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Isotope-Exchange Dynamics in Isostructural Decametalates with Profound Differences in Reactivity

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Abstract: Rates of oxygen-isotope exchange at all structural sites in two isostructural polyoxometalates, $[H_xNb_{10}O_{28}]^{(6-x)-}$ and $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$, show that small changes in structure have surprising and profound effects: a single-site substitution of Ti(IV) for Nb(V) inverts the pH dependencies for rates throughout the structures. Within a given structure, all oxygens exhibit similar pH dependencies although they react over a range greater than $\sim 10^4$, indicating that pathways involve concerted motions of the entire lattices. Profound sensitivity to changes in structure and composition suggests reaction pathways in polyoxometalate ions will be highly variable even within structural classes. The results also require new thinking about how ab initio simulations are used to understand reaction pathways involving extended structures, like the mineral−water interface. Our data indicate that reactions proceed via metastable intermediates and that the simulations must be structurally faithful or will miss the essential chemistry.

Introduction

The reaction dynamics of polyoxometalates (POMs) in solution are poorly understood in spite of their wide range of applications.[1−4] Only a few POMs, such as the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ and decavanadate $[H_xV_{10}O_{28}]^{(6-x)-}$ ions,[5−9] have been investigated comprehensively in terms of fundamental reactions, like the isotope exchange between structural oxygens and bulk water. Niobium-based decametalate ions are sufficiently stable and inert that isotope-exchange experiments can be easily conducted using both ^{17}O NMR and ESI-MS methods.[8] Trends in reactivity were found to be surprising in that the rates of isotope exchange at almost all structural oxygens in the decaniobate ion respond to changes in solution pH, even when the molecule is unprotonated. Furthermore, the relatively inert μ_3-oxo was found to be key for the dissociation of the molecule.[8]

Here we probe this idea further by expanding these experiments to include a molecule that is isostructural, but not isovalent, to the decaniobate ion, with two Ti(IV) atoms replacing the two central Nb(V) atoms, which reduces the valence charge on the key μ_3-oxos. With this dititanoniobate ion, $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ (Figure 1), we show that this single, small change increases the stability of the molecule and reduces the overall reactivity at alkaline pH. All oxygens in the dititanoniobate ion respond similarly to changes in solution pH, as though the pathways for isotope exchange involve concerted motions of much of the structure, and the molecule seems to react as a unit even though the rates of isotopic exchange span a considerable range.

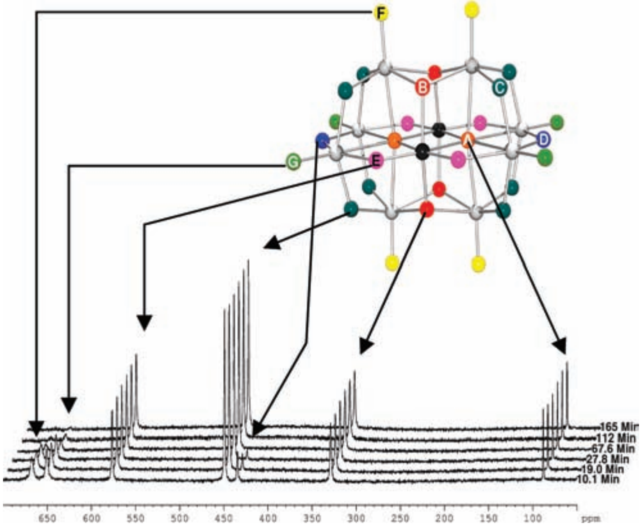

Figure 1. ^{17}O NMR stacked spectra showing signals for all seven structural oxygens of the dititanoniobate ion $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ (ion shown in the top right). As the structural oxygens exchange with bulk water, the individual signal intensities decrease with time. This stacked spectra shows that the fast-reacting oxygens (μ_2-oxo site D and terminal sites F and G) are gone in less than 3 h.

