AN ABSTRACT OF THE DISSERTATION OF

<u>Dylan J. Sures</u> for the degree of <u>Doctor of Philosophy</u> in <u>Chemistry</u> presented on February 19, 2018.

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Abstract approved:

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Polyoxometalates are discrete anionic oxo clusters of the Group V and VI transition metals that can be conceptualized as molecular metal oxides. Because they are pairable with any alkali cation, a great deal of fundamental chemistry can be gleaned from their study, including solubility trends and insight into cation binding behavior at metal oxide surfaces. This thesis primarily compares the aqueous solution behavior of the two hexacoltanates – hexaniobate and hexatantalate $([Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-})$. Crystalline cesium salts of niobo-tungstates $([Nb_xW_{6-x}O_{19}]^{(2+x)-})$ exhibited a trend of decreasing Cs^+ association in the solid state with decreasing charge and increasing tungsten character of the clusters, which was coupled with a narrowing HOMO-LUMO energy gap. The aqueous behavior of alkali and tetramethylammonium salts of the hexacoltanates was investigated via calorimetry, revealing a heightened concentration-dependence on enthalpy of dissolution for the cesium salts compared to the lighter alkali salts. Quadrupolar relaxation NMR and x-ray total scattering experiments were also performed on the cesium salts of the hexacoltanates, revealing a greater degree of Cs^+ ion-pairing with hexatantalate. This was corroborated by computational bond energy decomposition calculations, indicating that a greater contribution by the orbital interaction energy term arising from relativistic effects in hexatanalate was responsible for the difference. Finally, attempts at analogous studies with decaniobate ($[Nb_{10}O_{28}]^{6-}$) revealed a speciation process into much larger niobium clusters driven primarily by alkali cation association. In light of their observed heightened solubilities and unusual speciation in the presence of alkali cations (especially Cs⁺), polycoltanates constitute model systems in which alkali countercations do not have purely ionic character and instead induce partially-covalent orbital mixing effects. This thesis illuminates the unusual behavior of alkali cations in aqueous polyoxometalate solutions, further highlighting the necessity to consider counterions in order to arrive at complete characterizations of solution processes including speciation, solubility, ion-association, aggregation, and crystallization. These fundamental studies can then be applied to finding effective, reliable mechanisms for sequestering radioactive cesium that has leached into the environment from nuclear reactor meltdowns such as the Fukushima Daiichi disaster. [©]Copyright by Dylan J. Sures February 19, 2018 Attribution 4.0 (CC BY 4.0)

Probing Aqueous Ion-Pairing and Speciation of Group V Polyoxometalates

by

Dylan J. Sures

A DISSERTATION

submitted to

Oregon State University

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Dylan J. Sures, Author

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Chapter 1: An Introduction to Anomalous Cesium Ion Behavior¹

1.1 Introduction

On March 20, 2011, a magnitude 9.0 earthquake off the coast of Japan severely damaged the Fukushima Daiichi nuclear power plant, resulting in a month-long release of radioactive materials into the atmosphere and soil.² The most concerning of these materials is cesium-137 (¹³⁷Cs). It is the most mobile radionuclide in liquid and solid nuclear wastes, 3,4 has high radioactivity and persists in the environment (half life = 30.1 years), and as an environmental contaminant has potentially deleterious effects on agriculture and farming.⁵ Cesium is soluble in ground and seawater, enhancing its global dispersion via ocean currents.⁶ Additionally, the seawater that was used to cool the melted nuclear cores of the power plant requires treatment and safe disposal. In solution, it is readily entrained into plants and animals via multiple routes due to its chemical similarity to potassium, an essential nutrient.⁷ In addition, Cs and other radionuclides can bind to suspended particles such as anionic clays, causing sedimentary contamination and transport as colloidal material.^{8,9} Thus, efficient sequestration and removal of radioactive Cs from the environment is crucial for environmental and human well-being for both current and future generations. The periodic similarity of Cs⁺ to naturally abundant Na⁺ and K⁺ presents challenges to scientists and engineers. It is therefore important to understand Cs⁺'s solution behavior from a fundamental level, especially ion-association and bonding, in order to achieve separation from these far more abundant species in the natural environment and nuclear wastes. Existing technologies that separate Cs⁺ from Na⁺ in nuclear wastes exploit precipitation of poorly soluble Cs⁺ salts, Cs⁺-selective ion exchangers, designer ligands for solvent extraction, or readily-adsorbing minerals.

1.2 The Cesium Effect

1.2.1 The Cesium Effect in Organic Reactions

Cesium exists as Cs^+ in solution – the largest monovalent cation on the periodic table. Therefore, it has the lowest charge density of any monoatomic positively charged species, causing it to be highly polarizable and "soft". This unique property is thought to be at least partially responsible for unusual behaviors in polar aprotic solvents, collectively referred to as the 'cesium effect'.¹⁰ The most readily characterized Cs-effect characteristic is the high solubility of cesium salts of carbonate (as well certain other oxyanions) compared to the lighter alkali salts (367 mM and 4.4 mM for Cs_2CO_3 and Na_2CO_3 respectively in DMF).¹¹ This stark difference in solubility arises from the balance between electrostatic and solvation effects between the ions. The solvation enthalpy of Na⁺ does not exceed the electrostatic potential energy of the ion-pair.¹² Although the solvation enthalpy of Cs⁺ is lower than that of Na⁺, the much lower charge density of the former allows for its dissociation from the anion and complete solvation, allowing for more complete dissolution and higher solubility. The resultant formation of "naked" anions allows for greater catalytic capability in organic reactions. For instance, cesium salts of moderate bases such as carbonate (Cs_2CO_3) are used for cyclication and ring closure reactions via intramolecular anionic $S_N 2$ substitution.^{13–16} With Cs^+ as the counter-cation, higher yields are reported compared to reactions involving smaller alkali cations,¹⁷ attributed to the more complete solvation of Cs⁺ allowing the anion to freely interact with the reactants in solution.

Cesium hydroxide also exerts unusual effects in organic reactions, such as the controlled alkylation of amines.¹⁸ In this instance, the cesium ion itself is explicitly involved in the reaction. The hydroxide base promotes an alkylation of a primary amine, while the Cs⁺ ion weakly coordinates to the amine such that further alkylation is inhibited, preventing formation of dialkyl and trialkyl amines.¹⁹ This process was very effective compared to a control experiment that omitted CsOH, with 89% monoalkylated product compared to 25% (the other product being an unwanted dialkylated analogue).¹⁸ Furthermore, cesium carboxylates are used in the preparation of Merrifield resins²⁰ for solid-state protein synthesis,²¹ in which cesium again inhibits excessive alklylation of amines. This is desirable, as the overabundance of quarternary amines causes premature termination of peptide chains. Thus, the Cs⁺ ion is able to exert intriguing effects in its own right beyond simply being solvated away from the "real action".

Both cesium and sodium carbonate are more soluble in water than in organic solvents. The cesium salt is yet significantly more soluble, but the difference is not so stark (8.0 M and 0.57 M for Cs_2CO_3 and Na_2CO_3 , respectively) as their solubility differences in organic solvent.²² Water's higher polarity yields higher solvation enthalpies for the cations such that the electrostatic energy between the ions is exceeded even in the sodium salt. Furthermore, cesium and sodium salts of similarly sized monovalent oxoanions exhibit opposite solubility trends – $CsClO_4$ and $NaClO_4$ have aqueous solubilities of 0.085 and 17.1 M, respectively.²³ This is due to the electrostatic enthalpy between the ions and the solvation enthalpy of perchlorate being sufficiently low such that sodium's greater hydration enthalpy dominates, increasing the solubility of the sodium salt beyond that of the cesium salt.

Cesium's low electrophilicity²⁴ and high polarizability²⁵ that arise from its low charge



Figure 1.1: Coordination environment of Cs^+ in the crystal structure of cesium bis(perfluoro-triphenylborane)amide, highlighting the 16 Cs–F bonding contacts. Cs = purple, F = green, C = gray, B = orange, N = blue.

density allow it to sometimes achieve extremely high coordination numbers. Cesium is able to make an unprecedented tetracosahedral arrangement of 16 Cs···F bonding contacts with the weakly-coordinating fluorines in the bis(perfluoro-triphenylborane)amide anion ($[H_2NB_2(C_6F_5)_6]^-$)²⁶ – more than any other cation is capable of in any observed compound (Figure 1.1).²⁶ For instance, the Rb⁺ salt of the same anion was found to have an coordination number of merely ten. Within this coordination complex, Cs⁺ has the formal 32-electron closed-shell configuration of radon. This strong binding affinity and poor aqueous solubility of the resultant complex allows for nearly quantitative separation of Cs⁺ from water, suggesting that $[H_2NB_2(C_6F_5)_6]^-$ would effectively remove ¹³⁷Cs from nuclear wastes. A myriad of existing ¹³⁷Cs sequestration and sequestration methods will be discussed in detail in the following section.

1.3 Existing ¹³⁷Cs Sequestration/Removal Methods

1.3.1 Metathesis Reactions

Ion-association processes are central to all existing Cs^+ sequestration methods. The primary difficulty with the removal of ¹³⁷Cs from the environment lies in its periodic similarity to Na^+ and K^+ , which are both far more abundant and benign. However, Cs⁺'s subtle chemical differences has been exploited in several optimized technologies. The first line of attack that scientists have historically used is simple metathesis reactions with anions that have soluble sodium and potassium salts, but highly insoluble cesium salts. For instance, the tetraphenylborate anion has been used to separate ppm levels of Cs⁺ from nuclear waste solutions containing more than 3 molar Na⁺ due to the extreme difference in solubilities of tetraphenylborate's sodium and cesium salts (Ksp = 0.48 and 3.29 $\times 10^{-11}$, respectively).²⁷ ¹³⁷Cs has also been experimentally removed from synthetic wastewater (consisting partially of Bud Light[®] beer). Stable ¹³³CsCl was added to raise the Cs^+ concentration, and both isotopes were co-precipitated by metathesis with sodium tetraphenylborate.²⁸ Potassium tetraphenylborate has also been used as the adsorption-active component in a composite calcium alginate matrix for the adsorption of Cs^+ ions.²⁹ In competitive adsorption experiments, a 0.01 M each Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ solution was run through a column containing the alginatetetraphenylborate composite. The former two ions were negligibly adsorbed, while Cs⁺ was adsorbed at a modestly higher rate than Rb^+ (0.82 and 0.54 mmol per gram of composite, respectively). However, potassium tetraphenylborate is also fairly insoluble $(K_{sp} = 2.49 \times 10^{-8})$, so the use of the sodium salt in environmental aqueous solutions would also lead to precipitation of potassium ions, decreasing the efficiency of the process and depleting the water of necessary ions for plant survival. While this potential problem could be mitigated by using the potassium salt of tetraphenylborate for cesium ion exchange, it would require far more material, decreasing the efficiency of the process. Use of potassium cobalt hexacyanoferrate ($K_2[CoFe(CN)_6]$) as the ion-exchanger also results in stoichiometric ion-exchange with cesium.³⁰ The drawback of this technology is Co^{2+} ions may leach into the solution; the degree to which is dictated by pH and ionic strength of the solution.

1.3.2 Minerals

An assortment of clay materials and minerals have also been tested for their Cs^+ adsorption capabilities due to their large surface areas, chemical and mechanical strengths, layered structures, and high exchange capacities.³¹ These materials are already present in the environment and play an important role in both the sequestration and transport of ¹³⁷Cs in groundwater. In general, Cs^+ adsorbs, absorbs and/or ion exchanges onto clay minerals to balance the negative charge on the aluminosilicate layers. Sericites are one such clay material, composed primarily of silanol (Si-OH) and aluminol (Al-OH) groups, also containing potassium, magnesium, calcium, iron, and sodium. Cs^+ was found to ion-exchange with the acidic protons of the silanol and aluminol at the surfaces, so maintaining a pH above 5.0 played a role in efficient Cs^+ uptake in order to deprotonate the Si-OH, yielding a negative charge.³² However, these surface sites only constitute a fraction of potential Cs^+ adsorption sites – the edges of the interlayers (between alumina and silicate layers) and the internal interlayers are also initially charge-balanced by K⁺ ions, though the degree to which these ions can be exchanged varies.

Illite is a class of sericites of interest to scientists, since it is a primary component of

the of the argillaceous (clay-containing) rock proposed as host rock formations to mitigate the effects of radiocesium via natural attenuation.³³ The adsorption of Cs⁺ onto illite is likely determined by a relatively small number of "exchange sites" that have a high affinity for Cs⁺ while still maintaining the structural integrity of the material, ³⁴ resulting in a preferential amount of interlayer collapse to allow for cesium selectivity. These minerals' selectivities for Cs⁺ are largely due to the cation's low hydration enthalpy, which allows it to entirely shed its hydration shell upon intercalating into the clavs, resulting in interlayer dehydration. The layers then collapse onto and sequester Cs⁺ selectively. The larger hydration spheres of other alkali cations would not result in such an interlayer collapse and direct bond formation between the alkali and oxo ligands of the aluminosilicate layer. However only the K⁺ ions on the mineral surface and in the edge sites are exchangeable – removal of the interlayer K⁺ ions would result in excessive interlayer collapse, inhibiting Cs⁺ adsorption. Thus, for solutions containing trace Cs⁺, illites are good candidates for adsorbing Cs^+ due to the very high selectivity of the limited number of edge sites. However, in more concentrated solutions, these edge sites become quickly saturated, causing adsorption to fall off rapidly.³⁵

Other minerals perform better in concentrated Cs^+ solutions, but are overall less selective for Cs^+ than illite. Cesium selectivity is largely dictated by the charges on the silicate and aluminate layers. Vermiculites have a high layer charges due the substitution of Al^{3+} for Si^{4+} tetrahedral sites³⁶ and collapse to ~ 10.8 Å upon Cs^+ saturation, which is a particularly suitable spacing for its sequestration. On the other hand, montmorillonites have lower layer charges from the more prevalent substitution of Mg^{2+} for Al^{3+} at octahedral sites,³⁷ causing interlayer collapses to 12-18 Å instead, making Cs^+ uptake less selective, but increasing overall cation adsorption capacities.³⁸ Thus, layered minerals such as these are defined by a delicate balance between Cs^+ selectivity and cation adsorption capacity arising from the charges of the aluminate and silicate layers, with different minerals more optimally removing Cs^+ based on the specific solution conditions.³⁴ If we consider only the clay minerals that are found in the soil around the Fukushima site, weathered biotite (partially-vermiculized biotite) is the most promising candidate for the adsorption of radiocesium, compared to the other present minerals (fresh biotite, illite, smectite, kaolinite, halloysite, allophane, and imogolite). Weathered biotite is capable of depleting radiocesium from solution and is the most selective in its sorption of Cs^+ . The sorbed ¹³⁷Cs did not undergo leaching in 0.1 M hydrochloric acid, indicating irreversible sequestration. The other montmorillonites that were tested did not sorb Cs^+ nearly as effectively upon exposure to aqueous solutions containing ¹³⁷Cs.³⁹ Thus, in environments with high concentrations of smaller cations with large hydration spheres (such as in ocean water), minerals with higher layer charges and, thus, smaller interlayer distances upon Cs^+ intercalation perform better.

1.3.3 Synthetic Ion-Exchangers

Synthetic ion-exchangers can also be employed to remove 137 Cs from solution by more complicated processes than simple metathesis and are often inspired by clay materials. Tobermorites are another class of silicates with layered structures 40,41 that can be synthesized hydrothermally from fly ash (a product of coal combustion) to achieve separation, immobilization, and disposal of radioactive Cs⁺. When synthesized from fly ashes with higher aluminate compositions, the synthetic tobermorites exhibited superior Cs⁺ selectivity. The smaller interlayer spacing in the Al-substitute tobermorites restricts hydrated Ca²⁺ ions from competing with Cs⁺ for adsorption sites.³⁶ Zeolites have also shown promise as a means of removing ¹³⁷Cs from seawater. Systematic crystallographic investigations were performed on the origin of Cs^+ selectivity using seven single crystals of fully dehydrated and partially Cs^+ exchanged zeolite A with varying Cs^+/Na^+ ratios. Cs^+ is energetically preferred in the eight-oxygen ring sites and thus occupy those sites first. Once those sites are filled, additional Cs^+ begins to fill six-oxygen rings. Thus zeolites with greater amounts of eight-oxygen ring sites such as zeolite Rho perform better for Cs^+ removal from both deionized water and seawater, compared to materials with fewer such sites.³⁶

Crystalline silicotitanate (CST, $H_2Ti_2SiO_7 \cdot 1.5H_2O$) has a framework structure consisting of tunnels that are ideal for binding Cs⁺. It exhibits marked ion-exchange selectivity for Cs⁺ via a two-step process driven by conformational changes in the framework that "unlock" the adsorption sites and increase the overall capacity and selectivity of the material. Repulsive forces between Cs^+ and the H_2O dipole moment cause a realignment of a water molecule into cesium's hydration sphere. This forces the positive side of the water molecule closer to the protonated oxygen atoms in the structure, causing a 0.55Å displacement of the -OH groups, and resulting in a rotation of the TiO_6 columns, opening up an additional site for Cs⁺ occupancy.⁴² CST remains selective for Cs⁺ and retains its structure without breaking down even in highly alkaline environments and strong radiation fields,⁴³ making it ideal for Cs⁺ removal from the highly alkaline tank wastes stored at Hanford and the Savannah River Site. Upon the substitution of one niobium atom per two formula units of sodium-CST $(Na_{1.5}Nb_{0.5}Ti_{1.5}O_3SiO_4 \cdot 2H_2O)$, the uptake of Cs⁺ is significantly improved due to the higher coordination numbers of cesium incorporated into the structure. This is made possible by the replacement of Na^+ by H_2O to compensate for the substitution of Nb^{5+} for Ti^{4+} , decreasing the charge repulsion and increasing the Cs⁺ exchange capacity.⁴⁴

On the acidic end, while antimony silicates $([Sb_2O_5(H_2SiO_3)_6)] \cdot nH_2O)$ perform well

for 85 Sr uptake, they do not perform as well for 137 Cs adsorption. However, at low niobium substitution ratios (Si:Nb > 0.1), the uptake of 137 Cs is improved by a factor of three over the non-doped material. Greater degrees of Nb substitution caused poorer performance. The best results were obtained by doping with tungsten, which resulted in a performance increase by an order of magnitude while the original structure was retained.⁴⁵

Mesoporous carbons have large surface areas and uniform pore sizes, as well as being biocompatible, chemically inert, and radiologically and thermally stable. ⁴⁶ However, they are hydrophobic and thus do not disperse well in aqueous media, leading to potential secondary pollution.⁴⁷ Introduction of oxygen-containing groups can circumvent this problem, improving the hydrophilicity and surface area of these materials. ⁴⁸ By coupling mesoporous carbon with superparamagnetic Fe_3O_4 nanoparticles, the abundance of polar groups on the surface of the resultant adsorbent material allows for efficient and rapid removal of Cs⁺ from solution without leaching iron. ⁴⁹ This material outperforms a host of other materials in its maximum adsorption capacity, including Prussian blue-coated magnetic nanoparticles, ^{50,51} magnetic graphene oxides ^{52,53} certain zeolites, ⁵⁴ trititanate nanofibers and nanotubes, ⁵⁵ and layered metal sulfides. ^{56,57}

1.3.4 Designer Solvents and Ligands

Solvent extraction techniques have also been used for the sequestration of radioactive cesium from aqueous environments. Ionic liquids are nonflammable, chemically tunable, and exert negligible vapor pressure, leading to their designation as "designer solvents" for use as alternatives to potentially hazardous volatile organic compounds.^{58–60} Some ambient-temperature ionic liquids are hydrophobic and thus remain in a separate phase

from water while still retaining ionic characteristics.⁶¹ Because the conjugated ions that make up ionic liquids exhibit much more favorable solvation of metal cations compared to conventional solvents,^{62,63} ionic liquids are unique and intriguing materials for aqueous solvent extractions of metal cations.

