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An ^{17}O NMR Study of Hydrolyzed Nb(V) in Weakly Acidic and Basic Aqueous Solution

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Abstract

Time-dependent ^{17}O NMR spectra of basified decaniobate ($\text{Nb}_{10}\text{O}_{28}^{6-}$) solutions displayed intense resonances assigned to the well-known protonated hexaniobate anion ($\text{Nb}_6\text{O}_{19}^{8-}$) and two other species identified as heptaniobate ($\text{Nb}_7\text{O}_{22}^{9-}$) and protonated tetracosaniobate ($\text{Nb}_{24}\text{O}_{72}^{24-}$) anions. The decaniobate ion showed no sign of protonation from pH 6 – 10, in contrast with the hexaniobate ion which was protonated at doubly-bridging oxygen sites at pH 10–13. Most (> 90%) of the heptaniobate formed 1 h after basification was transformed into other species after 3 weeks. Tetracosaniobate was formed reversibly from decaniobate, but only when KOH, NaOH and $[(\text{CH}_3)_4\text{N}]\text{OH}$ were employed; none was observed after basification with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$. Moreover, far more tetracosaniobate was formed from KOH than from $[(\text{CH}_3)_4\text{N}]\text{OH}$. This effect was attributed to a tetracosaniobate cation binding site that binds K^+ more readily than $(\text{CH}_3)_4\text{N}^+$ but is too small to accommodate $(n\text{-C}_4\text{H}_9)_4\text{N}^+$.

Keywords

Polyoxometalates; Niobium; ^{17}O NMR

Introduction

Hatchett^[1] was the first to investigate aqueous niobate chemistry when, in 1802, he prepared strongly basic aqueous solutions of what is today known to be Nb(V). He acidified these solutions, forming a white precipitate now called “niobic acid,” and demonstrated that this material dissolved in strong base to form aqueous solutions having the same properties as the original basic solutions. Reproducible conditions for crystallization of polyniobates from aqueous solution were not described until 1866 when Marignac reported a salt having the empirical composition $\text{K}_8\text{Nb}_6\text{O}_{19} \cdot 16\text{H}_2\text{O}$.^[2] Reliable preparations of the remaining alkali metal hexametalate salts followed in the early twentieth century.^[3] Solid state structural characterization of the hexaniobate ion $\text{Nb}_6\text{O}_{19}^{8-}$ was achieved in 1952^[4] (see Figure 1a), and in the following decades this structure was shown to persist in aqueous solution using a variety of in situ techniques, including potentiometric titration,^[5] light scattering,^[6] ultracentrifugation,^[6] Raman scattering,^[7] and ^{17}O NMR spectroscopy.^[8]

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Dedicated to Prof. Michael T. Pope on the occasion of his 80th birthday

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Supporting Information. Notes on preparation of the decaniobate ion, preparation of niobic acid, preparation of TMA **1** hexahydrate from niobic acid, NMR spectra and IR spectra (Figures S1–S3).

Until the 1970's, isopolyniobate and heteropolyniobate^[9] synthesis was restricted to strongly basic aqueous solution, since acidification of basic hexaniobate solutions persistently yielded insoluble "niobic acid" or what Süe^[10] called (colloidal) "pseudosolutions." The breakthrough into weakly acidic and weakly basic solution was achieved independently through nonaqueous syntheses of water-soluble tetramethylammonium salts by Dosch^[11] in 1971 and Marty, Abdmeziem, and Spinner^[12] in 1976. These materials proved to contain the decaniobate ion $\text{Nb}_{10}\text{O}_{28}^{6-}$ (**1**) which was structurally characterized in 1977 by Graeber and Morosin^[13] (see Figure 1b). Stability of the decaniobate ion in aqueous and nonaqueous solution was established much later using ^{17}O NMR spectroscopy.^[14, 15]

Several years ago, Marek studied the acidification and basification of aqueous decaniobate solutions using ^{17}O NMR spectroscopy, and he was able to identify two new polyniobates designated polyniobate X and polyniobate Y.^[14] These species could not be formulated, as the only structurally-characterized polyniobates known at the time were the hexaniobate and decaniobate ions. Since then, further isopolyniobates have been prepared from aqueous and nonaqueous solution and structurally characterized in the solid state,^[16–21] thus allowing for formulation of polyniobates X and Y - the subject of the present paper.

Results

Reaction of the Decaniobate Ion with Aqueous Acid and Base

Aqueous solutions of $[(\text{CH}_3)_4\text{N}]_6\text{Nb}_{10}\text{O}_{28}$ (TMA **1**) were slightly acidic (pH~6). After two months' storage at ambient temperature, ca. 0.05 M solutions remained clear, showing no Tyndall effect, and their ^{17}O NMR spectra revealed no evidence of decomposition. Such was not the case, however, if these solutions were acidified or basified.

Addition of strong acid to aqueous solutions of TMA **1** yielded precipitates of "niobic acid." Slightly acidic solutions aqueous solutions 0.02 M in TMA **1** could be prepared, however, by mixing solutions of TMA **1** with appropriately buffered acetate and phosphate solutions. Solutions with pH > 5 remained clear for at least 12 h after preparation. Precipitates and/or colloids, detected visually by the Tyndall effect, appeared within seconds at pH < 4.

Aqueous solutions of TMA **1** remained clear for at least 6 weeks at ambient temperature after addition of KOH and $[(\text{CH}_3)_4\text{N}]\text{OH}$ (TMAOH), and an ^{17}O NMR study was performed in an effort to identify the species present these solutions. Eight solutions were prepared by adding 1, 3, 4, and 10 equiv of KOH and TMAOH to TMA **1** such that the total niobium concentration was in each case 0.6 M. The spectrum of each solution was recorded 1 h and 3 weeks after sample preparation such that a total of 16 spectra were obtained. The solution pH, both after 1 h and after 3 weeks, was 10 after addition of 1 equiv of base, 11 after addition of 3 and 4 equiv of base, and 13 after addition of 10 equiv of base.

Both decaniobate and hexaniobate resonances appeared in ^{17}O NMR spectra of solutions prepared by addition of aqueous KOH and TMAOH to TMA **1**. The intense decaniobate resonances labeled A–G in Figure 2a and e were observed only in those spectra measured 1 h after addition of 1 equiv of base, and they were assigned to the oxygen centers in $\text{Nb}_{10}\text{O}_{28}^{6-}$ as labeled in Figure 1b by analogy with the assignment of $\text{V}_{10}\text{O}_{28}^{6-}$ resonances given in reference [22]. Their chemical shifts, linewidths, and relative intensities were the same as those observed at lower pH. When spectra of these two solutions were measured 3 weeks later, the decaniobate resonances had lost >95% of their original intensity. Only three polyniobate resonances were observed after addition of 10 equiv KOH (see Figure 2d), and these resonances had the same chemical shifts and relative intensities observed for the hexaniobate ion in aqueous solutions of $\text{K}_7\text{HfNb}_6\text{O}_{19}$.^[8] They were therefore assigned to the

three types of symmetry-equivalent oxygen atoms in the hexaniobate ion labeled a–c in Figure 1a. Hexaniobate resonances were observed in all 16 of the spectra recorded in the present study, but their chemical shifts and linewidths varied according to which base and how much base was added (see Figure 2 and Table 1). After a given time interval, their intensities increased relative to the intensities of other polyniobate resonances with addition of increasing amounts of a given base.