These decametalate ions comprise a class of isostructural molecules with three types of metal sites and seven structural oxygen sites. Most familiar is perhaps the decavanadate ion $[H_xV_{10}O_{28}]^{(6-x)-}$,[5−7,9] which has been explored in terms of

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biological activity but is stable only over a narrow pH range.[10] The decaniobate ion is isovalent to the decavanadate ion but is stable over a larger pH range.[8] In addition, isostructural analogues can also be made by substituting Ti(IV) for Nb(V) at the central metal sites, yielding either $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ or $[H_xTiNb_9O_{28}]^{(7-x)-}$.[11,12]

This substitution of Ti(IV) for Nb(V) is at the metal site that is bonded to the four key μ_3-oxos. These overbonded oxygens were identified as key to the dissociation of the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion to the hexaniobate $[H_xNb_6O_{28}]^{(8-x)-}$ ion.[8] Here we use "overbonding" to refer to Pauling's bond valence rule; the formal 2− charge on the oxide is overcompensated by bonding to three Nb(V), each with 5/6+ charge.[13] The Nb(V)-to-Ti(IV) substitution reduces the overbonding from +0.5 to +0.33 valence bond unit at the μ_3-oxo (Site B) and is associated with a significant change in chemistry, as will be shown.

Experimental Section

Synthesis. To probe the effect of substitution on the reactivity of the molecule, we synthesized the sodium salt of dititanoniobate, $Na_8[Ti_2Nb_8O_{28}]$. This synthesis was modified from the original synthesis by Nyman et al.:[12] 112 mg of sodium hydroxide, 0.3 mL of titanium(IV) isopropoxide, and 350 mg of hydrous niobium oxide were mixed in 5 mL of $H_2{}^{17}O$ (40% ^{17}O) and put into a PTFE-lined pressure vessel. It was then allowed to react in a 200 °C oven for a minimum of 10 h. After cooling, the excess water was removed *in vacuo* until the product was dry. This product was then extracted from the residue in boiling, isotopically normal water and filtered hot through a medium fritted filter to eliminate any titanium(IV) oxide.

The filtrate was concentrated *in vacuo* to ∼5 mL and allowed to cool. Methanol was then used to precipitate the $Na_8[Ti_2Nb_8O_{28}]$. The precipitate was isolated by filtration through a medium fritted filter, washed repeatedly with methanol, and dried. This product contains ^{17}O in the μ_3-oxo and the μ_6-oxo sites (sites B and A, respectively). Complete enrichment of this product was achieved by dissolving it in 2 mL of $H_2{}^{17}O$ (40% ^{17}O) and heating it at 120 °C in a PTFE-lined pressure vessel for 5 days. The product was isolated by drying *in vacuo*.

^{17}O NMR. The solution-state ^{17}O NMR experiments were conducted with a 500 MHz Bruker Avance spectrometer located at the UCD NMR facility. This spectrometer is based on an 11.7 T magnet ($\nu_o = 67.8$ MHz for ^{17}O) and is fitted with a 10-mm broadband probe. The ^{17}O NMR spectra were taken with single-pulse excitation using 20 μs pulses and recycle delays of 6 ms. Depending upon the sample concentration and rate of reaction, 5000−15000 acquisitions were required to establish an adequate signal-to-noise ratio. The time-domain data were digitized at 10 kHz. We employed a 0.3 M $TbCl_3$ solution as an external intensity standard, which was included in the 10-mm NMR tube as a coaxial insert. The temperature was measured by replacing the sample with a copper-constantan thermocouple fitted into an NMR tube. The accuracy of the measured temperature was about ±0.1 °C. Peak positions are reported relative to the bulk water peak, which was assigned to 0 ppm.

Rate experiments were conducted by dissolving ∼10 mg of the ^{17}O-enriched $Na_8Ti_2Nb_8O_{28}$ into 2 mL of an isotopically normal solution containing pH buffer and 0.1 M $[N(CH_3)_4]Cl$. The ^{17}O NMR signal intensities for each structural oxygen decreased as the isotopically normal $H_2{}^{16}O$ exchanged with the individual oxygen sites and were followed as a function of time to yield the rates of isotopic exchange. Breakdown or oligomerization of the dititanoniobate ion is easily detected as a decline in the intensity for the central μ_6-oxo site, which is otherwise constant in intensity. Only at pH ≤ 7.5 does the ^{17}O NMR intensity for this site diminish with time (Figure 2), indicating that the dititanoniobate ion is being converted into a new species. Simultaneously we observe a new ^{17}O NMR signal growing into the region of the spectrum that is typical for μ_6-oxo in niobate ions but shifted upfield. We interpret this new peak to be a yet unidentified niobate or titanoniobate ion that inherited its central μ_6-oxo from the reacting dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion. Above pH 7.5, the dititanoniobate ion stays intact.