Calixarene crown ethers are "cup-shaped" with cavities that are optimal for extracting Cs⁺ from both acidic and alkaline environments, ⁶⁴ so their use in ionic liquid media can drastically increase selectivity for and overall uptake of Cs⁺. ⁶⁵ Ionic liquid solutions of one such calixarene, BOBCalixC6 (Figure 1.2), provide efficient and selective extraction of Cs⁺ over Na⁺ (although K⁺ was concomitantly extracted) from aqueous solutions, whereas analogous experiments using organic solvents yielded negligible extraction and depended on coextraction of the anion. ^{66,67} Ionic liquids with shorter alkyl chains generally result in more efficient extraction due to increasing ion-exchange capability with decreasing hydrophobicity. However, calixarenes are very hydrophobic and are therefore more soluble in ionic liquids with longer alkyl chains, forcing a compromise in the optimal ionic liquid for extraction.



Figure 1.2: Structure of the calixarene BOBCalixC6, including an extracted Cs⁺ ion (large maroon sphere).

Chapter 2: Cs⁺, Polyoxometalates, and Ion-Pairing

2.1 Two Classes of Polyoxometalates

Polyoxometalates (POMs), discrete, anionic, water-soluble metal-oxo clusters of Group V and VI d^0 metals, provide a model system to observe fundamental ion-association trends in solution. These clusters can be synthesized with any countercation, including Cs⁺, providing a controlled series of compounds for investigation.^{68,69} Because they are molecular metal oxides, POMs also provide insight into processes at metal oxide surfaces.⁷⁰ Thus, by studying solutions of Cs⁺ salts of POMs, we can gain insight into the fundamental processes that govern Cs⁺'s behavior in solution and its eventual precipitation.

Alkali salts of polyoxometalates are ideal for probing ion-association processes, especially with respect to Cs^{+} .⁷¹ Ion-pairing between POMs and their alkali cations is a complex set of processes. It is affected by the organization of water molecules into hydration spheres, the self-buffering (proton/hydroxide/water exchanging) behavior of the POMs, and the identity of the counter-cations. It is particularly complex in natural and/or fluctuating systems and controls the organization of biological and inorganic macromolecules as well as other supramolecular assembly processes.^{72–74} In light of this complexity, we do not entirely understand what drives solubility trends with respect to their alkali counter-cations. Typical solubility trends in aqueous solutions can be predicted by the hydration sphere of the ions, which would suggest that Li⁺-salts of POMs are highly soluble in water whereas salts with larger alkalis (*i.e.* Cs⁺) would always be

insoluble.^{75,76}

POMs of vanadium, molybdenum, and tungsten indeed follow this trend. However, this solubility trend is reversed for polycoltanates⁷⁷ (niobium and tantalum POMs), with Cs⁺ salts being highly soluble and Li⁺ salts being only sparingly soluble.^{69,78–80} The stark difference between these two classes of POMs provides two opposing model systems for studying Cs⁺ ion-association in water. Furthermore, Group V and VI metals can be combined into single discrete POMs, allowing for the study of intermediate systems.^{81,82} Through the study of these extreme and intermediate cases of POMs, we hope to elucidate the precise processes by which Cs⁺ ion-association occurs and, by extension, the ideal solution environment, reagents, and conditions for its efficient sequestration and removal.

2.2 Ion-Pairing with POMs



Figure 2.1: The three ion-pairing motifs: (a) contact, (b) solvent-shared, and (c) solvent-separated ion-pairing.⁸³

The degree of ion-pairing between cations and anions can be loosely divided into three motifs⁸⁴ – contact, solvent-shared, and solvent-separated (Figure 2.1). As an initial approximation, solid state lattices usually dissociate homogeneously into free, separately hydrated ions when dissolved in water, meeting the criteria for solventseparated ion-pairing. However, in some cases including the the cesium salt of hexaniobate ($[Nb_6O_{19}]^{8-}$, Figure 2.1a), there are measurable degrees of contact ion-pairing, in which some degree of ion-association remains even in dilute aqueous environments.^{83,85} Cesium counter-cations associate directly to the three bridging oxygen atoms on the faces of hexaniobate's Lindqvist structure. Because the Lindqvist ion is a superoctahedron with eight faces, it allows for eight associating Cs⁺ – a complete neutralization of its 8charge (Figure 2.2). The intermediate case of solvent-shared ion-pairing occurs when a cation and an anion remain loosely associated by a shared hydration sphere.



Figure 2.2: Solid state cation coordination environments of (left) Li, (middle) K, and (right) Rb/Cs salts of hexaniobate, demonstrating the greater degree of ion-association with larger cations. Green polyhedra = $[NbO_6]$, isolated red spheres = lattice water, and pink, magenta, and purple spheres are Li⁺, K⁺, and Rb⁺/Cs⁺ cations, respectively.

The degree of ion-pairing in aqueous solutions can be predicted by the solid-state distances between POMs and their countercations. The solid state structures of the alkali salts of hexaniobate – $A_8[Nb_6O_{19}] \cdot nH_2O$ (A = Li, K, Rb, Cs) – exemplify this (Figure 2.2). All eight Cs⁺ and Rb⁺ countercations are bonded directly to the three bridging oxygen atoms on the faces of the Lindqvist superoctahedron in their respective crystal lattices. The potassium salt exhibits four K^+ ions being directly bonded and the other four being partially hydrated away from the cluster.⁶⁹ Finally, Li⁺ ions form adamantane-like clusters with water molecules, and direct bonding between the clusters and Li is minimal.⁸⁶

The solution structures that we have been able to probe by X-ray scattering parallel the solid state structures. Cesium hexaniobate exhibits contact ion-pairing with some of the Cs⁺ ions remaining associated to the faces of the POM.⁸⁵ Rb⁺ shows a similar structure in solution, but with less ion-association at the same concentration as an analogous cesium hexaniobate solution. Potassium also exhibits ion-pairing in solution to some degree, but is more likely solvent-mediated ion-pairing. Although lithium hexaniobate is difficult to study in the aqueous state due to its limited solubility, the reason for its insolubility is predictable from its solid state structure. Li⁺ is unable to form contact ion-pairs due to its high solvation enthalpy,⁸⁷ forcing it to bridge multiple highly-charged clusters via association to water molecules, thereby causing precipitation at much lower concentrations.

2.3 Overview of Experimental Ion-Pairing Measurement Techniques

2.3.1 Thermochemical Measurements and Calculations

Calorimetry can be used to find the change in enthalpy between the solid and aqueous states for cluster salts (Chapters 4 and 5). For the case of room temperature aqueous dissolution, the solvent was kept at a constant 25.000 °C. The calorimeter tracks the heat flow required to maintain this constant temperature, which is allowed to equilibrate

for at least eight hours to allow for a sufficiently constant background signal. Once equilibrium is reached, a known mass of solid sample is dropped into the calorimeter. The resultant dissolution either heats or cools the solution, which causes a change to the heat flow (measured in μ W) required to maintain the temperature at 25.000 °C. This results in either a dip (if endothermic) or rise (if exothermic) in the heat flow signal (Figure 2.3). The signal is allowed to return to the baseline (usually taking around 90 minutes) and a line of best fit is determined for the signal on either side of the peak.



Figure 2.3: Sample heat flow signal for the dissolution of $Cs_8[Ta_6O_{19}]$ in water (red curve) with the linear background signal for subtraction included (black dashed line).

Upon determining the line of best fit, this line is background-subtracted from the signal, which is subsequently integrated over time to obtain a value measured in µJ (Figure 2.4) and multiplied by a dimensionless calibration constant (determined previous from KCl pellets and their known molar enthalpy of dissolution):

$$K_{calibr}\left(\int_{t_i}^{t_f} q(t)dt\right) = \Delta H_{total}$$
(2.1)

where K_{calibr} is the calibration constant, t_i is the start of the measurement time, t_f is


Figure 2.4: Background-subtracted and integrated peak from Figure 2.3, which is subsequently processed to arrive at the molar enthalpy of dissolution.

the time of signal re-equilibration, and ΔH_{total} is the total change in enthalpy. ΔH_{total} can then be divided by the number of moles of sample to find the molar enthalpy of dissolution (ΔH_{dis}). For example, the peak in Figure 2.4 from a 16.4 mg (6.50 µmol) sample of Cs₈[Ta₆O₁₉]is processed as follows:

$$\frac{(-10.9803)(-59977.6\mu\text{J})}{6.50\mu\text{mol}} = 101.3\,\text{kJ}\,\text{mol}^{-1}$$
(2.2)

where $K_{calibr} = -10.9803$. This value is the molar enthalpy of dissolution before correcting for lattice water, which is demonstrated in Appendix B. The integration process for hightemperature oxide-decomposition calorimetry is similar.

2.3.2 133 Cs NMR – T_1 Relaxation

NMR can be used to measure the relative magnitudes of ion-pairing between Cs⁺ and various anions (Chapters 6 and 7).^{88,89} At time $\tau = 0$, a 180° pulse inverts the magnetization vector M_z such that it lies along the negative-z axis (i.e. $M_z = -M_0$). The



Figure 2.5: A model relaxation curve for a theoretical solution ($T_1 = 5.0$ seconds) with a red line denoting the point at which T_1 is reached.

spin-lattice relaxation causes M_z to increase from its inverted value $-M_0$, through 0, and asymptotically approach its initial value M_0 (Figure 2.5). Thus, M_z can be found at any time τ by using the formula:

$$\frac{M_z}{M_0} = I[0] - Pe^{-\frac{\tau}{T_1}} = I[0] - Pe^{-\tau R_{QR}}$$
(2.3)

where P denotes a pre-exponential factor typically close in value to 2 (complete inversion of M_z to $-M_z$), I[0] is the asymptote of the graph (thermodynamic equilibrium) as a fraction of M_0 (typically close in value to 1), and τ is time in seconds.

This longitudinal relaxation can be halted by applying a 90° pulse at some time τ after the 180° pulse. This pulse rotates M_z so that it now lies in the transverse plane. By measuring the magnitude of the signal (appearing as a single peak) at a set of values of τ and fitting the data to Equation 2.3, T_1 (the time at which M_z has returned to $1 - \frac{2}{e} \approx 26.4\%$ of its positive equilibrium value) can be obtained.

The electric field gradient q_z is provided by an asymmetric distribution of electron

density around a quadrupolar nucleus. It is expressed as the second spatial derivative of the electrostatic potential (V), namely:

$$q_z = \frac{\partial^2 V(x)}{\partial x_z^2} \tag{2.4}$$

and thus has a x^{-3} dependence, where x_z is the distance between the source of negative charge and the cesium nucleus. Because the electric field gradient term in the quadrupolar relaxation rate expression is the only distance-dependent term and is squared, R_{QR} R_{QR} (the reciprocal of T_1) has a x^{-6} distance dependence, making it especially sensitive to relative degrees of contact ion-pairing while being less sensitive to solvent-separated ion-aggregation.

Because cesium's predominant isotope has a nuclear spin greater than $\frac{1}{2}$ (¹³³Cs, $I = \frac{7}{2}$)⁹⁰, it has a quadrupole moment.⁹¹ Thus, cesium's nucleus can measurably interact with the electric field gradient arising from an asymmetric distribution of charge around it,⁹² *i.e.*, from nearby charged anionic clusters. This interaction allows for an efficient relaxation mechanism, greatly outweighing weaker dipolar methods of relaxation to the point that they can be ignored,^{93,94} including the Nuclear Overhauser Effect.⁹⁵ In light of this, the spin-lattice relaxation time parameter, T₁, and its reciprocal relaxation rate, R_{QR} , can be described entirely by quadrupole relaxation:

$$R_{QR} = \frac{1}{T_{1(QR)}} = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2 Qq_z}{h}\right)^2 \tau_c$$
(2.5)

where η is an electric field gradient asymmetry parameter, q_z is the transverse electric field gradient, Q is the electric quadrupole moment of the nucleus, e is the electronic charge, τ_c is the molecular correlation time, and I is the nuclear spin.⁹⁶

The molecular correlation time (τ_c) is expressed as:

$$\tau_c = \frac{4\pi\eta_0 r^3}{3kT} \tag{2.6}$$

where η_0 is the viscosity of the solution, r is the effective hydrodynamic radius of Cs⁺, k is the Boltzmann constant, and T is the temperature of the solution.

Chapter 3: Cesium Salts Of Niobo-Tungstate Isopolyanions With Intermediate Group V - Group VI Character

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3.0 Abstract

Alkali metal salts of polyoxometalates (POMs) of the group VI elements (W and Mo) and polycoltanates (Nb and Ta POMs) exhibit opposing trends in their solubility in water and ion-association in solution. Mixed clusters of these two group V metals and tungsten provide an opportunity to probe the reversal in these trends and to understand their origin. A review of a classic study of mixed Nb/W clusters and our own work in Ta/W polyanions, have led us to isolate Cs^+/Na^+ salt of $[Nb_4W_2O_{19}]^{6-}$ and two salts, Cs^+/Na^+ and pure Cs^+ , of $[Nb_2W_4O_{19}]^{4-}$ by using peroxoniobate $([Nb(O_2)_4]^{3-})$ instead of hexaniobate $([Nb_6O_{19}]^{8-})$ as the niobium source. Crystallographic analysis shows that Cs⁺-bonding to clusters increases with Nb-content, following the trend observed in our previous studies of hexaniobate in solution. Fragmentation by ESI-MS suggests that niobium-rich $[Nb_4W_2O_{19}]^{6-}$ is less stable than isostructural $[Nb_2W_4O_{19}]^{4-}$ and this technique, together with FTIR, confirms the predominance of the cis- isomer in the cluster structures. The mixed-metal composition of these isopolyanions is reflected in the crystallographic bond lengths and in the positions of the absorption bands in the UV spectra. DFT calculations reveal that the HOMO-LUMO energy gap widens with increasing Nb content in the cluster framework – an effect ascribed to the overall poorer mixing of Nb_{4d} , versus W_{5d} , atomic orbitals with the corresponding O_{2p} orbitals.

3.1 Introduction

Ion-association is an extremely important phenomenon in natural and synthetic aqueous systems. The relationship between ions defines the structural transition between the solid and aqueous states of ionic materials and directly influences their self-assembly, as well as the solubility and stability of related compounds in solution. Alkali salts of polyoxometalates (POMs) provide a unique opportunity to study these processes. POMs are discrete anionic metal-oxo clusters of the early d^0 transition metals (W^{VI}, Mo^{V/VI}, V^V, Nb^V, Ta^V).⁹⁷ This family of clusters displays a range of functional properties⁹⁸ and may be divided into two distinct subsets with regard to their predominant self-assembly conditions, redox chemistry, charge density, and solubility properties. Group VI POMs (W^{VI} and Mo^{V/VI}) self-assemble via acidification of aqueous solutions, possess low charge-density, and exhibit rich redox chemistry. Group V (Nb^V and Ta^V) POMs are predominantly assembled and stable in base and possess poor redox character, consistent with their highly negative charge-densities.⁷¹ Meanwhile, V^V POMs have properties closer to those of Group VI POMs, exemplified by their rich redox character and acidic self-assembly conditions.