Spectra of polyniobate solutions prepared by addition of KOH and TMAOH to aqueous TMA **1** displayed numerous ^{17}O NMR resonances that could not be assigned to the hexaniobate and decaniobate ions. Among the most intense of these resonances, two sets of resonances exhibited similar chemical shifts, lineshapes, and relative intensities under different experimental conditions, suggesting their assignment to two specific polyoxoniobates designated polyniobate X and polyniobate Y.

Six resonances labeled y1 – y6 were assigned to polyniobate Y, four of which are evident in Figure 2g. They were observed at 28(y1), 272(y2), 437(y3), 449(y4), 627(y5), and 636(y6) ppm 1 h after addition of 10 equiv of TMAOH. Unless obscured by other resonances, all but one of these resonances had the same chemical shifts (within 2 ppm) and linewidths (within 10 Hz) in all four of the spectra measured 1 h after addition of 3 and 4 equiv of TMAOH and KOH. In the spectrum measured 1 h after addition of 3 equiv of TMAOH and only in this spectrum, resonance y3 appeared at 431 ppm and had a significantly larger linewidth than it did in the other three spectra. In all cases, resonance y4 had twice the intensity of resonance y3 and resonances y5 and y6 had equal intensity. After 3 weeks, all of the polyniobate Y resonances observed after 1 h had lost >90% of their original intensities, indicating that most of the polyniobate Y formed initially was converted into other polyniobates (see, for example, Figure 3).

Nine of the resonances assigned to polyniobate X were observed 1 h after addition of 3 equiv of TMAOH, and their chemical shifts were 29(x1), 277(x2), 306(x3), 439(x4), 443(x5), 451(x6), 472(x7), 476(x8), and 521(x9) ppm. Polyniobate X resonances were most intense in the four spectra measured 1 h and 3 weeks after addition of 3 and 4 equiv of KOH, where an additional δ 653 resonance was observed (see Figure 3). In these spectra, resonances x1–x9 had chemical shifts slightly different from those observed after addition of TMAOH such that resonances x7 and x8 could not be resolved, and only nine distinct resonances were observed at 31(x1), 279(x2), 302(x3), 444(x4), 449(x5), 454(x6), 475(x7/x8), 512(x9), and 653(x10) ppm. Polyniobate X resonances were not observed in any of the spectra measured after addition of 10 equiv of base. Solutions containing the same amount of base always showed more intense polyniobate X resonances after 1 day when KOH was used instead of TMAOH; the same held true after 3 weeks. Since the linewidths of the polyniobate X resonances were large, their relative intensities were difficult to quantify, but resonance x2 was significantly more intense than resonance x3, resonances x4 and x6 were more intense than resonance x5, and resonances x7, x8, and x9 had about the same intensity (see Figure 3). Polyniobate X resonances displayed the greatest intensity relative to hexaniobate resonances in the spectrum measured 3 weeks after addition of 3 equiv of KOH, where polyniobate X and hexaniobate resonances lying in the δ 350–550 chemical shift region had comparable intensities. In this spectrum, several very broad resonances were also observed in the 600 to 700 ppm region, but these were difficult to distinguish from the rolling baseline, and their apparent intensities and chemical shifts were sensitive to small changes in the phase correction applied to Fourier transformed spectra.

Oxygen-17 NMR spectra of aqueous polyniobate solutions were temperature-dependent. For example, no decaniobate resonances were detected in the spectrum measured six weeks after addition of 3 equiv of TMAOH to TMA **1** when the solution was stored at ambient

temperature, but all seven decaniobate resonances were observed at 75 °C after the aged solution was stored at 75 °C for 30–60 min. The decomposition of decaniobate was therefore a reversible process.

In order to obtain a significantly larger amount of pH-dependent ^{17}O NMR data without requiring a correspondingly large amount of ^{17}O enriched water, a set of ^{17}O NMR spectra was measured during a titration of aqueous TMA **1** with NaOH at ambient temperature. The results of this titration are summarized in Figure 4, where the chemical shifts of the most intense resonances observed after addition of 1–10 equiv of base are indicated. The chemical shift scale shown on the right side of Figure 4 was derived from the displayed chemical shift data in the same fashion employed to derive the polyoxomolybdate chemical shift scale provided in reference [23]. Increments of NaOH were added at 1 h intervals and spectra were recorded immediately after addition of each increment. The first 5 increments each contained 0.2 equiv of base per decaniobate ion, and the final 9 increments contained 1 equiv each; the total niobium concentration $[\text{Nb}]_{\text{tot}}$ decreased from 0.33 M to 0.27 M during the course of the titration. Under these conditions, the solution pH was 7 after addition of 0.2 equiv of NaOH, 8–9 after addition of 0.4–2.0 equiv, 10–12 after addition of 3.0 to 6.0 equiv, and >12 after addition of 7.0 to 10.0 equiv. Resonances slightly less intense than those included in Figure 7 were observed at 456 ppm after addition of 0.2 to 3.0 equiv of NaOH; at 446, 666 and 676 ppm after addition of >4.0 equiv of NaOH; and at 455, 465 and 642 ppm after addition of >6.0 equiv of NaOH. A very weak resonance became apparent in the 180–190 ppm region after addition of >1 equiv of base, and its chemical shift and intensity increased as the titration proceeded. This resonance was assigned to carbonate/bicarbonate ions resulting from exposure of the NMR sample to atmospheric CO_2 each time an increment of base was added (see below).

In order to more fully investigate the possibility that basification products might be cation-dependent, three solutions of 0.04 M aqueous $[(n\text{-C}_4\text{H}_9)_4\text{N}]_6\text{Nb}_{10}\text{O}_{28}$ (TBA **1**) were prepared containing 3, 4, and 10 equiv of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ (TBAOH). The ^{17}O NMR spectra of these three solutions were then recorded 5 h, 8 days and 22 days after preparation. In each spectrum, hexaniobate resonances were observed, but polyniobate Y resonances were observed only in those spectra measured 5 h after addition of 3 and 4 equiv of TBAOH. Polyniobate X resonances were not observed in any of the nine spectra.

Observation of the Decatantalate Ion

Numerous attempts were made to prepare tetraalkylammonium salts of the decatantalate ion $\text{Ta}_{10}\text{O}_{28}^{6-}$ by replacing pentaethylniobate with pentaethyltantalate in procedures used to prepare decaniobate salts (see Experimental Section), but these attempts were uniformly unsuccessful. Under some conditions, ^{17}O NMR spectra suggested formation of the $\text{Ta}_{10}\text{O}_{28}^{6-}$ ion in solution, but these solutions clearly contained other species as well. The spectrum shown in Figure 5, for example, contains eight relatively narrow resonances in addition to the water solvent resonance and several extremely broad resonances. Seven of these eight resonances, those labeled A–G in Figure 4, form a pattern very similar to the pattern of resonances characteristic of the decaniobate ion (see Figure 2e).