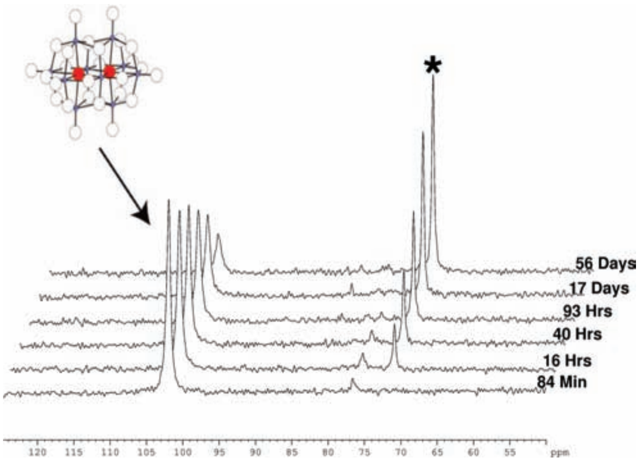

Figure 2. ^{17}O NMR stacked spectra of the μ_6-oxo region for the $[H_3Ti_2Nb_8O_{28}]^{5-}$ (shown at 102 ppm) at pH 6.61 at 35.5 °C (number of scans is 15000). The stacked spectra show the growth of the μ_6-oxo signal of the unknown niobate or titanoniobate ion (* at 73 ppm) with time. This new μ_6-oxo conserves almost all of the signal intensity from the original dititanoniobate ion μ_6-oxo, indicating that some of the structural oxygens, with their ^{17}O, are transferred intact to the newly formed product.

Results and Discussion

The order of oxygen reactivities is broadly similar between the isostructural dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ and decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ions (Figure 3). The reactivities of the structural oxygens in the dititanoniobate ion are ranked D(μ_2-oxo) > F(η-oxo) > G(η-oxo) ≫ C(μ_2-oxo) > E(μ_2-oxo) ≫ B(μ_3-oxo) > A(μ_6-oxo). By comparison to the decaniobate ion, only the terminal oxygens are switched in their order of reactivity. The rates of oxygen exchange for the D site are too fast to be measured in the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion at 35.5 °C below pH 7.5. However, in sharp contrast to results for the decaniobate ion, the rates of oxygen isotope exchange for the dititanoniobate ion steadily decrease with increasing pH, and the region of interconversion has changed from alkaline (decaniobate ion) to neutral/acidic pH (titanoniobate ion) (Figure 3b,f).

To further emphasize this difference, in Figure 4 we show the variation with pH of the rates of isotopic exchange of Site C, a set of μ_2-oxo on the corner of the molecule, away from the site of Ti(IV) for Nb(V) substitution. The apparent inversion of pH dependencies at alkaline conditions is general for all reactive oxygens in the decaniobate ion as compared with the dititanoniobate ion.

Substitution of Ti(IV) for Nb(V) at the two central sites of the molecule causes changes in the Brønsted acidity of the molecule. For the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion, approximate acidity constants are assignable from ^{51}V NMR and potentiometry studies of the isostructural and isovalent