A crucial and less commonly recognized difference between these two classes of POMs can be seen in their solubilities with respect to charge-balancing countercations. Group VI POMs exhibit solubility related to the hydration sphere and solvation energy of their cations, with Li-salts being the most soluble and Cs-salts being the least soluble. Likewise, this is the accepted 'normal' solubility trend for simple salts in water, since hydration of ions is the thermodynamic driving force for aqueous dissolution.⁸⁴ Conversely, Group V POMs of Nb and Ta have the opposite solubility trend, with greater cationic radius resulting in enhanced solubility, while polyvanadates exhibit solubility trends more typical of Group VI POMs.^{69,85,86} Given the distinct differences between POM chemistry of Nb & Ta compared to V, we have previously coined the term 'polycoltanate' (derived from coltan, abbreviation of columbite-tantalite – the ore from which Nb and Ta are extracted) to explicitly mean the POM chemistry of Nb & Ta.⁷⁷ This reverse solubility phenomenon of polycoltanates with counterions was initially recognized with the hexaniobate Lindqvist ion, $[Nb_6O_{19}]^{8-}$ – the most persistent aqueous species of sufficiently alkaline solutions of niobium oxide. ^{99,100} Understanding and exploiting this unusual trend remains a worthwhile goal, allowing us to more efficiently perform separations, assembly, and manipulation of inorganic materials in water. Moreover, there is particular interest in developing technologies for separating and sequestering Cs⁺, since ¹³⁷Cs remains the biggest challenge of legacy nuclear wastes, as well as the radionuclide of greatest concern in the more recent Fukushima nuclear disaster.¹⁰¹

A large number of metals¹⁰² and even non-metals¹⁰³ can replace W^{VI} and $Mo^{V/VI}$ in Group VI POMs. This strategy has increased the range of the properties of these polyanions.^{104,105} An illustrative example of this approach is displayed by the synthesis of the Nb-substituted series of hexatung state ($[W_6O_{19}]^{2-}$).¹⁰⁶ This compositional series of Linqvist-type Nb/W isopolyanions, $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$ (x = 1-4), was originally prepared 40 years ago by Dabbabi et al. from reactions of ${\rm K}_8[{\rm Nb}_6{\rm O}_{19}]$ and so dium tungstate in aqueous media under pH control and in the presence of H₂O₂.⁸¹ The original report did not include crystallographic analysis of the structures and just $[NbW_5O_{19}]^{3-}$ (as the TMA⁺/K⁺, ¹⁰⁷ and the TBA⁺ salt), ¹⁰⁸ $[Nb_2W_4O_{19}]^{4-}$, ¹⁰⁹ and a hybrid derivative of the latter¹¹⁰ have been structurally characterized so far. These highly symmetric clusters with mixed metal site occupancies present significant disorder, rendering proper structure interpretation challenging, but Cs⁺ may provide the advantage of orienting the clusters by preferred coordination to the more basic niobium-bonded oxo-ligands. More importantly, prior studies comparing arrangement of ions in the solid-state to their ionassociation in solution have presented an emerging trend that solution behavior remarkably mirrors solid-state structure.^{68,85,111,112} Structural characterization of these mixed metal POMs is thus a worthwhile effort as a foundation for future solution studies that focus specifically on ion-association and solubility.

This series of niobo-tungstate POMs bridging end-member Group V and Group VI clusters allows for insight into an intermediate set of trends in self-assembly and ion-pairing. Increasingly alkaline reaction conditions result in gradual Nb substitution for W centers, exemplifying the hybrid nature of these POMs.⁸¹ The Cs⁺ salts of the members of this series are of particular interest from an ion-association perspective, due to the stark contrast between the extreme solubility of $Cs_8[Nb_6O_{19}]$ (as high as 1.5 molar) and the insolubility of Cs⁺ polytungstates. Here we complement structural data with electrospray ionization mass spectroscopy (ESI-MS), vibrational spectroscopies, and compositional analysis to determine compositional and isomeric purity of the Lindqvist ions. UV-vis spectroscopy corroborated with simulations elucidate the origin of shifting HOMO-LUMO gaps with composition.

3.2 Experimental

3.2.1 Syntheses

Synthesis of the three reported compounds is detailed below, and instrumentation and additional crystallographic details are available in Appendix A.

$3.2.1.1 \quad Cs_4Na_2[Nb_4W_2O_{19}] \cdot 12H_2O \ (CsNa\{Nb_4W_2\})$

 $Na_2WO_4 \cdot 2H_2O$ (3.3 grams, 10.0 mmol) was added to 40 mL of H_2O at room temperature and stirred until dissolution. $Cs_3[Nb(O_2)_4]$ (2.9 grams, 4.7 mmol) was added to the solution, which was further stirred for 10 minutes. The suspension was then slowly acidified dropwise with 12 M HCl until the pH reached a value of 9, during which a white



Scheme 1: Reaction products for niobo- and tantalo-tungstates⁷⁷ in analogous conditions. Color code: Nb, green; Ta, blue; W, grey; O, red.

precipitate formed and redissolved. The solution was then refluxed for 4 h, microfiltered with a 0.45 µm nylon syringe filter, cooled to room temperature, and allowed to crystallize at 4 °C. Macroscopic colorless block-like crystals formed after 60 hours. The mother liquor was removed and the crystals were washed in 2-propanol and dried under vacuum.

Yield = 0.604 grams (27.6% by mass). Full formula: $Cs_4Na_2Nb_4W_2O_{31}H_{24}$. MW = 1838.8 g mol⁻¹. Atomic Ratios, calculated (found): W/Nb: 0.5 (0.5), Cs/Nb: 1.0 (1.0), Cs/W: 2.0 (2.1). Characteristic IR bands (cm⁻¹): 531 (s,br), 733 (s, br), 840 (s, sh), 874 (w), 884 (m), 907 (m, sh), 932 (m, sh). UV absorption: $\lambda_1 = 211$ nm, ε_1 = 1.87×10^5 L mol⁻¹ cm⁻¹, λ_2 ($n(O_b) \rightarrow \pi^*(M-O_b)$ transfer band) = 253 nm, $\varepsilon_2 =$ 1.51×10^5 L mol⁻¹ cm⁻¹. Water content (%), crystallographic (TGA 22-400 °C, in air): 12.1 (11.84).

Crystallographic Data: $Cs_4H_{24}O_{31}Na_2Nb_{3.89}W_{2.11}$; MW = 1846.70 g mol⁻¹; Size:

 $(0.16 \ge 0.14 \ge 0.08) \text{ mm}^3$, T = 150 K; crystal system: monoclinic; space group: P2₁/n, a = 9.5760(3) Å, b = 13.5844(4) Å, c = 12.3503(4) Å, $\beta = 90.0790(12)^\circ$, V = 1606.58(9) Å³; Z = 2; $D_c = 3.817 \text{ mg m}^{-3}$; $\mu = 13.446 \text{ mm}^{-1}$; F(000) = 1659; $2\theta_{max} = 80.0^\circ$; 45150 reflections; 9955 independent reflections [$R_{int} = 0.0299$]; $R_1 = 0.0310$, $wR_2 = 0.0917$ and GOF = 1.260 for 9955 reflections (248 parameters) with I > $2\sigma(I)$; $R_1 = 0.0318$, $wR_2 = 0.0921$ and GOF = 1.261 for all reflections; max/min residual electron density, $+2.644/-1.995 \text{ eÅ}^{-3}$.

3.2.1.2 $Cs_3Na[Nb_2W_4O_{19}] \cdot 10H_2O (CsNa\{Nb_2W_4\})$

 $Na_2WO_4 \cdot 2H_2O$ (3.3 grams, 10.0 mmol) was added to 40 mL of H_2O at room temperature and stirred to dissolve. $Cs_3[Nb(O_2)_4]$ (2.9 grams, 4.7 mmol) was added to the solution, which was further stirred for 10 minutes. The suspension was then slowly acidified dropwise with 12 M HCl until the pH reached a value of 8, during which a white precipitate formed and redissolved. The slightly yellow solution was then refluxed for 4 h, microfiltered with a 0.45 µm nylon syringe filter, cooled to room temperature, and allowed to crystallize at 4 °C. Small silvery-white flake-like crystals formed over two days. The solid was separated by vacuum filtration, washed in 2-propanol, and dried under vacuum.

Yield = 0.210 grams (4.9% by mass) from initial crystallization. More product can be obtained by boiling the mother liquor to half of its initial volume and cooling the solution again to 4 °C. Full formula: $Cs_3NaNb_2W_4O_{29}H_{20}$. MW = 1827.0 g/mol|. Atomic Ratios, calculated (found): W/Nb: 2.00 (1.98), Cs/Nb: 1.50 (1.52), W/Cs: 1.33 (1.30). Characteristic IR bands (cm⁻¹): 488 (vw), 529 (vw), 567 (m), 773 (s, br), 894 (s), 947 (s). UV absorption: $\lambda_1 = 198$ nm, $\varepsilon_1 = 1.74 \times 10^5$ L mol⁻¹ cm⁻¹, λ_2 ($n(O_b) \rightarrow$ $\pi^*(M-O_b)$ transfer band) = 269 nm, $\varepsilon_2 = 1.05 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. Water content (%), crystallographic (TGA 22-500 °C, in air): 9.2 (9.15).

Crystallographic Data: $Cs_3H_{20}NaO_{29}Nb_{2.14}W_{3.86}$; MW = 1814.67 g mol⁻¹, size: (0.09 x 0.07 x 0.04) mm³; T = 173 K; crystal system: trigonal; space group: R3; a = 11.6472(15) Å, b = 11.6472(15) Å, c = 19.117(2) Å, V = 2245.9(6) 3; Z = 3; $D_c = 4.025 \text{ mg m}^{-3}$; $\mu = 19.280 \text{ mm}^{-1}$; F(000) = 2404; $2\theta_{max} = 60.0^{\circ}$; 12477 reflections; 2686 independent reflections [$R_{int} = 0.0566$]; $R_1 = 0.0325$; $wR_2 = 0.0520$ and GOF = 1.008 for 2686 reflections (122 parameters) with I > $2\sigma(I)$, $R_1 = 0.0496$, $wR_2 = 0.0563$ and GOF = 1.009 for all reflections; max/min residual electron density: $+1.211/-1.167 \text{ eÅ}^{-3}$.

$3.2.1.3 \quad Cs_4[Nb_2W_4O_{19}] \cdot 4H_2O \ (Cs\{Nb_2W_4\})$

 $Na_2WO_4 \cdot 2H_2O$ (3.3 grams, 10.0 mmol) was added to 40 mL of H2O at room temperature and stirred until dissolution. $K_3[Nb(O_2)_4]$ (1.6 grams, 4.7 mmol) was added to the solution, which was further stirred for 10 minutes. The suspension was then slowly acidified dropwise with 12 M HCl, during which a white precipitate formed and redissolved until the pH reached a value of 7. Upon continued dropwise addition of HCl, the solution grew increasingly opaque and yellow until the pH reached a value of 2. The yellow suspension was then refluxed for 2 hours. The resulting solution was allowed to cool to room temperature and was then centrifuged. The supernatant was separated and microfiltered with a 0.45 µm nylon syringe filter. 6.0 grams of CsCl were then added to the supernatant and a cream-colored precipitate formed. This precipitate was isolated by centrifugation and removal of the supernatant liquid. The solid was dissolved in the minimum amount of boiling water ($\approx 120 \text{ mL} \cdot \text{g}^{-1}$) and allowed to recrystallize at 4 °C. After a day, small needle-like colorless crystals formed. The crystals were washed in 2-propanol and dried under vacuum.

Yield = 1.703 grams (39.6% by mass, crude product). MW = 1828.84 g mol⁻¹. Full formula: Cs₄Nb₂W₄O₂₃H₈. Atomic Ratios, calculated (found): W/Nb: 2.00 (2.02), Cs/Nb: 2.00 (1.93), W/Cs: 1.00 (1.04). Characteristic IR bands (cm⁻¹): 594 (m), 773 (s), 860 (w, sh), 947 (s, sh). UV absorption: $\lambda_1 = 196$ nm, $\varepsilon_1 = 1.64 \times 10^5$ L mol⁻¹ cm⁻¹, $\lambda_2 (n(O_b) \rightarrow \pi^*(M-O_b)$ transfer band) = 271 nm, $\varepsilon_2 = 1.03 \times 10^5$ L mol⁻¹ cm⁻¹. Water content (%), crystallographic (TGA 22-400 °C, in air): 4.0 (3.95).

Crystallographic Data: $Cs_4H_8O_{31}Nb_{1.97}W_{4.03}$; MW = 1832.11 g mol⁻¹, size: (0.16 x 0.14 x 0.08) mm³, T = 150 K; crystal system: monoclinic; space group: P2₁/*n*, *a* = 9.6119(8) Å, *b* = 11.8087(10) Å, *c* = 11.2532(9) Å, β = 90.929(18)°, V = 1277.12(18) Å³; Z = 2; D_c = 4.764 mg m⁻³; μ = 24.655 mm⁻¹; F(000) = 1582; $2\theta_{max}$ = 86.80°; 42881 reflections; 9627 independent reflections [R_{int} = 0.0744]; R_1 = 0.0468, wR_2 = 0.0869 and GOF = 1.016 for 9627 reflections (155 parameters) with I > 2 σ (I), R_1 = 0.0897, wR_2 = 0.1037 and GOF = 1.016 for all reflections; max/min residual electron density, +5.933/-4.251 eÅ⁻³.

3.3 Results and Discussion

3.3.1 Synthetic Variations

Departing from Dabbabi's hexaniobate-based syntheses, peroxoniobate $([Nb(O_2)_4]^{3-})^{113}$ was used as the Group V metal source for three Cs⁺ salts of POMs: Cs₄Na₂[Nb₄W₂O₁₉]· 12H₂O (CsNa{Nb₄W₂}), Cs₃Na[Nb₂W₄O₁₉]·10H₂O (CsNa{Nb₂W₄}), and Cs₄[Nb₂W₄-O₁₉]·4H₂O (Cs{Nb₂W₄}). Peroxide is important for maintaining solubility of niobium in slightly alkaline to acid conditions (*i.e.*, pH < 10). The use of peroxoniobate allows



Figure 3.1: (a) D_{4h} trans-isomer of {Nb₂W₄}. (b) C_{2v} cis-isomer of {Nb₂W₄}, vewied along a terminal-oxo bond. Color code: Nb, green; W, grey; O, red.

for greater control over these syntheses by providing minimal and consistent peroxide concentration. Peroxide is an unstable molecule with respect to heat, base and redox reactions, leading to potential inconsistent or uncontrolled results. This is particularly true because tungsten is likewise redox active.

The pH of the reaction controlled variance in the Nb:W ratio in each compound, thereby bridging the opposing self-assembly environments of Group V and Group VI POMs and paralleling Dabbabi's pioneering work on the $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$ series.⁸¹ While the general trend of increasing niobium content with higher pH was maintained, the actual pH ranges where members of the series were prevalent shifted with respect to reaction basicity. For instance, with peroxoniobate as the Group V metal source, the $[Nb_2W_4O_{19}]^{4-}$ species is formed at wide pH range (2 < pH < 8) instead of specifically at pH ≈ 5.5 .⁸¹ However, we do need to take into account the crystallizing countercations, as they can exhibit selectivity for crystallizing specific cluster compositions and isomers. Scheme 1 summarizes the reaction conditions under which these three Lindqvist salts were obtained, along with tantalo(niobo)-tungsten clusters from a prior study.⁷⁷ While the Cs{NbW₉} analogue of Cs{TaW₉} was successfully synthesized, attempts at making niobate forms of Cs{Ta₂W₈} and CsNa{Ta₃W₃} instead resulted in the formation of Cs{Nb₂W₄} and CsNa{Nb₂W₄}, respectively. CsNa{Nb₄W₂} was obtained by raising the pH from 8 to 9 in the CsNa{Nb₂W₄} reaction.

3.3.2 Structures

3.3.2.1 Isomer Determination

We can conclude that the cis-isomers of both clusters, $\{Nb_4W_2\}$ and $\{Nb_2W_4\}$, are the main crystalline products from the reaction mixtures. This is suggested by the number of absorption bands in the FTIR spectra (Figure 3.1).¹¹⁴ Focusing on the prominent terminal-oxo stretches (M-O_t) at 850-1000 cm⁻¹ (Figure 3.2), the low-symmetry C_{2v} cis-isomer exhibits six IR stretches (A₁ and B₁ from the two-site metal and 2A₁, B₁, and B₂ from the four-site metal). On the other hand, the high-symmetry D_{4h} trans-isomer would exhibit only two IR stretches (A_{2u} from the two-site metal and E_u from the four-site metal). All three compounds exhibit more than two IR stretching bands within this region, ruling out the high-symmetry D_{4h} trans structures. Thus, each ion must exist as the lower-symmetry C_{2v} cis-isomer. Although not all six peaks are immediately perceptible in the 850-1000 cm⁻¹ region of each IR spectrum, predominance of the D_{4h} structures can be ruled out due to the clear existence of more than two peaks. Bridging oxygen (M-O_b) stretching modes are primarily responsible for bands in the 500-850 cm⁻¹ region. Combinations of bridging oxygen and central oxygen (M-O_c) bending modes



Figure 3.2: IR spectra of $CsNa\{Nb_4W_2\}$, $Cs\{Nb_2W_4\}$, and $CsNa\{Nb_2W_4\}$, supporting the existence of more than two IR-active terminal-oxo stretching modes for each compound in the terminal-oxo stretching range. Regions for terminal-oxo stretches, bridging-oxo stretches, and bending modes involving the central-oxo are labeled. The full FTIR spectra are shown in Figure A4.



Figure 3.3: Representation of the crystal structures of $CsNa\{Nb_4W_2\}$, $Cs\{Nb_2W_4\}$, and $CsNa\{Nb_2W_4\}$ viewed along the crystallographic c axis. Color code: unit cell edges, dark green; MO_6 (M = Nb/W), grey; Cs^+ , pink and Na^+ , tan; O (from lattice water molecules), red.

Table 3.1: Nb/W occupancies for each cluster by free refinement of X-ray data and energy dispersive spectroscopy (EDX)

1 10 (/	
Cluster	Nb/W Occupancy	Nb/W Occupancy
	(Free Refinement)	(EDX)
$CsNa{Nb_4W_2}$	3.89/2.11	3.97(3)/2.03(3)
$Cs{Nb_2W_4}$	1.97/4/03	1.99(3)/4.01(3)
$CsNa{Nb_2W_4}$	2.14/3.86	2.05(4)/3.95(4)

result in the bands at lower wavenumbers.¹¹⁴ The disparity between the spectra of the two {Nb₂W₄} species, most prominently in the 890-910 cm⁻¹ range, can be attributed to the additional Cs⁺ in Cs{Nb₂W₄} associating to additional terminal oxygen atoms on the clusters, weakening their stretching signals (Figure 3.4).