Discussion

The Hexaniobate Ion in Aqueous Solution

When aqueous solutions of the hexaniobate ion $\text{Nb}_6\text{O}_{19}^{8-}$ are acidified, $\text{Nb}_6\text{O}_{19}\text{H}^{7-}$ ($\text{p}K_{\text{a}1} \approx 12\text{--}13$), $\text{Nb}_6\text{O}_{19}\text{H}_2^{6-}$ ($\text{p}K_{\text{a}2} \approx 10\text{--}11$), and $\text{Nb}_6\text{O}_{19}\text{H}_3^{5-}$ ($\text{p}K_{\text{a}3} \approx 9\text{--}10$) are formed.^[5, 24] and single crystal X-ray diffraction studies of the monoprotonated,^[25] diprotonated,^[25b, 26] and triprotonated^[27] species indicate that doubly bridging oxygen atoms, not terminal oxygen

atoms, are protonated in the solid state. It comes then as no surprise that ^{17}O NMR spectra of basified aqueous decaniobate solutions show that the hexaniobate is formed, the hexaniobate ion is stable in protonated form in aqueous solution, and hexaniobate protonation occurs predominantly at doubly bridging oxygen atoms. These conclusions may be drawn from the hexaniobate chemical shift data provided in Table 1, where the terminal oxygen resonance is seen to shift downfield and the doubly bridging oxygen resonance shift upfield with decreasing pH. Behavior of this type is characteristic of protonation at doubly bridging oxygen atoms in early transition metal polyoxoanions and has been observed in related group V polyoxometalates such as the hexametalates $\text{Nb}_2\text{W}_4\text{O}_{19}^{4-}$ [28] and $\text{V}_2\text{W}_4\text{O}_{19}^{4-}$ [29], the decavanadate $\text{V}_{10}\text{O}_{28}^{6-}$ [30], and the hexavanadate derivative $\text{V}_6\text{O}_{13}[(\text{OCH}_2)_3\text{CR}]_2^{2-}$. [31, 32] Linewidths of the doubly bridging oxygen resonances are also temperature- and pH-dependent, decreasing significantly with increasing temperature and with increasing pH. Although this is the behavior expected when rapid proton transfer averages the environments of protonated and unprotonated oxygen atoms, [30b] it is far from diagnostic since ^{17}O NMR lineshapes are also influenced directly by ^{17}O quadrupolar relaxation rates [8] and indirectly by ^{93}Nb quadrupolar relaxation rates through ^{17}O - ^{93}Nb spin-spin coupling. [22]

Several ^{17}O NMR spectra of aqueous sodium hexaniobate solutions used for oxygen-exchange studies have been reported [25b, 35] that differ significantly from hexaniobate spectra reported here and elsewhere [8, 36] by the presence of an additional resonance at 182–187 ppm assigned to protonated doubly bridging ONb_2 oxygen atoms. In the present study, a ~185 ppm resonance was only observed in spectra of solutions that had been exposed to atmospheric CO_2 , that is, spectra measured during the titration of aqueous TMA decaniobate with NaOH described above. The ~185 ppm resonance was assigned to CO_3^{2-} and CO_3H^- ions in dynamic equilibrium for two reasons. First, its chemical shift displayed pH dependence characteristic of the carbonate ion, [37] increasing from δ 186 at pH 8–9 to δ 194 at pH 10–12 as a consequence of bicarbonate deprotonation ($\text{p}K_{\text{a}2} \approx 9\text{--}10$ [37–38]). Second, its intensity increased as the titration progressed, reflecting increasing amounts of carbonate contamination, ultimately achieving about 1/5 the intensity of the hexniobate ONb_6 resonance. Villa, et al. [39] have reported that the carbonate ion affects oxygen rates of exchange between hexametalates, and as a result, oxygen exchange studies employing carbonate-contaminated solutions should be viewed with caution. [40]

The Decaniobate Ion in Aqueous Solution

The most striking feature of aqueous decaniobate ^{17}O NMR resonances is the insensitivity of their chemical shifts to pH: the chemical shifts of all seven resonances remain constant from pH 6 to pH 10. Given that ^{17}O NMR chemical shifts of early transition polyoxometalates are known to be extremely sensitive to protonation (see above), this indicates that protonated decaniobates are not present at significant concentrations under the conditions employed in the present study.

Identification of Polyniobate X and Polyniobate Y

At present, nine isopolyniobates have been structurally characterized in the solid state using X-ray crystallography, some of them in protonated form: $\text{Nb}_4\text{O}_{12}^{4-}$, [43] $\text{Nb}_6\text{O}_{19}^{8-}$, [4] $\text{Nb}_7\text{O}_{22}^{9-}$, [17] $\text{Nb}_{10}\text{O}_{28}^{6-}$, [13] $\text{Nb}_{12}\text{O}_{40}^{14-}$, [44] $\text{Nb}_{20}\text{O}_{54}^{8-}$, [18] $\text{Nb}_{24}\text{O}_{72}^{24-}$, [17a, 19] $\text{Nb}_{27}\text{O}_{76}^{17-}$, [20] and $\text{Nb}_{32}\text{O}_{96}^{32-}$. [19b] Four of these can be eliminated as identities of polyniobates X and Y: $\text{Nb}_4\text{O}_{12}^{4-}$ is water-sensitive; $\text{Nb}_{20}\text{O}_{54}^{8-}$ is obtained by acidification, not basification, of $\text{Nb}_{10}\text{O}_{28}^{6-}$; and ^{17}O NMR spectra of $\text{Nb}_6\text{O}_{19}^{8-}$ and $\text{Nb}_{10}\text{O}_{28}^{6-}$ have already been assigned. Two other candidates, $\text{Nb}_{12}\text{O}_{40}^{14-}$ and $\text{Nb}_{27}\text{O}_{76}^{17-}$, can be ruled out because they do not contain six-fold bridging oxygen atoms whereas both polyniobates X

and Y each display ONb₆ resonances (see Figure 4). This leaves only Nb₇O₂₂⁹⁻, Nb₂₄O₇₂²⁴⁻, and Nb₃₂O₉₆³²⁻ as viable candidates.