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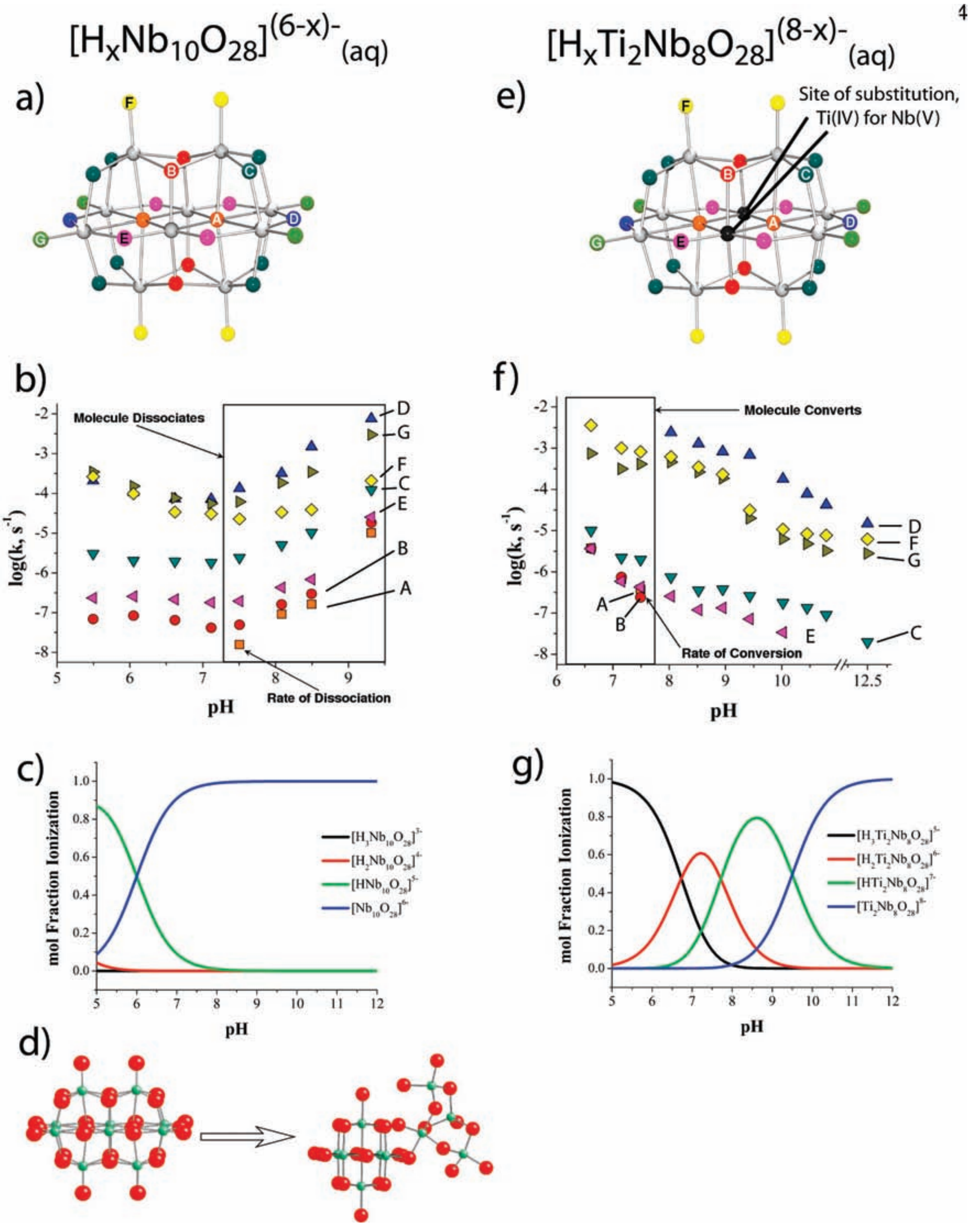

Figure 3. The $[H_xNb_{10}O_{28}]^{(6-x)-}$ (a) and $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ (e) ions are isostructural, and each has seven distinct oxygen sites, labeled A through G. In the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion, the central Nb(V) atoms have been substituted with two Ti(IV) atoms, where Nb(V) are shown as gray spheres and Ti(IV) are shown as black spheres. Rates of steady isotopic exchange in the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ (b) and the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ (f) ions span a range of over $\sim 10^4$. The boxes indicate dissociation in the decaniobate ion (b) and conversion in the dititanoniobate ion (f); moreover, rates for these side reactions are given by the rate of exchange for the central μ_6-oxo (Site A). In the boxed region for the decaniobate ion, pH ≥ 7.5 (b), we find that the decaniobate ion dissociates to the hexaniobate ion and that the μ_3-oxo is the hinge to that reaction (d). Speciation of the decaniobate and the dititanoniobate ions are shown in c and g, respectively. The speciation of the dititanoniobate ion is derived from titration data; however, the speciation of the decaniobate ion is inferred from the ^{51}V NMR and potentiometry studies done on the isostructural and isovalent decavanadate ion, $[H_xV_{10}O_{28}]^{(6-x)-}$.[9]