3.3.2.2 Crystallographic Structures

In each of the three studied phases, the free refinement of metal occupancies very closely matched the ratios found by energy-dispersive x-ray spectroscopy (EDX, Table 3.1). The fully-oxidized states of the metals were fixed since there is no evidence (i.e. color) for

Table 3.2: Summary of metal-oxo bond lengths in Lindqvist ions

Oxo-bond type	${Nb_6}$	$CsNa{Nb_4W_2}$	$Cs{Nb_2W_4}$	$CsNa{Nb_2W_4}$	$\{W_6\}$
M-O _t	1.804(9) Å	1.751-1.786 Å	1.726-1.759 Å	1.746-1.752 Å	1.689(6) Å
$M-O_b$	2.005(2) Å	1.951-1.981 Å	1.915-2.005 Å	1.919-1.991 Å	1.924(3) Å
M-O _c	2.381(1) Å	2.333-2.360 Å	2.341- 2.386 Å	2.333-2.337 Å	2.331(4) Å

reduction of W^{VI} and reduction of Nb^{V} is extremely rare in polyanions. Although Bond Valence Sum (BVS) calculations were attempted for all three structures, the degree of mixed-occupancy and disorder in each lattice significantly decreased the effectiveness of such calculations for determining atomic ratios.^{115–117} SEM-EDX was instead employed for this purpose, which is capable of giving very accurate ratios of heavy metals and these analyses confirmed the ratios obtained from free refinement of the site occupancies (Table 3.1). Additionally, the Nb/W ratios are confirmed by the number of fully-occupied countercations sites per cluster (six for the case of CsNa{Nb₄W₂} and four for the case of both {Nb₂W₄} structures), due to to the requirement for charge-balance. The BVS values of the bridging oxos are strictly greater than 1.720 in all three structures, likewise showing no protonation that would reduce the number of required countercations in each structure allows assignment of the metal occupancies to their nearest integer values with confidence.

Both CsNa{Nb₄W₂} and Cs{Nb₂W₄} crystallize in the orthorhombic crystal system with three symmetrically independent metal sites in the cluster unit (Figure 3.3). Nb and W are disordered over the six metal positions, with total occupancies summing to match the respective metal ratios in each cluster. The free refinement yielded an Nb/W ratio very close to 2:1 for CsNa{Nb₄W₂} and 1:2 for Cs{Nb₂W₄} (Table 3.1). Each of these ratios was supported by the atomic % ratio (EDX) and the crystallographic determination of the number of cations required to fully balance the charge on each



Figure 3.4: Representation of the coordination environments of the Cs^+ countercations in the structures of $CsNa\{Nb_4W_2\}$, $Cs\{Nb_2W_4\}$, and $CsNa\{Nb_2W_4\}$.

cluster (six and four, respectively). CsNa{Nb₂W₄} crystallizes in the trigonal space group R3 with only two symmetrically independent metal sites in the cluster unit. The free refinement again yielded an Nb:W occupancy ratio close to 1:2 and this ratio was further supported by the atomic % ratio, as well as the crystallographically determined number of cations.

In the CsNa{Nb₄W₂} structure, Lindqvist ion units are arranged in layers perpendicular to the c-axis. Cs⁺ coordinates to terminal and μ_2 bridging oxygens on the clusters and sodium countercations bonded to six water molecules each are interspersed between the cluster layers. The values for metal-oxygen distances for each of the three inequivalent oxygen types (Figure A9) fall in the expected range for an Nb/W mixed-metal cluster (Table 3.2). The bond distances between the mixed-metal sites and the terminal oxo ligands (O_t) are intermediate between those of terminal-oxo bond lengths in hexatungstate ({W₆}) and hexaniobate ({Nb₆}).¹¹⁸ The bond lengths are slightly closer to those in {Nb₆}, indicative of the greater Nb than W occupancy in each metal site. This trend is also observed for the bridging oxo bond lengths (M-O_b), which are on average slightly closer to the bond length of Nb-O_b than that of W-O_b. This is again the case for the bonds to the central oxygen (M-O_c). In the Cs{Nb₂W₄} structure, a similar stacking

arrangement of Lindqvist ions and countercations is seen, but with no sodium ions. The metal-oxygen distances for the three oxygen types are within the expected range for an Nb/W mixed cluster, but with bond lengths generally closer to those in $\{W_6\}$ to reflect the greater tungsten occupancy at each metal site. In CsNa $\{Nb_2W_4\}$, the M-O_t and M-O_b bond lengths fall within the ranges in Cs $\{Nb_2W_4\}$. The M-O_c bonds have lengths slightly shorter than those in Cs $\{Nb_2W_4\}$ and closer to those in $\{W_6\}$. The inclusion of Nb in the structure of $\{W_6\}$ therefore typically results in the lengthening of bond distances due to both the lower valency of Nb^V and the mixing of metals in the structure, which typically distorts the molecular framework.

Considering the countercation coordination environments with respect to only the POMs in the lattice, the two crystallographically distinct Cs^+ sites in $CsNa\{Nb_4W_2\}$ exhibit five-coordinate and six-coordinate bonding to the terminal and bridging oxygen atoms (Figure 3.4). Each Cs^+ additionally bridges to the sodium cations in the lattice via four water molecules (for total Cs⁺ coordination numbers of nine and ten). A similar Cs^+ bonding scheme is seen in $Cs\{Nb_2W_4\}$ with Cs^+ exhibiting six-coordinate bonding with respect to the oxygen atoms in their associated clusters (Figure 3.4). However, solvent water molecules instead bridge Cs⁺, since there is no sodium in the lattice. Cs⁺ sites in CsNa{Nb₂W₄} only have four bonds to the clusters' terminal and bridging oxygen atoms, and the remaining coordination is to water molecules (C.N.=11). Moreover, the bonding of Cs^+ to the clusters is primarily to the terminal oxos, suggesting the less basic nature of the bridging oxos in these W-rich sites. Meanwhile, Cs-cations of $Cs\{Nb_2W_4\}$ bond to both bridging and terminal oxos, likely because there is more Cs in the lattice (no sodium) and a surprising lack of lattice water (Figure 3.4). Alkali-cluster lattices typically contain ten or more water molecules per cluster. In the clusters with sodium countercations ($CsNa{Nb_4W_2}$ and $CsNa{Nb_2W_4}$), sodium ions only coordinate to



Figure 3.5: ESI-MS spectra of $CsNa\{Nb_4W_2\}$, $Cs\{Nb_2W_4\}$, and $CsNa\{Nb_2W_4\}$.

lattice water molecules and exhibit no coordination to cluster oxygen atoms. The cesiumoxygen bond distances of 3.0-3.6 Å were chosen to match the established range seen in ion-association to Lindqvist ions.⁸⁵ However, unlike the bonding of Cs^+ to the faces of the {Nb₆} superoctahedron,⁶⁹ Cs⁺ instead associates more loosely to bridging and terminal oxygen atoms in the currently studied niobo-tungstate clusters. The cation-only coordination environments with clusters removed are also highlighted (Figure A5).

3.3.3 Stability and Isomer Confirmation by ESI-MS

Electrospray-ionization mass-spectrometry (ESI-MS) was employed to explore the stability and confirm isomeric purity of the three compounds in solution and in the gas phase. This is also the most effective method to distinguish between a pure phase of mixed-metal clusters, and a mixture of co-crystallized clusters of different compositions. Spectra of CsNa{Nb₄W₂}, Cs{Nb₂W₄}, and CsNa{Nb₂W₄} were obtained in aqueous solution. The regions of interest in these spectra, along with labeled peak envelopes are shown in Figure 3.5. The spectrum of CsNa{Nb₄W₂} confirms the formula of the cluster as determined by crystallography and elemental analysis. Four peak envelopes can be assigned to the cluster, protonated and associated to Cs⁺ and Na⁺ countercations to different degrees. The envelope displaying the highest intensity is ascribed to an incomplete monoprotonated cluster in which one of the oxo ligands is missing. Hexacoltanate species in the gas phase missing one or more oxo ligands are fairly common, as reported in previous mass spectrometry studies.¹¹⁹ The high relative intensity of the [HWO₄]⁻ peak, when compared to the spectra discussed below, suggests that this polyanion is less stable in the gas phase than {Nb₂W₄}.

The spectra of the two salts of $\{Nb_2W_4\}$ also confirm the crystallographic/EDX formula despite the differences in the relative intensity of a number of peak envelopes. Seven and four peaks in the CsNa $\{Nb_2W_4\}$ and Cs $\{Nb_2W_4\}$ spectra respectively can be assigned to an intact $\{Nb_2W_4\}$ polyanion. The peaks showing the highest intensity in each spectrum are ascribed to a protonated intact cluster in the case of the CsNa $\{Nb_2W_4\}$ spectrum and to an adduct, formed by Cs⁺ and adventitious Na⁺ countercations associated to a protonated $\{Nb_2W_4\}$ cluster missing two oxo ligands, in the case of the Cs $\{Nb_2W_4\}$ spectrum. Interestingly, the presence of a $[W_3O_{10}]^{2-}$ fragment in both $\{Nb_2W_4\}$ spectra confirms the spectroscopic assignment of this cluster as the cis-isomer.

Table 3.3: λ_{max} values for $n(O_b) \rightarrow \pi^*$ (M-O_b) transitions in members of the $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$ series

Anion	$\lambda_{max}, \mathbf{nm}$
$\{Nb_6\}$	248
$\{Nb_4W_2\}$	253
$\{Nb_2W_4\}$	$269, 271^a$
$\{W_6\}$	278^{120}

^{*a*} CsNa{Nb₂W₄} and Cs{Nb₂W₄}, respectively.

3.3.4 Electronic Structure Trends by UV-Vis Spectroscopy

As tungsten occupancy in the isostructural $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$ series increases, a monotonic redshift trend is observed in the $n(O_b) \rightarrow \pi^*(M-O_b)$ transfer band (Table 3.3, Figure 3.6). This can be attributed to the $\pi^*(Nb-O_b)$ LUMO¹²¹ in {Nb₆} being higherlying (more destabilized) than the $\pi^*(W-O_b)$ LUMO in {W₆} with respect to their $n(O_b)$ HOMOs. 122 The higher-lying LUMO arises from the poorer mixing of $\rm Nb_{4d}$ than $\rm W_{5d}$ atomic orbitals with O_b , due to their atomic orbital energies being further apart.¹²³ The λ_{max} values in the $n(O_b) \rightarrow \pi^*(M-O_b)$ transitions for two other prominent hexametalate species, $[Ta_6O_{19}]^{8-}$ and $[Mo_6O_{19}]^{2-}$, are 215 nm and 326 nm, respectively.^{121,124} Comparing these transitions to those in $\{Nb_6\}$ and $\{W_6\}$, the redshift across a period is larger than the blueshift going down a group (Table 4). This arises from the significant lowering of atomic orbital energies due to the additional proton in each Group VI metal center (e.g., from Ta to W). The relative similarity in energy allows W_{5d} orbitals to have better π -mixing with oxygen's 2p orbitals. This stabilizing effect is greater than the destabilization resulting from poorer orbital overlap of the 5d orbitals with 2p orbitals, compared to 4d orbitals in the same group (e.g., from Nb to Ta) with 2p orbitals. The absorption peak positions of the niobo-tungstate clusters are indicative of the mixed occupancy of niobium and tungsten at each metal site, constituting an intermediate level



Figure 3.6: UV-visible spectra of CsNa{Nb₄W₂}, Cs{Nb₂W₄}, and CsNa{Nb₂W₄} (0.1 mM aqueous solutions). The higher-wavelength peaks correspond to $n(O_b) \rightarrow \pi^*(M-O_b)$ charge transfer bands.

Table 3.4: λ_{max} values for $n(O_b) \to \pi^*$ (M-O_b) transitions in $[M_6O_{19}]^{n-}$ (M = Nb, Mo, Ta, W)

	Group V, λ_{max}	Group VI, λ_{max}
4d	$[Nb_6O_{19}]^{8-}, 248 \text{ nm}$	$[Mo_6O_{19}]^{2-}, 326 \text{ nm}$
5d	$[Ta_6O_{19}]^{8-}, 215 \text{ nm}$	$[W_6O_{19}]^{2-}, 278 \text{ nm}$

of M_{nd} -O_b orbital mixing. This results in the LUMOs for the mixed-metal species lying between those in {Nb₆} and {W₆}, with greater tungsten occupancy resulting in smaller energy gaps. The electronic properties of these mixed Nb/W POMs are thus indicative of hybrids of {Nb₆} and {W₆}.

3.3.5 Computational Characterization

The electronic structure and properties of both cis- and trans-isomers of $\{Nb_4W_2\}$ and $\{Nb_2W_4\}$ were studied using first-principles calculations at the PBE and B3LYP lev-



Figure 3.7: HOMO, LUMO, and E_{gap} energies of CsNa{Nb₄W₂}, Cs{Nb₂W₄}, and CsNa{Nb₂W₄} in eV. The O_b atomic orbital contributions to the LUMOs are shown in parentheses.

els of theory. Identifying the proper isomers of each structure is complicated by the crystallographic disorder of these highly-symmetric species, warranting verification by computational methods. The relative electronic energies for the cis- and trans-isomers of $\{Nb_4W_2\}$ and $\{Nb_2W_4\}$ indicated slightly greater stability (on the order of 1-2 kcal·mol⁻¹) in the cis-isomer of each structure, confirming the predictions from IR spectra and group theory.

The historically well-characterized {Nb₆} and {W₆} structures were also investigated in order to properly elucidate the mixed-metal polyanions in the context of their intermediate properties between those of their single-metal congeners. In each hexametalate structure, the HOMO and LUMO are composed of the occupied O_{2p} and empty antibonding $\pi^*(M-O_b)$ orbitals, respectively. Combining Nb and W within the same structure resulted in intermediate electronic structures between the two pure hexametalate species, as predicted by the UV-vis spectra. Increased Nb occupancy resulted in greater energy

Table 3.5: Experimental and calculated (B3LYP) energy gaps (E_{gap}) for {Nb₆}, {Nb₄W₂}, {Nb₂W₄}, and {W₆}

Cluster	Calc. E_{gap}	Calc. Excitation	Exp. E_{gap}
	(eV)	Energy $(eV)^a$	$(eV)^b$
$\{Nb_6\}$	5.278	4.451	4.999
$\{Nb_4W_2\}$	5.082	4.419	4.901
$\{Nb_2W_4\}$	5.011	4.347	$4.609, 4.575^c$
$\{W_6\}$	4.876	4.235	4.460

^a Average excitation energy (3 lowest excitations) from TD-DFT calculations.

^b Calculated as $E = \frac{hc}{\lambda}$, where λ is the value of wavelength for the absorption ascribed to the $n(O_b) \rightarrow \pi^*(M-O_b)$ charge transfer across bridging oxygen bonds.

^c CsNa{Nb₂W₄} and Cs{Nb₂W₄}, respectively

gaps due to generally poorer mixing between M_{nd} and O_{2p} atomic orbitals (Figure 3.7). This poor mixing arises from the disparate atomic orbital energies of Nb_{4d} and O_{2p} (-2.95 eV and -9.82 eV for a niobium atom and an oxygen atom, respectively) and results in higher-lying LUMOs with less O_{2p} character. The energy required to promote electrons from the fully- O_{2p} nonbonding orbitals is thus increased. The atomic orbital energy of W_{5d} is closer to that of O_{2p} (-4.34 eV for a tungsten atom), resulting in LUMOs with more O_{2p} character.

Our calculated HOMO-LUMO gaps are overestimated by both PBE and B3LYP with respect to those inferred by the UV-Vis spectra (Table 3.5). This disparity can be attributed to the dependency of the molecular orbital energies, and hence the HOMO-LUMO gap, on the DFT functional.¹²⁵ Nonetheless, the trend of smaller HOMO-LUMO gaps with increasing tungsten occupancy is maintained in all forms of computational and experimental characterization.

3.4 Conclusions

Through a combination of experimental and computational methods, three cesium salts of members of the $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$ series were shown to exhibit intermediate solidstate bond distances and electronic properties between those of Group V and Group VI POMs. Their resultant properties highlight the nature of their mixed character. By combining these two disparate classes of POMs, advanced materials with unique, hybrid properties are attainable from water. The potential thus arises for tuning the solubility and base-catalytic capabilities of Group V POMs with the electrochemical activity of Group VI POMs, among other properties. In order to fully harness this, the requisite understanding of structures from this study must be supplemented by aqueous state evaluation of self-assembly and ion-pairing patterns, especially with Cs^+ . ¹³³Cs T₁ inversion-recovery experiments are underway to evaluate the relative degrees of contact ion-pairing between various Group V and VI mixed-metal POMs and Cs⁺. This association data can then be related to electronic structures and solubilities. Additionally, solution-state thermochemical measurements are in progress to evaluate the energetic differences between the solid and aqueous states of POMs. The results of our ongoing investigations on these topics will be presented in future publications.

3.5 Acknowledgements

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Chapter 4: Distinctive Interactions Between Cesium and Hexaniobate In Water

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4.0 Abstract

The Cs-effect is exploited in organic synthesis and influences behavior in water, most notably radioactive ¹³⁷Cs in nuclear wastes or the environment. Niobium polyoxometalates (Nb-POMs) provide a unique opportunity to probe aqueous phase ion-pairing responsible for cesium's solution behavior, because Nb-POMs are most soluble in conditions of maximum ion-association. Moreover, POMs broadly resemble metal-oxide surfaces representative of interfaces found in the environment and industrial processes. Aqueous dissolution calorimetry reveals that Cs-Nb-POM exhibits greater concentration dependence in its endothermic dissolution, compared to the lighter alkali analogues. This phenomenon is attributed to persistent ion-pairs upon dissolution, even in very dilute and otherwise ion-free solutions. While dissociation of these cation-anion interactions in the crystalline lattice is the dominant endothermic step of dissolution, deprotonation of the Nb-POM is the most exothermic. These studies highlight the importance of the competing effects of aqueous ion association and acid-base chemistry that control solubility of compounds from simple oxoanions to metal-oxo clusters to supramolecular assemblies to solid metal oxides.