As shown in Figure 4, six resonances labeled y1 – y6 were assigned to polyniobate Y: one ONb₆ resonance, one ONb₃ resonance, two ONb₂ resonances with a 1:2 intensity ratio, and a single ONb resonance. These resonances may be assigned to the Nb₆O₁₉⁸⁻ subunit of the C_{3v} Nb₇O₂₂⁹⁻ structure shown in Figure 1c where the y1 resonance is assigned to the Y1 oxygen atom, y2 is assigned to the Y2 oxygen atoms, y3 to the Y3 atoms, y4 to the Y4 atoms, etc. Only six of the seven anticipated resonances were observed, however, indicating either that the resonance for the third type of ONb oxygen atoms could not be identified or that polyniobate Y is in fact not Nb₇O₂₂⁹⁻. For example, polyniobate Y could be Nb₁₃O₃₈¹¹⁻ = Nb(Nb₆O₁₉)₂¹¹⁻, an isopolyniobate analogue of the D_{3d}-Mn(Nb₆O₁₉)₂¹²⁻ heteropolyanion.^[9c] Three further observations are relevant here. First, the C_{3v} hexaniobate derivatives (Nb₆O₁₉)Mn(CO)₃⁷⁻,^[36] (Nb₆O₁₉)Re(CO)₃⁷⁻,^[36] and (Nb₆O₁₉)Ru(*p*-cymene)₆⁶⁻^[45] display ¹⁷O NMR spectra very similar to the polyniobate Y spectrum. Second, Villa, et al.^[15a] have also observed four transient ¹⁷O NMR resonances upon basification of ¹⁷O-enriched decaniobate ion in unenriched water, and they too have assigned these resonances to the heptaniobate ion. They also observed fragments of the Nb₇O₂₂⁹⁻ anion ex situ in ESI mass spectra. Finally, Niu, et al. dissolved heptaniobate salts into water, measured Raman spectra of the solutions formed, and observed only hexaniobate ions, not heptaniobate ions, in their Raman spectra.^[17a]

The (protonated) Nb₂₄O₇₂²⁴⁻ and Nb₃₂O₉₆³²⁻ frameworks have very similar cyclic structures where Nb₇O₂₂⁹⁻ units (see Figure 1c) are linked together as indicated in Figure 1d. In the Nb₂₄ case, three Nb₇ units are linked together by *trans*-NbO(OH₂)³⁺ groups such that a cyclic, trimeric C_{3v}[(NbO₂)(Nb₇O₂₂)]₃²⁴⁻ metal-oxygen framework is formed where each Nb₇O₂₂⁹⁻ subunit retains local C_s symmetry. Polyniobate X can be assigned the Nb₂₄O₇₂²⁴⁻ framework structure since the ONb₆ resonance x1 can be assigned to the ONb₆ oxygen atom labeled X1 in Figure 1d; the two ONb₃ resonances, x2 and x3, can be assigned to the ONb₃ oxygen atoms labeled X2 and X3; the six ONb₂ resonances x4–x9 can be assigned to six of the seven ONb₂ oxygen atoms labeled X4–X10; and the ONb resonance x10 can be assigned to one of the five types of terminal oxygen atoms in the structure. In the Nb₃₂ case, four Nb₇ units are linked together by *cis*-NbO₂ groups such that a cyclic tetrameric C_{2h}[(NbO₂)(Nb₇O₂₂)]₄³²⁻ framework is formed where each Nb₇O₂₂⁹⁻ subunit has no rigorous local symmetry whatsoever. The Nb₃₂O₉₆³²⁻ framework is therefore expected to display a far more complex spectrum than the Nb₂₄O₇₂²⁴⁻ framework, but since the local Nb₇O₂₂⁹⁻ symmetry approximates C_s symmetry, the possibility that polyniobate X has the Nb₃₂O₉₆³²⁻ framework structure cannot be ruled out. This possibility is unlikely, however, given the relatively narrow linewidths observed for some of the ONb₂ resonances, namely, the x4 and x6 resonances (see Figure 3).

Even though water-soluble salts of both anions have been observed ex situ using ESI-MS,^[19b] a choice between the protonated Nb₂₄O₇₂²⁴⁻ and Nb₃₂O₉₆³²⁻ candidates for structural assignment of polyniobate X can also be made by noting that the stability of polyniobate X is very cation-dependent. Titration of TMA 1 with KOH yielded higher concentrations of polyniobate X than titration with TMAOH under the same conditions and titration with TBAOH yielded no detectable amounts of polyniobate X (see above). The Nb₂₄O₇₂²⁴⁻ framework contains a cation binding pocket occupied in the solid state by K⁺ [17a, 19b, 19c] or the ammonium cation of protonated ethylenediamine;^[17a, 19a] the Nb₃₂O₉₆³²⁻ framework contains no such pocket. The Nb₂₄O₇₂²⁴⁻ framework's cation binding pocket has the appropriate dimensions for binding small cations like K⁺ and, less favorably, (CH₃)₄N⁺, but it is too small to accommodate large cations such as (n-C₄H₉)₄N⁺. Polyniobate X is therefore readily identified with the Nb₂₄O₇₂²⁴⁻ framework structure.

There is precedent for this type of behavior in the cyclic $P_5W_{30}O_{110}^{15-}$ anion, which is stable only in the presence of small cations.^[46]

A more detailed assignment of the polyniobate X and polyniobate Y spectra than that given above can be achieved by considering the chemical shift correlation diagram shown in Figure 6. When an electron withdrawing group is bonded to surface oxygen atoms of an early transition metal polyoxoanion, the ^{17}O NMR chemical shifts of π -bonded oxygen atoms at the binding site are displaced upfield while the chemical shifts of the remaining oxygen atoms are displaced downfield, reflecting weaker and stronger π -bonding, respectively.^[47]

Viewing the $Nb_7O_{22}^{9-}$ anion (Figure 1c) as an NbO_3^- adduct of the $Nb_6O_{19}^{8-}$ anion (Figure 1a), (1) the resonance y2 already assigned to heptaniobate Y2 oxygen atoms should lie upfield from the hexaniobate b oxygen atoms' resonance, (2) the resonances y3 and y4 already assigned to the Y3 and Y4 oxygen atoms should be displaced downfield relative to the b oxygen atoms' resonance, and (3) the y5 and y6 resonances already assigned to the Y5 and Y6 oxygen atoms should lie downfield from the c oxygen atoms' resonance. This is in fact observed in all three cases (see Figure 6). Since the Y3 oxygen atoms are more remote from the NbO_3^- binding site than the Y4 oxygen atoms, the resonance assigned to the Y3 oxygen atoms might be expected to lie upfield from the resonance assigned to the Y6 oxygen atoms, and resonances y3 and y4 should be assigned to the Y3 and Y4 oxygen atoms, respectively, as indicated in Figure 6. For the same reason, the resonance assigned to the Y5 oxygen atoms is expected to lie upfield from the resonance assigned to the Y6 oxygen atoms, that is, resonances y5 and y6 should be assigned to the Y5 and Y6 oxygen atoms, respectively, as shown in Figure 6. Note that assignment of the y3 and y4 resonances is consistent with the relative intensities of the resonances y3 and y4. It is also consistent with the observation that resonance y3, not resonance y4, is shifted upfield upon protonation of polyniobate Y: if protonation occurs at twofold-bridging oxygen atom as in $Nb_6O_{19}^{8-}$ (see above) and $Nb_2W_4O_{19}^{4-}$,^[28] the ONb_2 oxygen atoms more remote from the electron withdrawing NbO_3^- group are expected to be more basic.