$[H_xV_{10}O_{28}]^{(6-x)-}$ molecule with pK_a values of pK_{a1}= 1.6, pK_{a2} = 3.7, and pK_{a3} = 6.0 (I=0.6 M);[7,9] however, the decaniobate ion is not stable in solution below pH 5. Using these equilibrium constants, the $[HNb_{10}O_{28}]^{5-}$ species becomes important only at pH < 6.5 (Figure 3c), consistent with the pH variation of isotope-exchange rates. Potentiometric titration of the dititanoniobate ion also indicates three pK_a values of pK_{a1}= 6.7, pK_{a2} = 7.7, and pK_{a3} = 9.5 (titration conducted in 0.1 M tetramethylammonium chloride as background electrolyte) (Figure 3g). At pH ≈ pK_{a1} and pH ≈ pK_{a2}, we also observe dramatic broadening for ^{17}O peaks corresponding to both the D site and the E site μ_2-oxygens in the dititanoniobate ion (Figure 5). Simultaneously, we see a large upfield shift in the peak positions of sites D and E with decreasing pH, suggesting that these sites are the primary

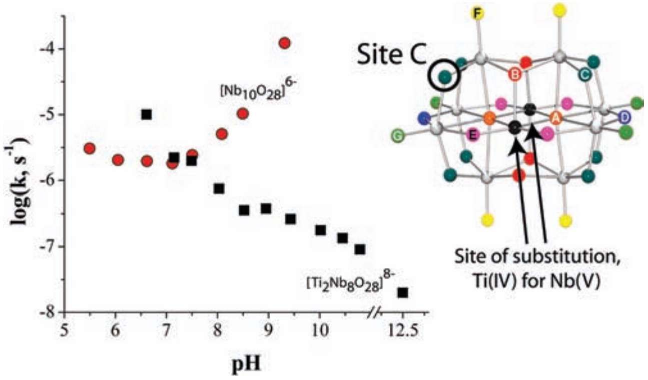

Figure 4. Comparison of the rates of isotopic oxygen exchange for the μ_2-oxo site (Site C) at 35.5 °C, where the data for the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion are in black squares and those for the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion are in red circles. The apparent inversion of pH dependencies is general across the molecule. The dititanoniobate ion on the right shows the site of Ti(IV) substitution on the central metal site, where the Nb(V) atoms are in gray and the Ti(IV) atoms are in black.

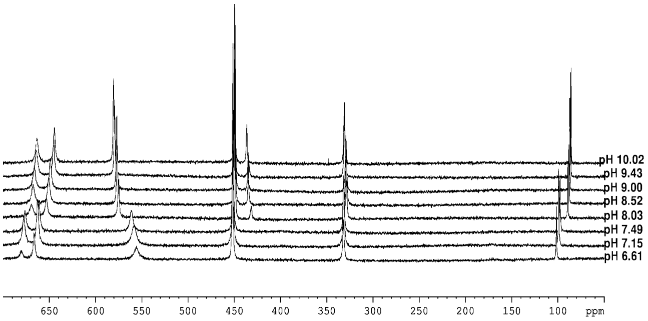

Figure 5. ^{17}O NMR stacked spectra of the pH shifts (in ppm) of the individual oxygen signals of the $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion at 35.5 °C (number of scans is 5000 and the bulk water peak is set to zero). Signals for the μ_2-oxos (sites D and E, ~430 and ~560 ppm, respectively) shift upfield, and broaden as the pH decreases; the signal for the μ_6-oxo (site A, ~90 ppm) and signals for both terminal oxygens (sites G and F; ~660 and ~675 ppm, respectively) shift downfield as the pH decreases. The B site μ_3-oxo (~325 ppm) and the C site μ_2-oxo (~450 ppm) do not change much.

loci of protonation. The highest pK_{a3} is difficult to assign because it is associated with a subtle inflection in the potentiometric curve; however, above this pH the terminal oxygen signals become sharper and there is a corresponding drop in their reactivities.

There are several immediate comparisons between the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion and the isostructural decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion. First, when compared at the same pH, the rates of exchange of the individual oxygen sites in the dititanoniobate ion are generally faster than the rates of the same oxygens sites in the decaniobate ion (under conditions where the side reactions are minimal, such as at pH 7.5).

Second, in both molecules, all sets of structural oxygens react in concert. The fact that the pH dependencies of these oxygen isotope-exchange reactions vary similarly across the dititanoniobate molecule indicate that activation is not local to one or two oxygens near the site of protonation.