4.1 Introduction

Cesium departs from Group IA character: it is the only alkali with frontier f-orbitals and is the largest metal cation on the periodic table in its common oxidation state. These characteristics may play a role in the 'Cs-effect', the efficacy of cesium salts to catalyze organic reactions, where the lighter alkalis are not nearly so effective.^{126,127} The stoichiometric or catalytic role of Cs^+ in such reactions is not well-understood and explanations include its ability to pre-organize reactants due to strong ion-association and bonding behavior, or simply possessing higher solubility in organic solvents. In addition, the ¹³⁷Cs⁺ radioisotope has attracted considerable attention and concern as the most mobile radionuclide in liquid and solid nuclear wastes and spent nuclear fuel, both in controlled materials¹²⁸ and uncontrolled contamination⁴ in the environment. More recently, the Fukushima accident has produced widespread Cs-contamination in soil, seawater, and groundwater.¹²⁹ It is therefore important to understand Cs's solution behavior, especially ion-association and bonding, in order to achieve separation from Na⁺ and K⁺, which are far more abundant in the natural environment and nuclear wastes. Technologies that separate Cs⁺ from Na⁺ in nuclear wastes exploit precipitation of poorly soluble Cs⁺ salts^{29,130} or Cs⁺-selective ion exchangers.^{42,44} The partial covalent bonding character of Cs⁺ leading to strong ion-association in solution and at interfaces is likely an important factor in the efficacy of these technologies.



Figure 4.1: Solid-state bonding of $\{Nb_6\}$ with K^+ (top left, orange), Cs^+ or Rb^+ (top right, magenta) and TMA^+ (bottom) counter-cations. The lattermost case exhibits cluster linking via hydrogen bonding of the $[H_3Nb_6O_{19}]^{5-}$ clusters.⁶⁸ Green polyhedra are NbO₆.

Ion-association in water is particularly complex: it is affected by the concomitant organization of water molecules, self-buffering behavior (binding and releasing protons) of dissolved oxo-species, and the presence of multiple ion types, particularly in complex, natural and/or fluctuating systems.^{72–74,131} Ion-assocation affects phenomena ranging from chemical reactivity and transport of ions in nature to dissolution of metal oxides. More broadly, ion-association controls organization of biological and inorganic macromolecules, and other supramolecular assembly processes. Polyoxometalates (POMs, discrete, anionic metal-oxo clusters of Groups V and VI d^0 metals) offer a unique opportunity to investigate ion-association because the clusters can be synthesized with any countercation, providing a controlled series of compounds.^{68,69} Additionally, they are intermediate in size between infinite metal oxide lattices and simple oxoanions and hence they possess characteristics of each. Additionally, POMs are considered model metal oxide surfaces, and useful for computational and experimental studies at the interface. The Cs⁺ salt of $[Nb_6O_{19}]^{8-}$ (abbreviated $\{Nb_6\}$, Figure 4.1), due to both its unusually high water solubility in conditions of maximum ion-association, is especially useful for study.^{80,85} The solubility trend of $\{Nb_6\}$ and most Nb-POMs is opposite to that of all other polyoxoanions including Group VI POMs and the uranyl peroxide clusters,^{80,132} as well as that of anionic colloids and proteins, in accordance with the Hofmeister series.⁷⁶ To better understand the atomic level interrelated phenomena of ion-association, acid-base behavior, and solubility; we conducted thermochemical measurements of $\{Nb_6\}$ -POM dissolution. Here we quantify the enthalpy of aqueous dissolution of Cs⁺, Rb⁺, K⁺, Li^+ and tetramethylammonium (TMA⁺, $[CH_3]_4N^+$) salts of Nb₆ in both pure water and parent hydroxide solutions. Dissolution in hydroxide represents more controlled conditions that has been prior corroberated with SAXS,⁸⁵ with maximum deprotonation of the clusters and maximum ion-association. Counterintuitively, dissolution in water is more complex with many interrelated processes that are summarized in Scheme 2. This is the first investigation of the dissolution behavior of $\{Nb_6\}$ in pure water. The main finding regarding ion-association shows that the Cs⁺-salt of $\{Nb_6\}$ displays unique concentration-dependent dissolution enthalpy that differs from the other alkalis and also questions prior data that suggest Rb and Cs are similar in aqueous conditions.

4.2 Results And Discussion

As an initial approach, the enthalpy of formation (ΔH_f^{ox}) of the alkali hexaniobates (denoted Li{Nb₆}, K{Nb₆}, Rb{Nb₆} and Cs{Nb₆}) from their parent oxides (Nb₂O₅ and A₂O) were measured by dissolution into molten sodium molybdate at 700 °C to obtain the enthalpy of drop solution (ΔH_{ds}) (A=alkali; see Appendix B, thermochemical cycles). The Na analogue was not included in the series because it crystallizes from aqueous solution with seven alkali counterions, whereas the other four analogues are all obtained with eight. However, these four analogues are sufficient to reveal series trends. Upon normalization for lattice water, ΔH_f^{ox} for all species are strongly negative, with a trend of increasing exothermicity from Li to Cs (Table 4.1). The ΔH_f^{ox} of K{Nb₆}, Rb{Nb₆} and Cs{Nb₆} exhibit a relatively small stepwise difference (~20 kJ mol⁻¹) between the alkali analogues while ΔH_f^{ox} of Li{Nb₆} is substantially less exothermic. This trend is the same for ΔH_{ds} of A₂O and reflects the greater number of bonds formed by the larger alkalis in the solid-state lattices (Table 4.1). ¹³³⁻¹³⁵

Next, we measured the enthalpy of dissolution (Figure 4.2) of Li{Nb₆}, K{Nb₆}, Rb{Nb₆} and Cs{Nb₆} in water, (ΔH_{dis} , kJ mol⁻¹ cluster) which is a complex sum of endothermic and exothermic processes (Scheme 4.1). The main endothermic events include the dissociation of the A-O_{cluster} bonds (a) and the hydrogen bonds in the crystal



Scheme 2: Summary of all processes involved in the dissolution of solid $\{{\rm Nb}_6\}$ clusters in water.

lattice between water molecules with each other and with the oxo-ligands of the clusters (not shown). Exothermic processes (bond formation) include hydration of the dissociated alkalis (b) and of the clusters (c). An additional endothermic process upon dissolution of $\{Nb_6\}$ is the protonation of the clusters (e),^{69,136} which is evidenced by the increase in pH (up to 12, depending on $\{Nb6\}$ concentration) upon dissolution:

$$[Nb_6O_{19}]^{8-} + xH_2O \longrightarrow [H_xNb_6O_{19}]^{7-} + xOH^-$$

$$(4.1)$$

bates and related data				
Structure Formula	$Li_6[Nb_6O_{19}]$	$K_8[Nb_6O_{19}]$	$Rb_8[Nb_6O_{19}]$	$Cs_8[Nb_6O_{19}]$
	$. xH_2O$	$.16{ m H}_2{ m O}^{69}$	$.14 {\rm H_2O^{69}}$	$.14 \mathrm{H_2O^{69}}$
$H_2O/cluster^{[a]}$	23.5	16.0	14.1	14.8
Total A-O bonds	None available,	56	62	68
in structure	likely 40 ^{86,137}			
Average A-O	None available,	$7/K^+$	$7.75/{ m Rb^{+}}$	$8.5/\mathrm{Cs}^+$
in structure	likely $5/Li^+$			
ΔH_f^{ox} [b]	-137.2(4.8)	-262.7(5.0)	-279.3(5.9)	-298.7(4.2)
$\Delta H_{ds} (A_2O, kJ mol^{-1})^{138-140}$	-90.3(2.5)	-318.0(3.1)	-332.6(2.2)	-348.9(1.7)
$\Delta H_{hydration}, \mathrm{A}^+ (\mathrm{kJ} \mathrm{mol}^{-1})^{87}$	-519(3)	-322(3)	-293(3)	-264(3)

Table 4.1: ΔH_f^{ox} (enthalpy of formation from oxides, kJ(mol Nb)⁻¹ of the alkali hexaniobates and related data

^[a]Determined from thermogravimetry, ^[b]Corrected for ΔH_{ds} of lattice water

The experimentally observed net effect is endothermic dissolution of all the alkali analogues. Li{Nb₆} has the least endothermic ΔH_{dis} , likely reflecting the much greater exothermic enthalpy of hydration of Li⁺ (Table 4.1). The endothermic dissolution of all four alkali-{Nb₆} salts is due to domination of the endothermic processes of breaking the A-O_{cluster} bonds in the lattice and protonation of the basic clusters (Eq. 4.1). At the lowest concentration measured (~0.05 mM), ΔH_{dis} for the K, Rb and Cs analogues when normalized for number of water molecules are very similar (around 90-95 kJ mol⁻¹) and overlap up to 0.4 mM. Since the hydration enthalpies of the alkalis are inherently different and predictable (exothermic: K⁺ > Rb⁺ > Cs⁺), as are the measured lattice energies (exothermic: K{Nb₆} < Rb{Nb₆} < Cs{Nb₆}), we expect the dissolution-hydration to yield a distinct trend of increasing ΔH_{dis} endothermicity of K{Nb₆} < Rb{Nb₆} < Cs{Nb₆}. Therefore, some other phenomena are contributing to the ΔH_{dis} values, producing similarity at lower concentrations. Hence, we revise our dissolution model to suggest that two correlated phenomena, retained alkali-{Nb₆} association (Cs{Nb₆} > Rb{Nb₆} > K{Nb₆}) and inhibited cluster protonation, reduce endothermicity of ΔH_{dis} in pure water – even at very low concentrations. Higher concentrations (up to 1.40 mM) reveal a trend towards less endothermic ΔH_{dis} for all four A{Nb₆}. This indicates that {Nb₆} and alkalis are undergoing less correlated cluster-protonation and/or alkali-cluster dissociation.

The ΔH_{dis} concentration dependence for Li{Nb₆}, K{Nb₆}, and Rb{Nb₆} are similar, while Cs{Nb₆} exhibits greater concentration dependence (Figure 4.2). This is particularly surprising, because solid-state structures⁶⁹ and prior SAXS⁸⁵ studies indicate greater similarity between Rb{Nb₆} and Cs{Nb₆}. The current study suggests similarity between K{Nb₆} and Rb{Nb₆}, while Cs{Nb₆} is distinctive. However, we note that this current study is in much different conditions. The current study of dissolution in pure water at very low concentrations that should not favor substantial ion-association. Therefore the differences between the alkali salts become more pronounced.

We also measured ΔH_{dis} in the parent alkali hydroxide solutions (1 M) for K{Nb₆}, Rb{Nb₆} and Cs{Nb₆} (Figure 4.2), whereas Li{Nb₆} is too insoluble in LiOH for practical execution. This dissolution medium simplifies the aqueous phase behavior of {Nb₆}, as the protonation of the cluster upon dissolution is minimized.⁸⁵ With great excess of alkalis in solution, ion-association is maximized and independent of cluster concentration, as shown in the prior SAXS studies.^{80,85} Indeed, there is minimal concentration dependence, with slightly decreasing endothermicity for Cs{Nb₆}, negligible change for



Figure 4.2: **top**: Enthalpy of aqueous dissolution (ΔH_{dis}) of Li{Nb₆}, K{Nb₆}, Rb{Nb₆} and Cs{Nb₆} in water and **bottom**: in the parent alkali hydroxide (1 M) solutions, normalized for lattice water (*i.e.* representing dissolution of the dehydrated forms Li₈[Nb₆O₁₉], K₈[Nb₆O₁₉], Rb₈[Nb₆O₁₉] and Cs₈[Nb₆O₁₉]; the hydrated enthalpies are shown in Figure B.1). Trend lines for dissolution in the parent hydroxides are only a guide for the eye.
Rb{Nb₆}, and very slightly increasing endothermicity for K{Nb₆}. The values of ΔH_{dis} are considerably more exothermic for all {Nb₆} salts in their parent hydroxide solutions than in water, likely due to decreased proton transfer from the water to the cluster upon dissolution (Eq. 4.1). The distinct relationship of ΔH_{dis} with increasing endothermicity K{Nb₆} < Cs{Nb₆} < Rb{Nb₆} is unexpected. Again, the departure from an expected periodic trend of increasing endothermicity (K < Rb < Cs) with increasing energy required to dissociate A-O bonds can be related to anomalous behavior of Cs{Nb₆}. Because ΔH_{dis} of Cs{Nb₆} is considerably less endothermic than that of Rb{Nb₆}, we can conclude that the ions remain more associated upon aqueous dissolution and the short range order reminiscent of the solid-state lattice is less disrupted. Again, this distinction was not made in the prior SAXS studies,⁸⁵ likely due to sensitivity of the technique to differentiate between similar states. For example, {Nb₆} associated with anywhere from 4-8 alkalis in solution might look similar by SAXS, as would the average scattering of {Nb₆} clusters with different numbers of alkalis associated.

Next we turn our attention to ΔH_{dis} of TMA⁺ salts of {Nb₆} in both water and its parent hydroxide. While high temeprature calorimetry is meaningless due to the organic, combustible counterions; aqueous dissolution calorimetry is valuable to delineate the behavior and role of the alkali counterions in dissolution and to confirm our hypotheses of the observed trends. TMA⁺, being bulkier and less charge-dense than the alkali metal ions, provides both minimal bonding in the lattice and minimal ion-association in solution, and likewise minimal exothermic hydration enthalpy of the cations upon dissolution. The enthalpy of hydration of TMA⁺ is -105.2(2.8) kJ mol⁻¹,¹⁴¹ considerably less exothermic than that of alkali cations (Table 4.1). The ΔH_{dis} of TMA-{Nb₆} in both water and TMA hydroxide is exothermic, and becomes slightly less negative with increasing concentration, differing in both features from the dissolution energetics of the



Figure 4.3: Enthalpy of dissolution of $TMA\{Nb_6\}$ in water and in 1M TMAOH.

alkali salts. The solid-state arrangement of these triprotonated clusters $[H_3Nb_6O_{19}]^{5-}$ is a linear chain (Figure 4.1), via H-bonding of the protonated faces, owed to the minimal TMA+-cluster association during crystallization.⁶⁸ Prior studies by X-ray scattering also suggest that the association of clusters upon dissolution in water is partially retained and more structuring is observed in solution with increasing concentration.⁶⁸ This is consistent with decreasing exothermicity as concentration increases, as they retain the H-bonded state with increasing concentration. Dissolution in TMAOH follows the same trend: less negative dissolution enthalpy with higher order of structuring in solution at higher concentrations (Figure 4.3). Overall, ΔH_{dis} is considerably more exothermic in TMAOH than in water. This is because deprotonation of clusters breaks up the hydrogen-bonded cluster chains and therefore a greater degree of exothermic hydration results. Deprotonation of the cluster is a neutralization reaction, which is also exothermic; *i.e.*:

$$[H_3Nb_6O_{19}]^{5-} + OH^- \longrightarrow [H_2Nb_6O_{19}]^{6-} + H_2O$$
 (4.2)

4.3 Conclusion

This data represents the first critical quantitative evaluation of lattice and dissolution energy of water-soluble metal-oxo clusters, and it reveals the correlation between ionassociation and acid-base behavior in dissolution processes. The current and follow-on studies of different metal-oxo compositions provides quantitative data that can be correlated with molecular dynamical and density functional theory simulations of these processes. Broadly we conclude that the energy required to dissociate Nb-POM lattices held together by alkali-oxo bonds exceeds energy released upon hydration of the dissociated ions (endothermic dissolution). Conversely, dissolution of alkali-free lattices held together by only H-oxo bonds is exothermic. Additionally; in conditions where alkalioxo bonding is retained in solution, formation of H-oxo bond formation is supressed, and vice versa. We will broaden the compositional scope of our thermochemical investigations and delineate the relationship between composition, charge density, and solubility with POMs exhibiting opposite and intermediate solubility trends to that of Nb-POMs (Group VI POMs, uranyl peroxide polyanions, mixed Group V/VI POMs).^{77,82} We will also elucidate the fundamental differences between aqueous Ta and Nb chemistries via thermochemistry.^{80,142} While prior X-ray scattering studies⁸⁵ and solid-state structure suggested the association of Rb^+ and Cs^+ to $\{Nb_6\}$ is identical, the current technique reveals distinct differences, highlighting the better ability of Cs⁺ to retain strong association to an anion in solution and to depart from trends based on periodicity. This we attribute to Cs's more covalent bonding character, derived from frontier f-orbitals.

Moreover, thermochemistry has enabled us to study dissolution processes in very simple solutions containing just the cluster salt and water. We have learned that the deceptively simple solutions represent the most complex dissolution processes, which we will follow-on with ¹³³Cs NMR, UV-vis, SAXS and computational studies. Complementary techniques allow access to different solution conditions and therefore provide a more complete understanding of the fundamental phenomena of acid-base and ion-pairing behavior in water. Charged, water-soluble metal-oxo clusters are excellent models to study ubiquitous processes at the water-metal oxide interface in synthetic, natural and industrial conditions.

Tables of drop solution enthalpies, thermochemical cycles, and tables and graphs of the hydrated (uncorrected for lattice water) dissolution enthalpies in water and in the parent hydroxide for each alkali hexaniobate are included in Appendix B. Syntheses, thermogravimetric analysis (TGA) plots, and elemental analyses are also included.

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Chapter 5: Thermochemical Measurements of Alkali Cation Association to Hexatantalate

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5.0 Abstract

The ion-pairing behavior of cesium with hexaniobate has previously been studied by calorimetric measurements. Like the niobium polyoxometalates, tantalum polyoxometalates exhibit the highest solubility in conditions of maximum ion-association, providing a unique opportunity to probe aqueous ion pairing at a large range of concentrations, especially at high concentrations where ion pairing is the most dominant. High temperature oxide melt calorimetry of alkali salts of hextantalate reveals that the enthalpies of formation from oxides of the K, Rb, and Cs salts are more similar to each other than they are for their niobate analogues. Aqueous dissolution calorimetry reveals that the cesium salt of hexatantalate has a similar concentration dependence on its enthalpy of dissolution to that of hexaniobate. However, unlike rubidium hexaniobate, rubidium hexatantalate also has an increased concentration dependence, indicating that hextantalate can also undergo increased ion-pairing with alkali salts other than cesium, despite the dilute environments studied. These studies again illuminate the importance of considering ion-pairing among the interrelated processes in the aqueous dissolution of ionic salts, as well as for arriving at a model of cation association to metal oxide surfaces.