Viewing the $Nb_{24}O_{72}^{24-}$ anion as a cyclic trimer of $Nb_7O_{22}^{9-}$ anions (Figure 1c) linked together by electron withdrawing $NbO(OH_2)^{3+}$ groups as described above to form a cyclic trimer (Figure 1d), the chemical shifts of the oxygen atoms in the $Nb_{24}O_{72}^{24-}$ anion should correlate with the chemical shifts for the $Nb_7O_{22}^{9-}$ in the same fashion that chemical shifts of $Nb_7O_{22}^{9-}$ and $Nb_6O_{19}^{8-}$ resonances correlated in the case just discussed. The resonances assigned to the X2 and X3 oxygen atoms should lie downfield from the resonance assigned to the Y2 oxygen atoms; the resonance assigned to the X3 oxygen atoms should lie downfield from the resonance assigned to the X2 oxygen atoms, that is, the x2 and x3 resonances should be assigned to oxygen atoms X2 and X3, respectively. This assignment is consistent with the observed relative intensities of the x2 and x3 resonances. The two $Nb_{24}O_{72}^{24-}$ ONb_2 resonances with the smallest (downfield) chemical shifts, resonance x4 and x5, cannot be assigned to oxygen atoms derived from the y4 resonance because they lie upfield from resonance y4, the resonance assigned to the Y4 oxygen atoms. This implies assignment of these two resonances to the Y3-derived oxygen atoms X4 and X5 since the x4 and x5 resonances lie downfield from the y3 resonance. The detailed assignment given in Figure 6 is based on the relative intensities of resonances x4 and x5 (see Figure 3).

Given that the hexaniobate ion is a structural subunit of the heptaniobate ion and that base hydrolysis of decaniobate yields the hexaniobate ion, it is tempting to propose a simple dissociative mechanism for base hydrolysis of the decaniobate ion involving dissociation of the appropriate metal and oxygen centers from the decaniobate ion to generate the hexaniobate ion.^[15a, 48] We have resisted this temptation since ^{17}O labeling studies have

shown that base hydrolysis of the $\text{TiNb}_9\text{O}_{28}^{8-}$ decametallate anion also yields the hexaniobate ion even though the hexaniobate ion is *not* a structural subunit of the $\text{TiNb}_9\text{O}_{28}^{8-}$ ion.^[49] Given that base hydrolysis of the $\text{TiNb}_9\text{O}_{28}^{8-}$ ion does not proceed by a simple dissociative mechanism, there is no compelling reason to believe that base hydrolysis of the isostructural $\text{Nb}_{10}\text{O}_{28}^{6-}$ does.

Conclusions

The present ^{17}O NMR study provides strong evidence for the presence of unprotonated $\text{Nb}_{10}\text{O}_{28}^{6-}$, protonated and unprotonated $\text{Nb}_7\text{O}_{22}^{9-}$, protonated $\text{Nb}_{24}\text{O}_{72}^{24-}$, and protonated $\text{Nb}_6\text{O}_{19}^{8-}$ in aqueous solution upon addition of 0 to 10 equiv of hydroxylic base to aqueous $\text{Nb}_{10}\text{O}_{28}^{6-}$ solutions. This is not to say that ^{17}O resonances arising from other polyniobates were not observed, only that these resonances could not be assigned to specific species. A more complete analysis of decaniobate base hydrolysis will undoubtedly reveal a far richer chemistry than the one described here, particularly in the pH~9 region which has not been addressed in the present study. Finally, it should be noted that aqueous polyniobate chemistry at pH<5 remains to be explored. Just as Hatchett's observation that acidification of strongly basic niobate solutions yielded insoluble "niobic acid" did not imply that polyniobates were unstable at lower pH, so should the observation that acidification of weakly acidic aqueous niobate solutions yielded insoluble "niobic acid" not be taken to imply that polyniobates are intrinsically unstable at pH<5.

Experimental Section

Reagents, Solvents, and General Procedures

Deionized water was obtained from a Millipore MilliQ UV Plus water filtration system. Pentaethyl niobate (99.999%) and pentaethyl tantalate (99.999%) were purchased from Alfa Aesar Company and used without further purification. Sodium hydroxide pellets (ACS Grade), 85 wt % potassium hydroxide pellets (ACS Grade), and concentrated hydrochloric acid (37.5 wt %, Certified ACS Plus Grade) were purchased from Fisher Scientific and used without further purification. Molecular sieves (3 Å Linde Type A, Grace Davison) were activated by heating at 250°C for at least 24 h and cooling under vacuum. Absolute ethanol was purchased from McCormick Distilling Company, Inc. and stored over activated molecular sieves. Acetonitrile (HPLC Grade), Nb_2O_5 (99.99%), tetramethylammonium hydroxide (TMAOH) pentahydrate (97%), aqueous TMAOH (25 wt %), methanolic TMAOH (25 wt %), 1.0 M tetra-*n*-butylammonium hydroxide (TBAOH) in methanol, and ^{17}O -enriched water (2 – 10 at % ^{17}O) were purchased from Aldrich Chemical Company. Acetonitrile was dried over activated molecular sieves, refluxed over CaH_2 , and freshly distilled immediately before use. The concentrations of TMAOH and TBAOH solutions were determined by titration of benzoic acid in 2-propanol using thymol blue indicator. Buffered aqueous solutions were prepared as described in reference [50]. Solutions of TBAOH in acetonitrile were prepared by evaporating a 1 M methanolic TBAOH solution to a viscous liquid on a rotary evaporator at 30–35°C, adding a volume of acetonitrile equal to one half of the original volume of the original methanol solution, repeating this evaporation-dilution cycle a total of seven times, and diluting the resulting solution to ca. 1M in acetonitrile. The hydroxide concentration of this faint yellow, clear solution was determined by titration against benzoic acid in 2-propanol. The absence (<1%) of methanol and other organic impurities was confirmed by ^1H and ^{13}C NMR spectroscopy.

Water, when used as ^{17}O NMR solvent, and all decaniobate ^{17}O NMR samples were enriched in ^{17}O unless specified otherwise. Enriched decaniobate samples were prepared following the procedures described below using ^{17}O -enriched water. All manipulations of ^{17}O -enriched materials described below were performed in a nitrogen atmosphere to

avoid isotopic dilution by atmospheric moisture. Polytetrafluoroethylene NMR sample tube inserts were used for all ^{17}O NMR studies of basic aqueous niobate solutions.

All glassware was cleaned in ethanolic KOH, rinsed with 6 M HCl, rinsed with deionized water, and oven dried for at least 12 h at 120°C before use.

