adsorbed from air during the crystallization process. Both also contain K^+ in lacunary-like pockets, similar to the Na^+ in the pocket of (2), see Fig. 5. These unique PONb clusters can only be obtained in the presence of dibenzylthiocarbamate, but neither this organic anion nor its decomposition byproducts are located in their crystal lattices. While the exact role of this crucial anion could not be determined, the take-home message is that spectator ligands such as dibenzylthiocarbamate, if explored in a systematic fashion, may allow for the isolation of other unprecedented PONb geometries.

The second example is a mineral called menezesite found in Brazil with an ideal formula $Ba_2MgZr_6[BaNb_{12}O_{42}] \cdot 12H_2O$ (with minor substitutions of K, Ca, rare-earths, Mn, Fe, Ti, Th, Ta and Si).⁷⁵ The PONb cluster, $[BaNb_{12}O_{42}]^{22-}$ featured in this mineral has six sets of two face-sharing NbO_6 octahedra that are arranged in an octahedral fashion around the central 12-coordinate barium (Fig. 10). While repeated attempts to synthesize some analogue of this heteropolyniobate did not yield anything,⁷⁶ a tungstate analogue, $[MgW_{12}O_{42}]^{10-}$ was obtained over two decades ago as a Mn, Fe, Co or Ni salt by simply heating the pure metal powders plus tungstic acid in boiling water.⁷⁷ There are three main reasons the analogous synthesis of this simple reaction would not work with niobate: (1) niobate is not soluble as an acid, (2) $Nb(v)$ does not have easily accessible redox chemistry that is probably necessary to dissolve the metal powders as cations, and (3) the aqueous alkaline conditions required to dissolve niobate would result in the precipitation of the transition metals as hydroxides. Another point to consider is that perhaps $Nb(v)$ is too large with too high charge to readily form phases with face-sharing octahedra, except under the high-pressure conditions in which this mineral was formed. However, this mineral heteropolyniobate illustrates an important point in relation to PONb chemistry: perhaps investigating synthetic conditions in which face-sharing of polyhedra is obtainable would be another route to expand

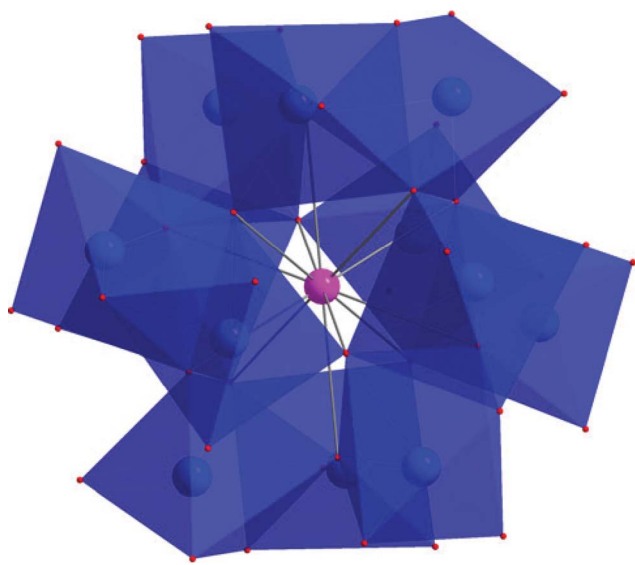


Fig. 10 $[BaNb_{12}O_{42}]^{22-}$ PONb observed in the mineral menezesite from Brazil. This unusual PONb formed in nature features six sets of face-sharing Nb -octahedra arranged in an octahedral fashion around a central Ba^{2+} . The blue octahedra are NbO_6 and the pink sphere is Ba^{2+} .

accessible PONb geometries. In particular, high-pressure syntheses or flux syntheses might be explored.

9. Conclusions

Potentially the most important outcome of writing this Perspective Article is identifying the logical paths forward to continue expanding polyoxoniobate (and also polyoxotantalate) chemistry. In general, synthetic investigations with the most potential are those that utilize organic counterions; in both aqueous and non-aqueous media. The miscellaneous works of Casey, Niu and others show that these can indeed produce larger, more intricate clusters and new cluster geometries. The trick to obtaining these is often crystallization, but identification in solution *via* techniques such as ESI-MS could greatly expedite success. Heteropolyniobates (*i.e.* Keggin derivatives) are still greatly underdeveloped. These need to be characterized better in solution, to understand their formation process and behavior. Again, different counterions should be investigated more in-depth. In addition to the organic counterions, Cs and Rb should be considered for the Keggin derivatives; particularly since Cs and Rb provide such great solubility to the Lindqvist ions. Finally, as mentioned in the prior section, high pressure or flux syntheses may produce new ways to assemble niobate polyhedra that are not readily obtainable in less extreme conditions.

Finally, what would spur more rapid development of this chemistry would be the potential for applications. This is another challenge for POM chemists, in that some of the more useful characteristics of POW, POMo and POV are not easily accessible for PONb and POTa: in particular redox chemistry, acidic behavior, colorometric response, catalysis, and metal binding capabilities. Rather than struggling to identify behavior in PONb chemistry that is readily obtainable in more traditional POM chemistry, it would serve us well to exploit some of the more unique characteristics of PONb (POTa) chemistry that are identified in this review. For instance, the alkaline nature of the dissolved Lindqvist ions may be exploited in some base catalysis reactions or CO_2 separation/sequestration. The strong and unique ion-association/solubility trends may be further explored in supermolecular assembly, surface functionalization, or ion separations. Finally, while microbiological applications did not prove too promising in initial studies, this may change as a greater diversity of PONb clusters become available through creative and tenacious synthetic research.

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