5.1 Introduction

Aqueous ion behavior is driven by many fundamental and interrelated physical processes. The solubility of ionic salts in water is predictable to some degree by the "hardness" or "softness" of the component cations and anions, which arises from their degrees of hydration upon dissolution, electron density in the frontier molecular orbitals, overall charge, and charge-density.^{143–146} Typically, close interactions between cations and anions (ion pairing) in solutions predicates precipitation, with larger hydration spheres from more charge-dense species (*i.e.*, Li⁺) maintaining solubility according to the Hoffmeister series.⁷⁶ This factor competes with lattice energy, in which similarly-sized cations and anions stabilize each other to the greatest degree, decreasing solubility. However, these factors alone fail to fully explain the anomalous solubilities of some species, most notably certain alkali salts of prominent oxoanions such as carbonate,¹² which are further complicated by protonation in solution. We define anomalous solubility to mean solubility increases with increased ion-pairing, rather than leads to precipitation. A more complete picture of the mechanisms behind ion association helps to provide more complex models for thermodynamic data calculations. Additionally, the solubility of cations in water is important for driving their adsorption onto transition metal and metal oxide surfaces,¹⁴⁷ which can be used to fine-tune the electronic properties and chemical reactivities of catalysts, as well as design ion-specific sorbents.^{148–150}

Polyoxometalates (POMs), nanoscale discrete oxoanions of Group V and VI metals in their highest oxidation states, can be synthesized with any alkali cation, thus providing an excellent model for ion-pairing in water and at metal oxide surfaces.^{151,152} These "molecular metal oxides" exhibit a wide range of aqueous behaviors that depend on their metal centers and, crucially, their countercations.¹⁵³ Thus, fundamental studies of these behaviors are important to more fully understand the aqueous chemistry of ionic species. The isostructural and isovalent hexaniobate ($[Nb_6O_{19}]^{8-}$, Nb₆) and hexatantalate ($[Ta_6O_{19}]^{8-}$, Ta₆) POMs exhibit very similar reactivities, pH stabilities, and aqueous solubilities with respect to alkali countercations.^{121,154,155} In particular, Cs⁺ undergoes significant ion-pairing with these POMs, which increases their solubilities due to each Cs⁺ more favorably interacting with a single cluster rather than coordinating to multiple, wherein binding to a single cluster inhibits aggregation and precipitation



Figure 5.1: Solid state ΔH_f^{ox} (enthalpy of formation from oxides, kJ(mol-Nb)¹) values for alkali salts of Ta₆ (this study) and Nb₆ (a previous study).

even at relatively high concentrations.¹⁵⁶ However, subtle differences have been found in their degrees of ion-association with Cs^+ – Ta_6 undergoes an overall greater degree of ion pairing with Cs^+ at a large range of concentrations, even at low concentration. This was attributed to the presence of relativistic effects in Ta_6 , which results the orbital interaction term having a larger contribution to the total bonding energy.¹⁵⁶ In other words, electrostatics alone are insufficient to describe Cs^+ 's behavior in the presence of Group V POMs and covalent character must also be considered in order to arrive at a complete description of solution behavior.

5.2 Results and Discussion

We have previously conducted high-temperature oxide decomposition calorimetry on alkali (Li⁺, K⁺, Rb⁺, Cs⁺) salts of Nb₆.¹⁵⁷ Upon dropping pellets made from crystalline samples into molten sodium molybdate at 700 °C, we were able to ascertain a trend of

increasingly exothermic enthalpy of formation from oxides (ΔH_f^{ox}) with respect to alkali countercation size. To parallel this previous study, we performed measurements on the same alkali salts of Ta₆. Although the Na₈[Ta₆O₁₉] salt exists, it was not tested due to the lack of an analogous Nb₆ salt. ΔH_f^{ox} is less exothermic for each alkali Ta₆ analogue, compared to the Nb₆ analogue (Figure 6.1). We rationalize this as mixing of Ta_{5d} and O_{2p} orbitals in Ta₆ being poorer than the mixing between Nb_{4d} and O_{2p} in Nb₆,^{82,156} making the ΔH_f^{ox} inherently less exothermic. Additionally, Ta₂O₅ has more covalent character than Nb_2O_5 ,¹⁵⁸ resulting in a smaller change in electronic structure when converting to the hexametalate form. As a result of this greater covalent character, it is more difficult to convert Ta_2O_5 to Ta_6 than it is to convert between the Nb analogues. This is reflected by the existence of syntheses that directly convert Nb_2O_5 to Nb_6 in highly alkaline conditions,¹⁵² whereas no such procedure exists for Ta. Mirroring the trend in hexaniobate, the Li^+ salt of Ta_6 exhibits a far less exothermic (by more than a factor of two) ΔH_f^{ox} than the larger alkali salts. This can be rationalized by the structure of lithium hexaniobate.^{79,137} The hexaniobate lattice contains adamantanelike Li-water clusters, which prevents direct bonding between ${\rm Li}^+$ and ${\rm Ta}_6$ the solid state $(Li_8Ta_6O_{19} \cdot 18H_2O)$. A single crystal structure of Li-Ta₆ has never been possible due to poor crystal quality and perhaps disorder of the the hydrated lithium in the lattice. We surmise from these characteristics that it is likely not isostructural to the Li-Nb_6 analogue $(Li_8Nb_6O_{19} \cdot 22H_2O)$. However, Li is generally bonded to water in hydrated salt lattices, so we expect a similar effect on its formation enthalpy. Unlike Nb_6 , the K^+ , Rb^+ , and Cs^+ salts of Ta_6 do not exhibit a strict trend of increasing ΔH_f^{ox} (Figure 1). Instead, the three larger alkali salts are more similar in their ΔH_f^{ox} . This is a curious departure from the trend seen with Nb_6 , indicating that the larger alkali cations have similar bonding character to Ta_6 in the solid state, unlike Nb_6 with which alkali cations



Figure 5.2: Enthalpy of aqueous dissolution (ΔH_{dis}) of Li-Ta₆, K-Ta₆, Rb-Ta₆ and Cs-Ta₆ in water, normalized for lattice water (*i.e.*, representing dissolution of the dehydrated forms Li₈[Ta₆O₁₉], K₈[Ta₆O₁₉], Rb₈[Ta₆O₁₉] and Cs₈[Ta₆O₁₉]; the hydrated enthalpies are provided in Tables C.5-C.9.

have a progressively increasing bond strength and number with larger cations.

We have also previously measured the enthalpies of dissolution (ΔH_{dis}) at room temperature of the alkali salts of Nb6, elucidating the Cs-salt's greater concentration dependence. By extension, the degree of structural change was becoming less extensive at higher concentrations, indicating that the Cs⁺ underwent the most ion-pairing with Nb₆. These studies were repeated with Ta₆ and we again revealed a dependence of ΔH_{dis} on concentration for each alkali salt (Figure 2). Li⁺ again cannot be easily compared to the larger alkalis, due to its far more extensive coordination to water molecules in the solid state. This is reflected in its overall lower values of ΔH_{dis} compared to the other three alkali salts. However, the steeper slope of the Cs-Ta₆ trend was matched by the Rb⁺ salt, with K⁺ having a smaller slope. This indicates that rubidium and cesium undergo similar degrees of ion-pairing with Ta₆, constituting a departure from the Nb₆ trend in which the cesium salt clearly had the greatest dependence on concentration. Specifically, the ΔH_{dis} ranges from $\approx 70\text{-}100 \text{ kJ mol}^{-1}$ for Ta₆ salts (Rb, Cs) compared to $\approx 60{\text{-}}100 \text{ kJ} \text{ mol}^{-1}$ for Cs-Ta₆, in the same concentration range. Interestingly, the slope from Cs-Ta₆ is somewhat less than that from Cs-Nb₆ in our previous study (30) and 35 kJ mol⁻¹/mM, Figure 4.1). At first glance, this might indicate that Nb₆ undergoes more ion-pairing with Cs^+ at higher concentrations than Ta_6 . However, we have also determined by DFT calculations that the interaction between a single solvated Cs⁺ and a single solvated Ta_6 ion is more energetically favorable than that between Cs^+ and Nb_6 (Section 6.3.5). Therefore, the opposite process of dissociation would be more favorable for Cs-Nb₆. An additional Cs^+ remaining associated to Nb₆ would thus contribute more to the slope than the same process with Ta_6 , causing the Nb₆ line to be inherently more sloped with the same degree of ion-association. In other words, more Cs⁺ must remain associated to Ta₆ than to Nb₆ to achieve the same decrease in ΔH_{dis} . On the other hand, it has been noted that Nb_6 is more basic than Ta_6 , meaning it protonates upon dissolution in water, at the bridging oxos sites. Since protonation is an endothermic process that is not equal between the Ta_6 and Nb_6 , it is difficult to compare the dissolution enthalpy with exact certainty.

We dissolved the K, Rb and Cs Ta₆ salts in 1 molar solutions of each alkali cation's parent hydroxide (Figure 5.3). The Li⁺ salt was omitted due to its insolubility in LiOH. Like Nb₆, alkali salts of Ta₆ do not have a concentration dependence when dissolved in base, due to a lack of cluster protonation and the excess cations in solution forcing the "maximally associated" state at all concentrations. The generally more exothermic dissolution enthalpies can be related to the lack of protonation of the clusters with high concentration of base. There is a distinct trend in ΔH_{dis} with respect to alkali cation size with Cs-Ta₆ being most exothermic, followed by Rb-Ta₆ and then K-Ta₆. This trend suggested that less energy is required to dissociate the Cs-Ta₆ lattice adequately enough



Figure 5.3: Enthalpy of aqueous dissolution (ΔH_{dis}) of Li-Ta₆, K-Ta₆, Rb-Ta₆ and Cs-Ta₆ in their parent hydroxide (1 M) solutions, normalized for lattice water; the hydrated enthalpies are provided in Tables C.10-C.13.

to achieve dissolution, compared to the K and Rb analogues. This is exactly consistent with ion-pairing persisting in solution; increasing $K-Ta_6 < Rb-Ta_6 < Cs-Ta_6$.

Finally, we compared the ΔH_{dis} of the protonated tetramethylammonium salt of Ta₆ ([(CH₃)₄N]₆H₂O₁₉ · 21H₂O, TMA-Ta₆) in water and in 1 molar TMAOH to the previously-measured Nb analogue. As with the analogous TMA-Nb₆ case, ΔH_{dis} does not have a concentration dependence in either solution environment due to the lack of ion-association between TMA⁺ and Ta₆. However, ΔH_{dis} is less exothermic for TMA-Ta₆ (\approx -10 kJ mol⁻¹) than it is for TMA-Nb₆ (\approx -40 kJ mol⁻¹) in water. As described above, this is because Ta₆ is a weaker base than Nb₆,¹⁵⁹ resulting in a lesser degree of deprotonation, consistent with fewer exothermic events occurring in solution. The difference in ΔH_{dis} between TMA-Ta₆ and TMA-Nb₆ is greatly exacerbated in 1M TMAOH (\approx -35 kJ mol⁻¹ and -150 kJ mol⁻¹, respectively). This is due to the tendency for TMA-Nb₆ to form



Figure 5.4: Enthalpy of dissolution of $TMA-Ta_6$ in neat water and in 1M TMAOH.

oligomeric chains in neat water, whereas TMA-Ta₆ typically forms dimers.⁸³ Thus, the vast difference in exothermicity is further explained by the degree of hydrolysis of the respective assemblies – a far greater number of exothermic events occur in the breaking of long Nb₆ chains than in the breaking of the simpler Ta₆ dimers. ΔH_{dis} is nonetheless more exothermic for TMA-Ta₆ in 1M TMAOH than it is in neat water due to the disassembly of these dimers.

5.3 Conclusion

This study represents another quantitative evaluation of lattice and dissolution energy of water-soluble metal-oxo clusters, further revealing the correlation between ionassociation and acid-base behavior in dissolution processes. Following the groundwork laid by our previous study on hexaniobate, the enthalpies of dissolution of the alkali salts of hexatantalate indicated greater degrees of ion pairing as concentration increased, with Rb^+ exhibiting a similar increased degree of ion association to that of Cs^+ with $\{Ta_6\}$, whereas $\{Nb_6\}$ only presented this behavior with Cs^+ With these studies combined, we hope to achieve a quantitative, rigorous backing for a more complete set of solubility rules based on fundamental energetic processes. We also hope to arrive at an energetic model for the behavior of cations at metal-oxide surfaces.

Tables of drop solution enthalpies, thermochemical cycles, and tables and tables of the hydrated (uncorrected for lattice water) dissolution enthalpies in water and in the parent hydroxide for each alkali hexaniobate are included in Appendix C. Syntheses, thermogravimetric analysis (TGA) plots, and elemental analyses are also included.

5.4 Acknowledgements

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Chapter 6: Electronic And Relativistic Contributions To Ion-Pairing In Polyoxometalate Model Systems

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6.0 Abstract

Ion pairs and solubility related to ion-pairing in water influence many processes in nature and in synthesis including efficient drug delivery, contaminant transport in the environment, and self-assembly of materials in water. Ion pairs are difficult to observe spectroscopically because they generally do not persist unless extreme solution conditions are applied. Here we demonstrate two advanced techniques coupled with computational studies that quantify the persistence of ion pairs in simple solutions and offer explanations for observed solubility trends. The system of study, ([(CH₃)₄N]⁺,Cs)₈[M₆O₁₉] (M=Nb,Ta), is a set of unique polyoxometalate salts whose water solubility increases with increasing ion-pairing, contrary to most ionic salts. The techniques employed to characterize Cs^+ association with $[M_6O_{19}]^{8-}$ and related clusters in simple aqueous media are ¹³³Cs NMR (nuclear magnetic resonance) quadrupolar relaxation rate and PDF (pair distribution function) from X-ray scattering. The NMR measurements consistently showed more extensive ion-pairing of Cs⁺ with the Ta-analogue than the Nb-analogue, although the electrostatics of the ions should be identical. Computational studies also ascertained more persistent Cs^+ -[Ta₆O₁₉] ion pairs than Cs^+ -[Nb₆O₁₉] ion pairs, and bond energy decomposition analyses determined relativistic effects to be the differentiating factor between the two. These distinctions are likely responsible for many of the unexplained differences between aqueous Nb and Ta chemistry, while they are so similar in the solid state. The X-ray scattering studies show atomic level detail of this ion association that has not been prior observed, enabling confidence in our structures for calculations of Cs-cluster association energies. Moreover, detailed NMR studies allow quantification of the number of Cs⁺ associated with a single $[Nb_6O_{19}]^{8-}$ or $[Ta_6O_{19}]^{8-}$ anion which agrees with the PDF analyses.

6.1 Introduction

Preceding precipitation of ionic salts from water, soluble ion pairs and aggregates must form. When these increase in size and decrease in charge, they precipitate. Elucidating these processes is foundational to designing effective pharmaceuticals,¹⁶⁰ remediating contamination in the environment,¹⁶¹ optimizing materials synthesis in water,¹⁶² and growing biological and inorganic crystals from water.¹⁶³ Aqueous solubility and ionpairing is extremely complex because many phenomena are involved including the lattice energy of the crystallized or precipitated solid, the hydration sphere of both the cation and anion, the sum of ions present in solution, and pH effects if the cation and/or anion is a polyatomic oxo-ion.^{73,74,164} Alkali salts of polyoxometalates (POMs), the early d^0 Group V/VI metal-oxo clusters, are ideal for probing both ion association^{71,78,165–167} and crystal growth mechanisms, ^{168–173} and these two phenomena are intimately related. POMs scatter X-rays strongly due to their large size and to the high electronic denisty of the metals present in their structures. This has allowed observation of ion pair formation via small-angle X-ray scattering by determining the size of the scattering species.¹⁶⁵ In addition, POMs are molecular metal oxides,¹⁷⁴ so ion-pairing behavior at bulk metal oxide interfaces can be inferred from their study. We do not entirely understand what drives solubility trends of alkali salts. If we simply consider hydration spheres, Li⁺ carries a large hydration sphere and does not exhibit extensive ion-pairing, suggesting all Li-salts should be highly soluble in water.^{75,76}. Yet, some POMs are highly soluble as Li-salts and extremely insoluble as Cs-salts (normal solubility), while others exhibit exactly the opposite solubility trend (anomalous solubility).^{69,71,78–80} For instance, the Cs-salt of the hexaniobate POM ($[Nb_6O_{19}]^{8-}$, Figure 6.1) is soluble up to 1.5 M, whereas the lithium and sodium salts are only sparingly soluble. We can state, as an initial approximation,



Figure 6.1: Possible solution-state coordination environments of Cs⁺ with $[M_6O_{19}]^{8-}$ (M = Nb, Ta; left) and $[Nb_2W_4O_{19}]^{4-}$ (right) from the solid state structures.⁸²

that POMs of high charge density exhibit anomalous solubility while POMs of low charge density exhibit normal solubility. Alkali salts of highly charged oxoanions including CO_3^{2-} and PO_4^{3-} also exhibit anomalous solubility.^{10,172} Ultimately, we endeavor to explain the anomalous solubility trend in terms of the structuring of ions in solution and also determine exactly the charge density at which the trend reverses. An initial approach was to benchmark solutions in which ion association is forced by employing extreme conditions, including an excess of one of the ions to drive maximum ion association.^{83,165} However, these studies are not broadly representative of conditions in natural settings that are of low ionic strength and a complex mixture of ions, nor materials synthesis conditions in which metastable species could persist and be isolated.