Analytical Procedures

^{17}O NMR spectra were recorded from 10 mm sample tubes at 67.8 MHz using a Varian Unity Inova 500 wide bore spectrometer equipped with a ^{15}N - ^{31}P broadband probe and at 40.7 MHz using a General Electric GN300 wide bore spectrometer equipped with an $^{17}\text{O}\{\text{X}\}$ probe. Chemical shifts in ppm were externally referenced to fresh tap water using the sample replacement method and were reproducible within ± 2 ppm unless stated otherwise. Both 400 MHz ^1H and 100.6 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured using a Varian Unity 400 spectrometer. Infrared absorption spectra were recorded using a Nicolet 205 FT-IR spectrometer. Aqueous pH values were measured using a Fisher Scientific Accumet Model 15 pH meter equipped with a Cole Palmer Gel-Filled Pencil Electrode. Elemental analyses were performed by the University of Illinois School of Chemical Sciences Microanalytical Laboratory. Crystallographic data were obtained from a Bruker SMART CCD diffractometer at the University of Illinois School of Chemical Sciences X-ray Diffraction Laboratory.

Preparation of $[(\text{CH}_3)_4\text{N}]_6\text{Nb}_{10}\text{O}_{28}\cdot 6\text{H}_2\text{O}$ (TMA 1 Hexahydrate) from Pentaethyl Niobate

A 25 mL flask equipped with a stir bar and reflux condenser was charged with 0.701 g of TMAOH pentahydrate (3.59 mmol), 0.29 mL of H_2O (16 mmol), and 10 mL of ethanol. After a clear solution had been obtained, 1.00 mL (1.27 g, 3.98 mmol) of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ was added with stirring, causing the formation of a small amount of white precipitate. The reaction solution was then refluxed for 10 hours. A large amount of white precipitate formed during this time period, and after the system was cooled to ambient temperature, this precipitate was isolated by vacuum filtration through a medium glass frit or Whatman 50 filter paper, washed with cold methanol or ethanol, and dried in air (0.673 g, 88% based on Nb). Anal. Calcd for $[\text{N}(\text{CH}_3)_4]_6\text{Nb}_{10}\text{O}_{28}\cdot \text{H}_2\text{O}$: C, 14.94; H, 4.39; N, 4.35; Nb, 48.14. Found: C, 15.19; H, 4.00; N, 4.07; Nb, 48.27. IR (KBr pellet, 400–1000 cm^{-1} ; see Figure S1b): 433(m), 456(w), 489(sh,w), 505(m), 535(s), 582(w), 710(m,sh), 740(vs), 797(vs), 891(s), 910(m,sh), 951(m), 959(m,sh). ^{17}O NMR (67.8 MHz, H_2O , δ ; see Figure S3a): 724, 706, 557, 476, 470, 311, 69. ^{17}O NMR (67.8 MHz, CH_3OH , δ ; see Figure S2b): 718, 690, 555, 477, 473, 311, 68. TMA 1 hexahydrate was crystallized from methanol solution by adding 0.51 g of material to 1.4 mL of methanol, heating the mixture until a clear solution was obtained, allowing the solution to cool to ambient temperature, filtering the solution through a 0.45 μm polytetrafluoroethylene syringe filter, and storing the solution at 0°C for 48 h. The large, clear, needle-shaped crystals that formed were isolated by filtration on Whatman 50 filter paper, washed twice with portions of cold methanol, and allowed to dry in air (0.42 g, 82%). Crystals removed from the mother liquor were monoclinic, $a = 14.4476(2)$ Å, $b = 18.5686(1)$ Å, $c = 10.9752(2)$ Å, and $\beta = 92.955(1)^\circ$.^[13]

Preparation of Solvated $[(n\text{-C}_4\text{H}_9)_4\text{N}]_6\text{Nb}_{10}\text{O}_{28}$ (Solvated TBA 1)

A 50 mL three-neck, round-bottom flask was charged with a stirring bar, 14 mL of 0.5 M TBAOH in acetonitrile (7.0 mmol), and 0.86 mL H_2O (48 mmol). Pentaethyl niobate (3.0 mL, 12 mmol) was then added with vigorous stirring, and the clear solution obtained after about 10 sec was stored for 48 h at ambient temperature. ^{17}O NMR (40.7 MHz, CH_3CN , δ ; see Figure S3c): 710, 696, 557, 483, 476, 309, 66. Removal of volatiles under vacuum on a rotary evaporator at 30–35°C yielded a clear, slightly yellow, viscous oil that typically had the composition $3[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{O}\cdot 5\text{Nb}_2\text{O}_5\cdot 16\text{CH}_3\text{CN}\cdot 9\text{H}_2\text{O}\cdot 3\text{C}_2\text{H}_5\text{OH}$ according to elemental

analysis. Anal. Calcd for $C_{134}H_{300}N_{22}Nb_{10}O_{40}$: C, 42.47; H, 7.98; N, 8.13; Nb, 24.52. Found: C, 42.76; H, 7.65; N, 7.93; Nb, 24.81. IR (KBr pellet, 400–1000 cm^{-1} ; see Figure S1a): 433(m), 481(sh,w), 507(m), 534(s), 582(w), 619(w), 698(m,sh), 741(vs), 792(vs), 809(vs), 894(s). ^{17}O NMR (40.7 MHz, unenriched H_2O , δ ; see Figure S3d): 719, 703, 554, 472, 465, 307, 65.

Tetra-*n*-butylammonium Polytantalate Solutions

A 50 mL three-neck, round-bottom flask was charged with a stirring bar, 0.314 mL of 1.23 M TBAOH in acetonitrile (0.386 mmol), 27.8 μ L water (1.54 mmol), and 3 mL of acetonitrile. Pentaethyl tantalate (0.100 mL, 0.385 mmol) was then added with vigorous stirring, and the resulting clear solution stored at ambient temperature for 5 h. ^{17}O NMR (40.7 MHz, δ ; see Figure 5): 591, 571, 461, 398, 385, 324, 249, 26.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and Notes

1. Hatchett C. Philos. Trans. R. Soc. London. 1802; 92:49–66.
2. Marignac MC. Ann. Chim. Phys. 1866; 8:5–75.
3. a) Bedford MH. J. Am. Chem. Soc. 1905; 27:1216–1221. b) Balke CW, Smith EF. J. Am. Chem. Soc. 1908; 30:1637–1668.
4. Lindquist I. Ark. Kemi. 1952; 5:247–250.
5. Neumann G. Acta Chem. Scand. 1964; 18:278–280.
6. Nelson WH, Tobias RS. Can. J. Chem. 1964; 42:731–743.
7. Tobias RS. Can. J. Chem. 1965; 43:1222–1225.
8. Filowitz M, Ho RKC, Klemperer WG, Shum W. Inorg. Chem. 1979; 18:93–103.
9. a) Dale BW, Pope MT. Chem. Commun. 1967:792. b) Dale BW, Buckley JM, Pope MT. J. Chem. Soc. A. 1969:301–304. c) Flynn CM, Stucky GD. Inorg. Chem. 1969; 8:335–344. d) Flynn CM, Stucky GD. Inorg. Chem. 1969; 8:178–180. e) Flynn CM, Stucky GD. Inorg. Chem. 1969; 8:332–334.
10. Süe P. Ann. Chim. 1937; 7:493–592.
11. Dosch, RG. Ph.D. Thesis. The University of New Mexico; 1971.
12. Marty A, Abdmeziem K, Spinner B. C. R. Acad. Sci., Ser. C. 1976; 283:285–288.
13. Graeber EJ, Morosin B. Acta Cryst. 1977; B33:2137–2143.
14. Marek, KA. Ph.D. Thesis. University of Illinois at Urbana-Champaign; 2001.
15. a) Villa EM, Ohlin CA, Balogh E, Anderson TM, Nyman MD, Casey WH. Angew. Chem., Int. Ed. 2008; 47:4844–4846. b) Matsumoto M, Ozawa Y, Yagasaki A. Polyhedron. 2010; 29:2196–2201.
16. Recent reviews: Nyman M. Dalton Trans. 2011:8049–8058. [PubMed: 21670824] Nyman MD, Burns PC. Chem. Soc. Rev. 2012; 41:7354–7367. [PubMed: 22695929]