Third, in both molecules we find that the μ_3-oxo is key to the stability. The Ti(IV) substitution stabilizes the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion to high-pH conditions where the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion would dissociate into the hexaniobate $[H_xNb_6O_{19}]^{(8-x)-}$ ion. We find that the μ_3-oxo is inert to oxygen exchange in the dititanoniobate ion (except when it is converting to the new compound at lower pH); whereas in the decaniobate ion the μ_3-oxo exchanges extremely slowly and is the hinge for the conversion of $[H_xNb_{10}O_{28}]^{(6-x)-}$ to $[H_xNb_6O_{19}]^{(8-x)-}$ (Figure 3d). Thus, the Ti(IV) substitution in the dititanoniobate ion stabilizes the molecule and prevents transformation at high pH (Figure 3f). Conversely, the Ti(IV)-substituted molecule is now subject to acid transformation into another species at conditions where the decaniobate ion was stable.

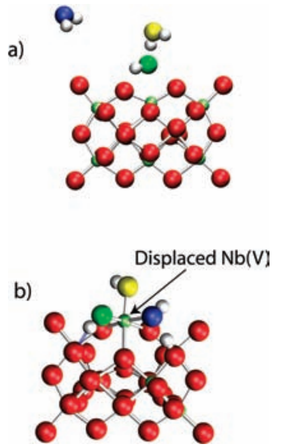

Figure 6. A conceptual model for isotope exchanges probably requires formation of a metastable intermediate form of the structure that allows relatively facile and reversible exchange of oxygens. Here we show one such idea where oxygens in the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion become reactive as the molecule begins to slowly dissociate at pH ≥ 7.5. Here we suggest one hypothesis that involves nucleophilic attack by a $[OH^-]$ at the Nb(V) bonded to Site B. This nucleophilic attack displaced the metal and forms a metastable form of the molecule with a temporarily underbonded Nb(V). The coordination sphere is filled by water molecules that can then distribute protons to other oxygens and allow them to exchange for waters or hydroxyls in bulk soluion. Increased electrostatic repulsion in the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion suppresses the initial $[OH^-]$ coordination.

Conclusions

The covariation of oxygen isotope-exchange rates across the molecules indicates that a metastable intermediate is probably forming that is incongruent with the stable structure, as was observed for the MAl_{12} series of aluminum hydroxide polyoxocation molecules.[14] A likely step to form this intermediate could be nucleophilic attack by a $[OH^-]$ ion on the metal center near Site B, the key μ_3-oxo, causing it to retract the trans bond to the μ_6-oxo and convert the adjacent, and key, Site B μ_3-oxo to a metastable μ_2-oxo (Figure 6). The central Nb(V) site is now no longer octahedrally coordinated, which allows incoming H_2O to add to the Nb(V) metal and then transfer protons to adjacent structural oxygens, labilizing them and making them susceptible to isotopic exchange. In this way, structural oxygens are labilized by protons without creating unreasonably high anionic charges on the structure.

Formation of such a metastable structure by nucleophilic attack would be greatly reduced after the Ti(IV) is substituted for Nb(V) because the increased anionic charge suppresses the initial $[OH^-]$ attack on the metal site (Figure 6). This result resonates with our previous studies. In work on isostructural aluminum polyoxocations, we showed that the inert, highly coordinated oxygens (μ_4-oxo) were key to the stability of the molecule and dramatically affected the rates of isotopic substitu-

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tion into μ_2-OH bridges.[14] For these molecules, oxygen isotope exchanges with bulk solution proceeded by transformation into a metastable dimer-like form of the polyoxocation, the extent of which was controlled by the strength of bonds in the central, inert core.[15]

The importance extends well beyond the individual molecules discussed here. There is intense interest among geochemists and environmental chemists in assigning reactivities to the surface oxygens on minerals, yet much of this work entails ab initio calculations or bond-valence models developed on molecular clusters of a few dozen atoms. We here show that the actual reaction dynamics at the nanometer scale, with a few dozen atoms, are often not intuitive and can be dramatically changed by single site substitutions. Simulations of the reaction dynamics must be structurally faithful and inherently dynamic or they will miss the essential chemistry.

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Supporting Information Available: Buffer composition; oxygen exchange rates (Tables S-1−2); stacked ^{17}O NMR plots; ^{17}O-exchange rates comparing the decaniobate and dititanoniobate ions; full width at half-maximum vs pH plots; titration data; and electrospray-ionization mass spectrometry (ESI-MS). This material is available free of charge via the Internet at http://pubs.acs.org.

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