Understanding Cs^+ 's ion association behavior in water is particularly important, as scientists and engineers are currently optimizing efficient technologies to remove radioactive ¹³⁷Cs from the various contaminated groundwater, seawater, and agricultural environments that are still emerging in the wake of the Fukushima-Daiichi nuclear disaster.^{2,5,6} Solubility and ion-pairing was used to separate ppm levels of Cs from nuclear wastes containing ~ 3 moles of Na — sodium tetraphenylborate is soluble while Cs tetraphenylborate is insoluble.²⁷ Of additional importance, Cs₈[Nb₆O₁₉] was used as a model system to computationally probe the base hydrolysis reactivity of [Nb₆O₁₉]⁸⁻, where the Cs-association is expected to simplify hydrolysis effects in both solution and solid state reactions.¹⁷⁵

Despite the similarities between hexaniobate ($\{Nb_6\}$) and hexatantalate ($\{Ta_6\}$) in the solid state, we and others have noted considerable differences in solution behavior,^{121,176–178} but the fundamental origin of these differences has never been explained, other than by inference to broadly defined effects of frontier f-orbitals present in $\{Ta_6\}$ but not $\{Nb_6\}$. Next to Zr and Hf, Nb and Ta are the two elements on the periodic table that are the most chemically similar as a direct consequence of the lanthanide effect. This report provides insight into how the lanthanide effect alters the solution behavior of post-lanthanide metals compared to their lighter counterparts. Here we utilize two advanced spectroscopies that permit probing solutions of relatively low ionicity and yield unprecedented details concerning solution phase ion association. POMs of this study provide a range of charge density while the structure remains similar or identical. These include Cs-salts of: $[M_6O_{19}]^{8-}$, $[Nb_4W_2O_{19}]^{6-}$, $[Nb_2W_4O_{19}]^{4-}$ and $[MW_9O_{32}]^{5-}$ (M=Nb,Ta).^{77,81,82} The quadrupolar relaxation rate of ¹³³Cs by Nuclear Magnetic Resonance (NMR) and X-ray total scattering, explained by computational models point towards the influence of relativistic effects in the formation of ion pairs and as a source of differences between Nb(V) and Ta(V) speciation in water. X-ray scattering revealed the structure of the Cs-POM association in solution. Furthermore, with detailed analysis of the NMR data, we quantified the average number of Cs⁺ associated with clusters in solution, which agrees with the model proposed by the X-ray scattering data. Taken together, these data support a proposed model for discrete ion pairs (meaning not bridged into large networks) paired with anomalously high solubility.

6.2 Experimental

6.2.1 Syntheses

 $\begin{array}{l} \mbox{Cs-salts of POMs } (\mbox{Cs}_8[\mbox{Nb}_6\mbox{O}_{19}] \cdot 14\,\mbox{H}_2\mbox{O}, \mbox{Cs}_8[\mbox{Ta}_6\mbox{O}_{19}] \cdot 14\,\mbox{H}_2\mbox{O}, \mbox{Cs}_5[\mbox{Ta}\mbox{W}_9\mbox{O}_{32}] \cdot 7\,\mbox{H}_2\mbox{O}, \\ \mbox{Cs}_5[\mbox{Ta}\mbox{W}_9\mbox{O}_{32}] \cdot 6.5\,\mbox{H}_2\mbox{O}, \mbox{Cs}_4[\mbox{Nb}_2\mbox{W}_4\mbox{O}_{19}] \cdot 4\,\mbox{H}_2\mbox{O}, \mbox{Cs}_4[\mbox{Nb}_4\mbox{W}_2\mbox{O}_{19}] \cdot 10\,\mbox{H}_2\mbox{O}, \\ \mbox{[(CH_3)}_4\mbox{N]}_5[\mbox{H}_3\mbox{Nb}_6\mbox{O}_{19}] \cdot 20\,\mbox{H}_2\mbox{O} \ (\mbox{TMA}\{\mbox{Nb}_6\}), \mbox{ and } [(\mbox{CH}_3)_4\mbox{N]}_6[\mbox{H}_2\mbox{Ta}_6\mbox{O}_{19}] \cdot 21\,\mbox{H}_2\mbox{O}, \\ \mbox{(TMA}\{\mbox{Ta}_6\})) \ \mbox{were synthesized by following the reported procedures}. \end{tabular}^{68,69,77,82,179} \ \mbox{These procedures are also described in detail in Appendix} \ . \end{array}$

6.2.2 Inversion-Recovery ¹³³Cs NMR

The ¹³³Cs spectra were recorded on a Bruker 400 MHz NMR spectrometer operating at the ¹³³Cs Larmor frequency (52.482 MHz) at a constant temperature of 25 °C (by means of a VTU temperature controller) in solutions of 90% H₂O and 10% D₂O. T₁ values were derived by inversion recovery experiments. Each value of T₁ was calculated by an exponential fit from 16 delay times of four scans each.

 T_1 inversion recovery was performed on 5 mM solutions that were prepared from each of the aforementioned Cs⁺ POM salts, as well as a range of solution concentrations (0.5 mM to 100 mM) of Cs₈Nb₆O₁₉ and Cs₈Ta₆O₁₉.

Solutions of 20 mM (TMA)₅ $H_3[Nb_6O_{19}]$ and (TMA)₆ $H_2[Ta_6O_{19}]$ in 200 mM TMAOH were also prepared to assure deprotonation of the clusters. A second series of such

solutions, *i.e.* 20 mM of either hexacoltanate $([M_6O_{19}]^{8-}, M = Nb, Ta)^{77}$ in 200 mM TMAOH, was replicated, this time with the addition of 240 mM CsCl. Thus, systematic mixing of these solutions afforded a range of Cs⁺ concentrations from 10 mM to 240 mM, with a constant hexacoltanate anion concentration of 20 mM.

6.2.3 CTAB Precipitation and Atomic Ratio Analysis

Solutions of 5 mM, 10 mM, and 20 mM $Cs_8M_6O_{19}$ (M = Nb, Ta) were combined with excess solid cetyltrimethylammonium bromide (CTAB, $C_{16}H_{31}(CH_3)_3NBr$) and a white precipitate was immediately observed. The white precipitate was separated by centrifugation and the resultant solid was dried under vacuum. The surface layer of the solid was scraped off and discarded in order to remove any excess surface Cs^+ and Atomic Ratio Analysis was performed on the bulk region of each white powder to determine the approximate ratio of bound Cs^+ per hexametalate unit (upon averaging five or more data points per sample) by EDX. EDX Spectra were obtained from a Quanta 600F instrument (FEI).

6.2.4 Viscometry

Viscosity measurements were taken with an Ostwald Viscosity Tube and a stopwatch at a constant temperature of 25 °C. A constant sample volume of 5.00 mL was held for each experiment. Densities were found by weighing 5.00 mL of each solution. Five efflux times were recorded for each sample and the averages of these times are reported along with solution density and relative viscosity to 10% $D_2O/90\%$ H₂O (see Appendix D.2). The mixed Group V-Group VI POM solutions are not corrected for viscosity due to the negligible variance at 5 mM.

6.2.5 PDF Analysis of X-Ray Total Scattering (XRTS)

The solutions of TMA{ M_6 } with added CsCl were prepared at 100 mM (with CsCl concentrations ranging from 100 to 1200 mM) in 200 mM TMAOH without D₂O. Raw x-ray scattering data were collected with a Rigaku Smartlab x-ray diffractometer with a Mo-K α source ($\lambda = 0.71073$ Å). For these solution X-ray scattering measurements, an aliquot of the solution was injected in a Kapton 1.5 mm capillary, sealed and positioned in the goniometer. Transmission mode of the data collection was applied, where 2θ range of 3.0-118.6° was used. Therefore, the maximum available Q-value is 15.2 Å⁻¹. The data collection time was $0.2^{\circ} \text{ min}^{-1}$ using a 0.01degree resolution. In order to eliminate the contribution of the solvent and the sample holder, Milli-Q water (Millipore, 18.2 M Ω cm at 25 °C) was also measured for background subtraction applying identical experimental parameters.

The solution scattering curves were transformed to the reduced structure functions, then they were Fourier transformed to obtain the reduced atomic pair distribution functions (PDF, denoted as G(r) on the graph). For the mathematical transformations and background subtractions we used the PDFgetX3 software.¹⁸⁰ Simulated PDF data were obtained with the solX software¹⁸¹ using the appropriate parameters.

6.2.6 Computational Methods

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations¹⁸² were performed on single instances of $Cs_x[Ta_6O_{19}]^{(8-x)-}$ and $Cs_x[Nb_6O_{19}]^{(8-x)-}$ (x = 0, 1, 4, 8), using the software package Gaussian09.¹⁸³ Additional supplementary calculations were carried out on the series $M_8[Ta_6O_{19}]$ (M = Rb, K, Na, Li). In all cases, the chosen methodology is identical to the one previously employed by Deblonde et al. to compute the UV-Vis spectra of $[Ta_6O_{19}]^{8-}$ and $[Nb_6O_{19}]^{8-}$ in implicit water, ¹²¹ leading to results that were in excellent agreement with experiment.

This particular approach consists of two distinct steps, both involving spin-restricted calculations, but not relying on molecular symmetry. To begin with, all species are structurally optimized using the PBE0 functional:¹⁸⁴ at this stage, oxygen electrons are treated using the D95 basis set,¹⁸⁵ whereas those on remaining elements are modeled using various Stuttgart-Dresden effective core potential and basis sets. More specifically, tantalum electrons are treated with MWB60,¹⁸⁶ niobium with MWB28,¹⁸⁶ and cesium with MWB46.¹⁸⁷ With respect to the supplementary calculations on the M₈[Ta₆O₁₉] series (M = Rb, K, Na, Li), rubidium electrons are treated with MWB28,¹⁸⁷ potassium with MWB10;¹⁸⁷ sodium with SDF10;¹⁸⁸ and lithium with SDF2.¹⁸⁸ With hexatantalate salts in particular, convergence problems are occasionally encountered during default¹⁸⁹ solution of the self-consistent field equations; these are always solved by automatically invoking the alternative quadratic convergence procedure developed by Bacskay.¹⁹⁰ Structures resulting at this stage are also verified to be true minima by means of frequency calculations, aiming to confirm the absence of imaginary vibrational modes.

In the second and final step, the UV-Vis spectrum of each optimized structure of $\{M_6\}$; $Cs\{M_6\}$; $Cs_4\{M_6\}$; and $Cs_8\{M_6\}$ (M = Nb, Ta) is subsequently computed by means of a single-point TD-DFT calculation:¹⁸² in this case, the PBE0 functional is retained, but electrons on all elements are treated with the def2-TZVP effective core potential and/or associated basis set.¹⁹¹ In the case of the supplementary $M_8[Ta_6O_{19}]$ series (M = Rb, K, Na, Li), the level of theory is identical, but UV-Vis spectra are not

derived, so only DFT calculations suffice. All orbital energies quoted and discussed in this work are actually those calculated during this second and final step.

Throughout both steps, water effects are implicitly included using the *polarizable* continuum model (PCM),¹⁹² which is readily implemented in Gaussian09. Moreover, to rule out the existence of lower-energy solutions of computed wavefunctions, these are always tested for any spatial- or spin-instability.¹⁹³

The Bonding Energy Decomposition analysis was performed using the ADF2012 program system.^{194,195} The PBE0¹⁸⁴ DFT GGA functional including scalar relativistic ZORA^{196,197} approach was used together with the Slater triple- ζ plus polarization basis sets (TZP) in all atoms, which included frozen cores up to 4p for Mo and 1s for O and C atoms. Solvent effects were introduced non-explicitly by means of the COSMO model.^{198,199} The values of the atomic radii correspond to the Van der Waals radii derived by Klamt.^{198,199} For Cs, a value of 3.205Å was used. A data set collection of input files and computational results is available in the ioChem-BD repository²⁰⁰ and can be accessed online.

6.3 Results and Discussion

6.3.1 NMR Theory

The hydrodynamic radius of Cs^+ in water can be assumed to be independent of environment in the relatively dilute conditions in which we perform these experiments.^{201,202} However, an assumption that viscosity varies negligibly between solutions of {Nb₆} and {Ta₆} cannot be made *a priori*. Further details regarding viscosity are discussed in Appendix D.2. Ion pairing provides an efficient relaxation mechanism for the ¹³³Cs nucleus. It is thus possible to quantify ion-pairing and observe ion pairs, with larger values of R_{QR} (faster relaxation rates) indicating greater degrees of ion-pairing in solution. Each 1D ¹³³Cs spectrum contains only a single peak (Figure D.1), indicating that the "free" and "bound" Cs⁺ environments are in rapid exchange. Dipolar effects are further determined to be negligible due to rapid molecular reorientations occurring such that the extreme narrowing conditions apply.²⁰³ The combined R_{QR} (upon adjusting for viscosity, R_{adj}) of the two Cs⁺ environments in solution is the weighted average of their relaxation rates:

$$R_{adj} = \chi_b R_b + \chi_f R_f \tag{6.1}$$

where χ_b and χ_f are the mole fractions of the bound and free environments and R_b and R_f are the quadrupolar relaxation rates of the bound and free environments, respectively. The value for R_f is the relaxation rate of ¹³³Cs at infinite dilution at 25 °C (0.086 s⁻¹).²⁰⁴ Therefore, the relaxation rate for Cs⁺ in an ion pair can be ascertained if the mole fractions of bound and free Cs⁺ are known.^{*}

6.3.2 Quantification of Cs⁺ Ion-Pairing as a Function of Charge Density

¹³³Cs inversion-recovery NMR was performed on 5 mM solutions of a series of Cssalts POMs with both Group V and Group VI metals $([TaW_9O_{32}]^{5-}, [NbW_9O_{32}]^{5-},$ $[Nb_2W_4O_{19}]^{4-}, [Nb_4W_2O_{19}]^{6-}, [Nb_6O_{19}]^{8-},$ and $[Ta_6O_{19}]^{8-})$ to provide a systematic range of charge-densities. The cluster salts do not all have the same Cs:cluster ratio.

^{*}Portions of this section were moved to Chapter 2.



Figure 6.2: ¹³³Cs quadrupolar relaxation rates of niobo- and tantalo-tungstates plotted with respect to (left) charge density of the anionic POM (total charge divided by the number of non-hydrogen atoms) and (right) the energy of the $n(O_{2p}) \rightarrow \pi^*(O_{2p}-M_{nd})$ charge transfer band measured by UV-Vis spectroscopy.^{82,97} The red line indicates the literature value⁸⁴ of the ¹³³Cs R_{QR} rate at infinite dilution.

Therefore this is a semiquantitative evaluation, since Cs-cations are likely to be in equilibrium between associated and free in solution. However, addition of excess Cs to the clusters of lower charge can induce precipitation. The POMs with more W(VI) centers have an overall lower charge and thus induce a smaller electric field gradient on nearby Cs⁺ nuclei. Nonetheless, a Cs⁺ in an ion pair with any of these anions will still have a significantly higher R_{QR} than the infinite dilution value due to the asymmetry of the charge distribution with respect to Cs⁺. However, a single Cs⁺ coordinated to multiple clusters in solution will exhibit an R_{QR} closer to the infinite dilution value due to the increased symmetry of the surrounding charge distribution (Figure 6.1).

Cs associated with POMs of lower charge-density (more W) exhibit lower R_{QR} values than those of higher charge-density (more Nb or Ta), with tungsten-based POMs approaching the infinite dilution relaxation rate (Figure 6.2). This is despite the fact that that there is higher Cs:cluster ratio for clusters of higher charge. As stated above, if all else is equal, a higher Cs:cluster ratio statistically means more Cs is free in so-

lution leading to a slower relaxation rate, approaching that of Cs at infinite dilution. For the lower charge-density clusters, each Cs⁺ is hydrated and separated from the anions or, at concentrations close to the solubility limit of the salt, presumably coordinated to multiple anions as observed in the structure of Cs₄Nb₂W₄O₁₉ (Figure 6.1),⁸² diminishing the quadrupolar relaxation rate. However, while there is a general trend of higher R_{QR} values (and thus greater average ion-pairing) with higher anionic charge density, the tantalum-containing POMs exhibit strictly faster quadrupolar relaxation rates than their niobium-containing counterparts of the same charge density in the case of both {M₆} (at the upper end) and {MW₉} (at the lower end). Thus, anionic chargedensity is insufficient to fully explain the ion-pairing trends of Cs⁺ in solution and more in-depth molecular obtial effects should be considered. Plotting R_{QR} instead against charge-transfer band energy (previously measured by UV-Vis spectroscopy) improves the monotonicity of the trend, although {TaW₉} remains an outlier (Figure 6.2).

6.3.3 Comparing the Cs⁺ Ion-Pairing of $\{Nb_6\}$ and $\{Ta_6\}$

By observing solutions of $Cs_8M_6O_{19}$ (M = Nb, Ta; $Cs\{M_6\}$) at a range of concentrations with inversion-recovery ¹³³Cs NMR, we can fully ascertain the differences between {Nb₆} and {Ta₆} in how they interact with Cs⁺ counter-cations. Previous thermochemical dissolution studies revealed that the enthalpy of dissolution for the Cs-salt of hexaniobate has a greater concentration dependence than for any other alkali salt, indicating different degrees of ion-pairing between dilute and more concentrated environments. ¹⁶⁴ Inversionrecovery NMR experiments revealed a similar dependence of ion-pairing on concentration (Figure 6.3). The quadrupolar relaxation rates of {Nb₆} and {Ta₆} exhibit an initial strong dependence on concentration, leveling out at higher concentrations. This



Figure 6.3: Adjusted quadrupolar relaxation rates (R_{adj}) of Cs{Nb₆} and Cs{Ta₆} compared to CsCl, demonstrating the greater average Cs⁺ ion pairing in {Ta₆}.

trend indicates that the number of "bound" Cs⁺ associated to each hexacoltanate anion increases with concentration, consistent with the previously observed decrease in dissolution with increasing Cs{Nb₆} concentration. Notably, Cs⁺ undergoes consistently faster relaxation when in solution with {Ta₆} than with {Nb₆}. This indicates that {Ta₆} undergoes a greater degree of ion-pairing with Cs⁺ counter-cations than {Nb₆} at all concentrations. CsCl undergoes no ion-pairing and thus exhibits a constant R_{QR} independent of concentration.