17. $\text{Nb}_7\text{O}_{22}^{9-}$: Niu J, Ma P, Niu H, Li J, Zhao J, Song Y, Wang J. *Chem. Eur. J.* 2007; 13:8739–8748. [PubMed: 17654454] Tan H, Chen W, Liu D, Li Y, Wang E. *Inorg. Chem. Commun.* 2010; 13:1354–1356.
18. $\text{Nb}_{20}\text{O}_{54}^{8-}$: Maekawa M, Ozawa Y, Yagasaki A. *Inorg. Chem.* 2006; 45:9608–9609. [PubMed: 17112246]
19. Protonated $\text{Nb}_{24}\text{O}_{72}^{24-}$: reference 17a and Bontchev RP, Nyman M. *Angew. Chem., Int. Ed.* 2006; 45:6670–6672. Huang P, Qin C, Su Z-M, Xing Y, Wang X-L, Shao K-Z, Lan Y-Q, Wang E-B. *J. Am. Chem. Soc.* 2012; 134:14004–14010. [PubMed: 22905866] Wang Z-L, Tan H-Q, Chen W-L, Li Y-G, Wang E-B. *Dalton Trans.* 2012; 41:9882–9884. [PubMed: 22763602]
20. Protonated $\text{Nb}_{27}\text{O}_{76}^{17-}$: Tsunashima R, Long D-L, Miras HN, Gabb D, Pradeep CP, Cronin L. *Angew. Chem., Int. Ed.* 2010; 49:113–116.
21. Protonated $\text{Nb}_{32}\text{O}_{96}^{32-}$: ref 19b.
22. Besecker CJ, Klemperer WG, Maltbie DJ, Wright DA. *Inorg. Chem.* 1985; 24:1027–1032.
23. Filowitz M, Klemperer WG, Messerle L, Shum W. *J. Am. Chem. Soc.* 1976; 98:2345–2346.
24. a) Spinner B. *Rev. Chim. Min.* 1968; 5:839–868. b) Etxebarria N, Fernandez LA, Madariaga JM. *J. Chem. Soc. Dalton Trans.* 1994:3055–3059.
25. a) Goiffon A, Philippot E, Maurin M. *Rev. Chim. Miner.* 1980; 17:466–476. b) Nyman M, Alam TM, Bonhomme F, Rodriguez MA, Frazer CS, Welk ME. *J. Cluster Sci.* 2006; 17:197–219.
26. Ozeki T, Yamase T, Naruke H, Sasaki Y. *Bull. Chem. Soc. Jpn.* 1994; 67:3249–3253.
27. Ohlin CA, Villa EM, Fettinger JC, Casey WH. *Angew. Chem., Int. Ed.* 2008; 47:8251–8254.
28. Day VW, Klemperer WG, Schwartz C. *J. Am. Chem. Soc.* 1987; 109:6030–6044.
29. Klemperer WG, Shum W. *J. Am. Chem. Soc.* 1978; 100:4891–4893.
30. a) Klemperer WG, Shum W. *J. Am. Chem. Soc.* 1977; 99:3544–3545. b) Day VW, Klemperer WG, Maltbie DJ. *J. Am. Chem. Soc.* 1987; 109:2991–3002.
31. Chen Q, Goshorn DP, Scholes CP, Tan X-L, Zubietta J. *J. Am. Chem. Soc.* 1992; 114:4667–4681.
32. In reference 31, Chen et al. described a protonated hexavanadate system in acetonitrile solution where ^{17}O NMR resonances 805 ppm and 331 ppm downfield from water (internal) were assigned to doubly bridging OV_2 and protonated doubly bridging OV_2H oxygen atoms, respectively, implying that proton transfer was slow on the NMR time scale. However, the NMR sample was known to contain dimethylformamide, and the chemical shifts of dimethylformamide (δ 320^[33]) and water (δ 11^[34]) in acetonitrile are separated by 331 ppm. The 331 ppm resonance can therefore be assigned to DMF, and assuming that proton exchange is rapid on the NMR time scale, the 805 ppm resonance can be assigned to the chemical exchange-averaged $\text{OV}_2/\text{OV}_2\text{H}$ resonance.
33. Gerothanassis IP, Vakka C. *J. Org. Chem.* 1994; 59:2341–2348.
34. Luz Z, Yagil G. *J. Phys. Chem.* 1966; 70:554–561.
35. a) Alam TM, Nyman M, Cherry BR, Segall JM, Lybarger LE. *J. Am. Chem. Soc.* 2004; 126:5610–5620. [PubMed: 15113233] b) Black JR, Nyman M, Casey WH. *J. Am. Chem. Soc.* 2006; 128:14712–14720. [PubMed: 17090059]
36. Besserguenev AV, Dickman MH, Pope MT. *Inorg. Chem.* 2001; 40:2582–2586. [PubMed: 11350237]
37. Allen PG, Bucher JJ, Clark DL, Edelstein NM, Ekberg SA, Gohdes JW, Hudson EA, Kaltsoyannis N, Lukens WW, Neu MP, Palmer PD, Reich T, Shuh DK, Tait CD, Zwick BD. *Inorg Chem.* 1995; 34:4797–4807.
38. Roy RN, Roy LN, Vogel KM, Porter-Moore C, Pearson T, Good CE, Millero FJ, Campbell DM. *Mar. Chem.* 1993; 44:249–267.
39. Villa EM, Ohlin CA, Casey WH. *Chem. Eur. J.* 2010; 16:8631–8634. [PubMed: 20602370]
40. The influence of CO_2 contamination^[10, 41] on polyniobate solutions and its remediation^[8, 42] is well-documented; stoichiometric reaction of CO_2 with polyniobates is reported in references [41] and [15b].
41. Smith EF, Van Haagen WK. *J. Am. Chem. Soc.* 1915; 37:1783–1797.
42. Reisman A, Holtzberg F, Berkenblit M. *J. Am. Chem. Soc.* 1951; 81:1292–1295.
43. Meyer G, Hoppe R. *Z. Anorg. Allg. Chemie.* 1977; 436:75–86.

44. Atencio D, Coutinho JMV, Doriguetto AC, Mascarenhas YP, Ellena J, Ferrari VC. *Am. Mineral.* 2008; 93:81–87.
45. Laurencin D, Thouvenot R, Boubekeur K, Proust A. *Dalton Trans.* 2007:1334–1345. [PubMed: 17372649]
46. Alizadeh MH, Harmalker SP, Jeannin Y, Martin-Frère J, Pope MT. *J. Am. Chem. Soc.* 1985; 107:2662–2669.
47. a) Besecker CJ, Day VW, Klemperer WG, Thompson MR. *J. Am. Chem. Soc.* 1984; 106:4125–4136. b) Besecker CJ, Day VW, Klemperer WG, Thompson MR. *Inorg. Chem.* 1985; 24:44–50. c) Day VW, Klemperer WG, Maltbie DJ. *Organometallics.* 1985; 4:104–111. d) Day VW, Klemperer WG. *Science (Washington, D.C.).* 1985; 228:533–541.
48. a) Villa EM, Ohlin CA, Rustad JR, Casey WH. *J. Am. Chem. Soc.* 2009; 131:16488–16492. [PubMed: 19658397] b) Casey WH, Rustad JR, Spiccia L. *Chem. Eur. J.* 2009; 15:4496–4515. [PubMed: 19347896]
49. Villa EM, Ohlin CA, Casey WH. *J. Am. Chem. Soc.* 2010; 132:5264–5272. [PubMed: 20302304]
50. Gordon, AJ.; Ford, RA. *The Chemist's Companion.* New York: Wiley; 1972. p. 71–74.

Figure 1.

Structures of (a) $\text{Nb}_6\text{O}_{19}^{8-}$, (b) $\text{Nb}_{10}\text{O}_{28}^{6-}$, (c) $\text{Nb}_7\text{O}_{22}^{9-}$, and (d) the $\text{Nb}_7\text{O}_{22}^{9-}$ subunit of the $\text{Nb}_{24}\text{O}_{72}^{24-}$ and $\text{Nb}_{32}\text{O}_{96}^{32-}$ plus the two Nb centers linking each subunit to its two nearest neighbors. In each structure, one member of each set of symmetry-equivalent oxygen atom is labeled. Niobium-oxygen bonds are drawn as double lines when $d(\text{Nb}-\text{O}) \leq 1.8 \text{ \AA}$, as single lines when $1.8 \text{ \AA} < d(\text{Nb}-\text{O}) < 2.2 \text{ \AA}$, and broken lines when $d(\text{Nb}-\text{O}) \geq 2.2 \text{ \AA}$.

Figure 2.

^{17}O solution NMR spectra measured 1 h after addition of (a) 1 equiv, (b) 3 equiv, (c) 4 equiv, and (d) 10 equiv of KOH and 1 h after addition of (e) 1 equiv, (f) 3 equiv, (g) 4 equiv, and (h) 10 equiv of TMAOH to aqueous TMA **1** such that in each case $[\text{Nb}]_{\text{tot}} = 0.6 \text{ M}$. Hexaniobate and decaniobate resonances are assigned using the labeling schemes shown in Figure 1a and 1b, respectively. All spectra were measured and plotted under the same instrumental conditions.

Figure 3.

^{17}O solution NMR spectra in the 430 – 520 ppm region measured (a) 1 h and (b) 3 weeks after addition of 3 equiv of KOH to aqueous TMA **1**, $[\text{Nb}]_{\text{tot}} = 0.6$ M. Resonances are assigned to polyniobate X and polyniobate Y using the labeling scheme given in the text. The vertical scales for (a) and (b) were chosen for purposes of clarity and do not reflect absolute intensities, only the relative intensities within each spectrum.

Figure 4.

Chemical shifts of the most intense ^{17}O resonances observed after addition of n equiv of NaOH to aqueous TMA **1**, $n = 0-10$. Resonances assigned to oxygen atoms in the decaniobate and hexaniobate ions are labeled with upper case and lower case letters, respectively, using the labeling schemes shown in Figure 1. Resonances assigned to polyniobate X and polyniobate Y are labeled x1–x10 and y1–y6, respectively as given in the text. Assignment of resonances in different chemical shift regions to terminal (ONb), doubly bridging (ONb_2), triply bridging (ONb_3), and sixfold bridging (ONb_6) oxygen atoms is shown on the right side of the Figure (see text).

Figure 5.

^{17}O solution NMR spectrum of a tetra-*n*-butylammonium polytantalate mixture in acetonitrile solution prepared as described in the Experimental Section. Seven resonances are assigned to the decatantalate ion using the decaniobate labeling scheme shown in Figure 1b. The 26 ppm resonance labeled "w" is assigned to water; the 326 ppm resonance labeled with an asterisk is unassigned.

Figure 6. ^{17}O NMR chemical shift correlation diagram for the $\text{Nb}_6\text{O}_{19}^{8-}$, $\text{Nb}_7\text{O}_{22}^{9-}$, and protonated $\text{Nb}_{24}\text{O}_{72}^{24-}$ anions. Resonances are assigned in the text using the labeling schemes given in Figure 1; the numbers in parentheses are the relative numbers of atoms in each symmetry-equivalent set of oxygen atoms. Chemical shift regions are delineated as in Figure 4.

Table 1

Hexaniobate ^{17}O Solution NMR Chemical Shifts Observed after Addition of KOH and TMAOH to Aqueous TMA 1.^[a]

chemical shifts in ppm (line widths fwhm in Hz) ^[b]				
equiv of base	pH	ONb	ONb ₂	ONb ₆
1 equiv KOH	10	648(380 ^[d])	--[c]	41(22 ^[d])
3 equiv KOH	11	629(167 ^[f])	382(374 ^[e])	37(29 ^[e])
4 equiv KOH	11	626(160 ^[f])	383(256 ^[f])	36(26 ^[e])
10 equiv KOH	13	607(153 ^[f])	393(139 ^[f])	29(24 ^[e])
1 equiv TMAOH	10	644(226 ^[f])	--[c]	41(38 ^[d])
3 equiv TMAOH	11	635(147 ^[f])	378(966 ^[e])	38(14 ^[f])
4 equiv TMAOH	11	631(150 ^[f])	380(522 ^[f])	38(12 ^[f])
10 equiv TMAOH	13	612(141 ^[f])	391(93 ^[f])	32(18 ^[f])

^aSpectra are shown in Figure 2; experimental details are given in the Results Section.

^bChemical shifts and line widths of the hexaniobate terminal oxygen (ONb), doubly bridging oxygen (ONb₂), and sixfold bridging oxygen (ONb₆) resonances.

[c] extremely broad resonance at 375 ± 10 ppm.

[d] $\pm 35\%$

[e] $\pm 15\%$

[f] $\pm 5\%$