A "snapshot" of the average degree of ion-pairing in solutions of $Cs\{M_6\}$ can be obtained by dissolving solid CTAB (cetyltrimethylammonium bromide; $C_{16}H_{31}(CH_3)_3NBr$) into the cluster solutions at a range of concentrations. The resulting floc contains $\{M_6\}$ anions with the ion-paired Cs⁺ from the solution. CTA⁺ balances the remaining charge and induces precipitation via interdigitiation of the hydrophobic surfactant tails. This is a departure from the typical behavior of most POM salts whose counter-cations are completely displaced by cationic surfactants.²⁰⁵ In the case of Cs $\{M_6\}$, the Cs can never

Starting Solution	Cs_{assoc}	R_{adj} (NMR)	R_b
$5 \text{ mM Cs}\{\text{Nb}_6\}$	1.14	$0.719 \ {\rm s}^{-1}$	$4.52 \ {\rm s}^{-1}$
$10 \text{ mM Cs}\{\text{Nb}_6\}$	1.49	$0.931 \ {\rm s}^{-1}$	$4.62 \ {\rm s}^{-1}$
$20~\mathrm{mM}~\mathrm{Cs}\{\mathrm{Nb}_6\}$	2.11	$1.169 \ {\rm s}^{-1}$	$4.19 \ {\rm s}^{-1}$
$5 \text{ mM Cs}{Ta_6}$	2.36	$1.450 \ {\rm s}^{-1}$	$4.71 \ {\rm s}^{-1}$
$10 \text{ mM Cs}\{\text{Ta}_6\}$	2.97	$1.712 \ {\rm s}^{-1}$	$4.46 \ {\rm s}^{-1}$
$20 \text{ mM Cs}\{\text{Ta}_6\}$	3.60	$2.089 \ {\rm s}^{-1}$	$4.53 \ {\rm s}^{-1}$

Table 6.1: $Cs^+/{M_6}$ ratios in surfactant-precipitated samples along with associated R_b .* Cs_{assoc} denotes the $Cs/{M_6}$ ratio of the precipitate

 $^{*}R_{b}$ values are calculated from Eq. 5.2

be fully displaced by this rapid precipitation process, giving an indication of how many Cs-cations are associated per cluster for any solution concentration. Therefore, we can directly compare the $Cs^+/\{M_6\}$ ratio for $\{Nb_6\}$ and $\{Ta_6\}$ at the same concentration to corroborate our observation by NMR that there is more Cs^+ associated to hexatantalate than hexaniobate in water. Indeed, at each concentration tested, there are more Cs^+ per $\{Ta_6\}$ than per $\{Nb_6\}$ (Table 6.1). Moreover, the trend of increased ion association with increased solution concentration is also apparent in these studies. Excess CTAB was also added to a solution of only CsCl as a control, which yielded negligible (indistinguishable from the baseline) precipitated Cs (Figure D.9).

Additionally, by considering the ratios of $[Cs^+]/[\{M_6\}]$ (Cs_{assoc}) in tandem with R_{adj} for Cs^+ in each solution, along with the known R_f value $(0.086 \, s^{-1})$,²⁰⁴ we can ascertain the value of R_b by rearranging Eq. 5.1 (after multiplying both sides by 8 to reflect the 8:1 Cs^+ :{ M_6 } ratio):

$$R_b = \frac{8R_{adj} - (8 - Cs_{assoc})R_f}{Cs_{assoc}}$$
(6.2)

Because both $\{Nb_6\}$ and $\{Ta_6\}$ have an 8- charge, they induce very nearly identical

electric field gradients on any Cs⁺ ion in solution. Additionally, distances of Cs to the cluster's bridging oxygen atoms to which they are bound in the solid state are very nearly identical for Cs₈Nb₆O₁₉ and Cs₈Ta₆O₁₉ (≈ 3.1 Å).^{69,179} The solution-state phase pairdistribution function data (PDF) described below for Cs{M₆} indicate the solid state structures are reliable models for solution ion-pairing, so the derived values for R_b in Table 6.1 are thus directly comparable. Upon averaging the values for R_b in Table 6.1, we estimate a value for the relaxation rate of a single Cs⁺ in an ion pair with {M₆}:

$$R_b = 4.51 \pm 0.18 \mathrm{s}^{-1} \tag{6.3}$$

From this value, we can calculate the relative populations of Cs^+ in an ion pair and "free" in solution for any solution of Cs^+ and $\{Nb_6\}$ or $\{Ta_6\}$ and thus the average number of Cs^+ ions in an ion pair per cluster in solutions of any concentration.

 Cs^+ ion association can also be quantified by titrating CsCl into solutions of 20 mM $(TMA)_5H_3Nb_6O_{19}$ and $(TMA)_6H_2Ta_6O_{19}$. TMA⁺ ions do not undergo any appreciable amount of ion-pairing with $\{M_6\}$, ^{68,164} so any added Cs⁺ may associate directly to the clusters without interference. However, the two compounds cannot be directly compared in neat water due to their differing protonation states and degrees of oligomerization in solution. In light of this, they are instead observed in 200 mM TMAOH to ensure complete deprotonation and predominance of $\{M_6\}$ monomers in solution, ⁶⁸ while still keeping the viscosity of the solutions relatively low.

Cs⁺ ion association as a function of Cs:{M₆} ratio (0.5-12) in 20 mM TMA{M₆} solutions was determined from ¹³³Cs R_{QR} measurements (Figure 6.4). We again observe strictly greater Cs⁺ ion association with {Ta₆} than with {Nb₆} at all Cs⁺ concentrations. Although average Cs⁺ ion association (*i.e.* the fraction of all Cs⁺ in solution that



Figure 6.4: Quadrupolar relaxation rates of 133 Cs in a range of Cs⁺/{M₆} ratios in 200 mM TMAOH, indicating the average degree of ion association upon the addition of CsCl.

is in an ion pair) decreases for solutions of both $\{Nb_6\}$ and $\{Ta_6\}$ with increasing Cs⁺ as shown by R_{adj} , this does not indicate that there are fewer Cs⁺ ions associated to any given cluster at higher $[Cs^+]/[\{M_6\}]$ ratios. Instead, it suggests an equilibrium between free and associated Cs⁺ and the equilibrium shifts more towards free Cs⁺ as equivalents are added. By considering R_{adj} for each solution along with our derived value for R_b , we can arrive an average Cs_{assoc} in solution for any solution, again by rearranging Eq. 5.2:

$$Cs_{assoc} = \frac{[Cs^+]}{[\{M_6\}]} \left(\frac{R_{adj} - R_f}{R_b - R_f}\right)$$
(6.4)

This yields a more intuitive picture of the degree of Cs^+ ion association that is presented in figure 5. Each curve also appears to approach a "carrying capacity" for associated Cs^+ , with that of {Ta₆} being approximately double that of {Nb₆}. Thus, {Ta₆} undergoes greater degrees of ion-pairing than {Nb₆} with Cs^+ for any amount of initial free Cs^+ in solution.



Figure 6.5: Number of associated Cs⁺ per cluster in 20 mM solutions of TMA{ M_6 } (M = Nb, Ta) and 10-240 mM CsCl in 200 mM TMAOH. Values were obtained using Equation 5.4.

6.3.4 The Structure of Solution Ion-Pairing Between Cs^+ and $\{M_6\}$

A distinct peak appears at 4.1 Å and becomes more intense with added CsCl. This distance is very close to the Ta-Cs distances seen in the solid state crystal structure of $Cs_8Ta_6O_{19}.14H_2O$,¹⁷⁹ confirming the similarity between the aqueous and solid state Cs^+ environments. Additionally, upon normalizing the peak heights at the trans Ta-Ta distance (4.8 Å), the Ta-Cs peak grows monotonically, reaching a maximum. This agrees with the determined 'carrying capacity' of Cs^+ from the above NMR experiments. The cis Ta-Ta distance at 3.4 Å, on the other hand, grows with added Cs^+ . This pair distance overlaps with those of Cs-O and Cl-O pairs, according to prior X-ray scattering studies of CsCl and KCl solutions.^{206,207} We can discount significant contribution from Cl-O due to both the disorder of water that is hydrogen-bonded to Cl^- ,²⁰⁸ as well as the relatively low electron density of this atom pair. On the other hand, the Cs-O pair produces significant scattering from Cs, and the number of Cs-O bonds formed is



Figure 6.6: PDF analysis of X-ray total scattering on solutions of 100 mM TMA{ Ta_6 } in 200 mM TMAOH with added CsCl (0 to 12 molar equivalents) – 'sim' indicates a simulated spectrum.

directly correlated with the number of Cs^+ in solution, regardless of whether they are bonded to water only, or bonded directly to the cluster, with the rest of its coordination sphere completed with water molecules. Another peak arises at 6.6 Å with added Cs^+ , attributable to either a trans Ta-Cs or Cs-Cs distance. The peak intensity monotonically increases with increasing Cs^+ concentration and does not exist in the absence of Cs^+ .

The analogous $\{Nb_6\}$ solutions were also tested and exhibited very similar behavior to the $\{Ta_6\}$ solutions, with distinct Nb-Cs and Cs-Cs peaks growing monotonically with added Cs⁺ at 4.1 Å and 6.7 Å (Figure D.2). Thus the computational studies can be approached with confidence of correct solution phase structures. Moreover, these data provide a rare example of atomic-level evidence for ion-pairing in simple solutions that do not contain an excess of either the cation or anion.

6.3.5 Computational Results



Figure 6.7: Structures of (left to right) $\{M_6\}$; $Cs\{M_6\}$; $Cs_4\{M_6\}$; and $Cs_8\{M_6\}$ (M = Nb, Ta); optimized at the PBE0/Stuttgart-Dresden/D95 level (DFT). Key: small red spheres: O; large purple spheres: Cs^+ ; blue polyhedra: M. Gray lines are guides for the eye, and do not represent formal chemical bonds. All structures are also available on-line.

A contact ion pair, though impermanent and prone to rapid exchange with free ions in solution, involves some degree of covalent bonding.²⁰⁹ The relative importance of pure ionic/electrostatic interactions versus covalent bonding can be ascertained within the framework of DFT, qualitatively from the analysis of the electronic structure and molecular orbitals (Kohn-Sham orbitals) composition, and semi-quantitatively by applying the Bonding Energy Decomposition Analysis (EDA), for instance. A visualization of the evolution of the molecular orbital energy levels is included in Figure 6.8, from single isolated {M₆} ions and Cs⁺, to 1-, 4- and 8-Cs⁺ ion pairs, consistent with Figure 6.7. The LUMO of {Ta₆} is considerably higher in energy than that of {Nb₆}. The origin of the destabilized LUMOs for {Ta₆} is the Ta_{5d} atomic orbitals mixing more poorly than Nb_{4d} with O_{2p} in the formation of $\pi^*(M_{nd}-O_{2p})$ frontier unoccupied molecular orbitals (Figure D.11-12).

Upon the association of a single Cs^+ with $\{Nb_6\}$ and with $\{Ta_6\}$ (Figure 6.7), the

Table 6.2: Bond Energy Decomposition terms for the interaction of a single Cs^+ ion with $\{Nb_6\}$ and $\{Ta_6\}$ and solvation energies. 'Non-Relativistic' refers to results obtained by cancelling relativistic scalar ZORA effects. All energy values are in kcal mol⁻¹

	$\{ND_6\}$		$\{1a_6\}$	
	ZORA	Non-Relativistic	ZORA	Non-Relativistic
Solvation Energy	-2184.6	-2186.7	-2187.3	-2188.3
		Cs^+		
		ZORA	Non-Relativistic	
Solvation Energy		-50.4	-50.4	
	$Cs - \{Nb_6\}$		$Cs-{Ta_6}$	
	ZORA	Non-Relativistic	ZORA	Non-Relativistic
Pauli repulsion	65.1	69.3	56.8	65.8
Electrostatic Interaction	-547.4	-551.5	-546.4	-548.4
Orbital Interactions (OI)	-19.2	-24.0	-28.8	-21.4
Bonding Energy (BE)	-501.5	-506.3	-518.4	-504.1
% OI/BE	3.8	4.7	5.6	4.3
Solvation energy	-1719.4	-1720.7	-1715.1	-1724.3
Δ (Solvation)	515.6	516.4	522.6	514.4
Total Interaction Energy	14.1	10.1	4.2	10.3

LUMOs of both are energetically stabilized (Figure 6.8, Table 6.2). The stabilization observed for the $Cs\{M_6\}$ LUMO in Figure 6.7 is an indirect consequence of the interaction of the HOMO (primarily O^{2-} orbital character) with Cs^+ . The contribution of Cs^+ to the HOMO can be seen clearly in figure 9, discussed further below. While some portion of this is attributable to the decrease in total charge from -8 to -7, stabilization of the {Ta₆} LUMOs is nonetheless significantly greater than that of the {Nb₆} molecular orbitals. When the number of associated Cs^+ ions is increased to four, we continue to see stabilization of both the HOMOs and LUMOs in both {Nb₆} and {Ta₆}. However, we observe a greater total stabilization of the HOMO rather than the LUMO, resulting in a re-widening of the HOMO-LUMO gaps by roughly the same amount in both cases. Thus, when four Cs^+ ions are in a contact ion pair with a {M₆} anion, the total stabilization of molecular orbital energies compared to when only one Cs^+ ion is associated is ascribable to the decrease in total charge of the assembly. In other words, the stabilization achieved



Figure 6.8: Frontier molecular orbital energies of (Left) {Nb₆} and (Right) {Ta₆}, with 0, 1, 4, and 8 Cs⁺ associated, as shown in Figure 6.7. Black lines indicate the $\pi^*(O_{2p}-M_{nd})$ frontier unoccupied molecular orbital.

upon forming a single $Cs\{M_6\}$ pair is largely diluted across the additional Cs^+ ions, rather than fully duplicated for each additional association. In the case where eight Cs^+ ions are associated (when the charge of the {M_6} is fully neutralized), we again see stabilization of both the HOMOs and LUMOs, but such that the HOMO-LUMO gap increases (Table D.11-12). Interestingly, the HOMO-LUMO gap of $Cs_8\{Nb_6\}$ is wider than that of {Nb₆}, but it is narrower in $Cs_8\{Ta_6\}$ than in {Ta₆}. This indicates that for any amount of associated Cs^+ , the LUMOs have still undergone more total stabilization than the HOMOs in {Ta₆}, whereas this is not the case for {Nb₆}. Electrostatic effects alone cannot explain this result.

The interaction between Cs^+ and both anions was analyzed in terms of the bond energy decomposition scheme.^{210–212} Within this framework, the interaction energy is decomposed into three terms: two accounting for the interaction of the two unperturbed electronic densities (the Pauli repulsion and the electrostatic interaction) and a third term that accounts for the energy released because of the electronic relaxation, which is
usually called "orbital interactions". This scheme is applied in the gas phase. Melgar et al. recently demonstrated that in order to apply this method to charged fragments in solution, the balance of solvation energies of all the species needs to be taken into account.²¹³ Following this protocol, the analysis was also carried out with and without including relativistic effects. As expected, the values in Table 2 show that the electrostatic term is by far the most important and contributes equally in both cases. This term is slightly larger for ${Nb_6}$, as is the Pauli repulsion term. Both terms account for the slightly higher negative charge of the oxygen atoms in $\{Nb_6\}$. Significantly, the orbital interaction term clearly favors $\{Ta_6\}$ over $\{Nb_6\}$. Whereas Pauli and electrostatic terms hardly change upon cancellation of relativistic effects, the difference in the orbital interaction term between $\{Ta_6\}$ and $\{Nb_6\}$ almost vanishes. The percentage of the orbital interaction with respect the Bonding Energy does not exceed 6% in $\{Ta_6\}$ and 4% in ${Nb_6}$. Both values decrease and equalize when relativistic effects are cancelled out. It is important to notice that the total interaction energy values are slightly positive. This is due to the inaccuracy in computing absolute solvation energies. For instance, for Cs⁺ we computed $-50.4 \text{ kcal mol}^{-1}$ while the experimental value is $-47.5 \text{ kcal mol}^{-1}$.²¹⁴ The subtle balance between the Δ (Solvation) term and Bonding Energy term finally generates a total interaction energy value of 4.2 kcal mol^{-1} for $\{\text{Ta}_6\}$ – a reasonably small number. Thus, relativistic effects clearly make the difference between $\{Ta_6\}$ and $\{Nb_6\}$.

Further, to obtain another perspective on the nature of Cs^+ bonding to {Ta₆}, we ran supplemental calculations on the series $M_8[Ta_6O_{19}]$, where M = Rb, K, Na, Li (in this case without deriving UV-Vis spectra). Analysis of atomic orbital contributions, as well as energy plots of frontier orbitals for this series, are reported in Appendix D.6. Analysis of atomic orbital contributions, as well as energy plots of frontier orbitals for this series, are also reported in Appendix D. As expected, results from these additional calculations



Figure 6.9: Representation of the HOMO of (left) $Cs_8[Ta_6O_{19}]$; (center) $K_8[Ta_6O_{19}]$; and (right) $Li_8[Ta_6O_{19}]$; all with isosurface 0.005. The decreasing degree of admixture of alkali metal orbitals (seen in the sizes of the lobes on the alkali metals – highlighted in magenta and light green) is evident when going from left to right.

also point to a markedly covalent character in $Cs_8[Ta_6O_{19}]$, which gradually decreases from Cs to Li. For example, Figure 6.9 depicts the HOMO of $Cs_8[Ta_6O_{19}]$, $K_8[Ta_6O_{19}]$, and $Li_8[Ta_6O_{19}]$, all with isosurface 0.005. Participation of Cs^+ orbitals is evident in the first case, much less pronounced in K⁺ orbitals of $K_8[Ta_6O_{19}]$ and completely absent in the case of $Li_8[Ta_6O_{19}]$, where the interaction of Li^+ with $\{Ta_6\}$ is purely electrostatic in nature.

6.4 Conclusion

Through a combination of experimental and computational methods, we have arrived at a more thorough understanding of the nature of Cs^+ ion-pairing with polyoxometalates in water. Here we considered effects beyond relatively simple Coulombic models that cannot explain observed differences when charge-density is identical, as in the case of $\{Nb_6\}$ and $\{Ta_6\}$. The partial covalent nature of the $Cs\{Ta_6\}$ contact ion-pair, as shown by the extent of the mixing of the Cs^+ and the $\{M_6\}$ orbitals, was demonstrated by the higher value of orbital interaction energy in $Cs{Ta_6}$ than in $Cs{Nb_6}$. We owe this difference to relativistic effects, which was clearly shown by bond energy decomposition.

While scientists accept that in the solid state, bonds are rarely purely ionic or covalent, this is less widely accepted when describing aqueous solutions where all interactions are presumed to be ionic in nature. However, by computational studies and unexplained differences in ion-pairing experiments of Cs^+ with $\{Nb_6\}$ and $\{Ta_6\}$, we have arrived at a conviction that covalency in ion-interactions in water are relevant. Finally we return to the issue of solubility and understanding how the $Cs-\{M_6\}$ salts can be extremely soluble with maximum ion-pairing, contrary to well-known trends. The PDF reveals a remarkably stable ion-interaction, in that it is rigid enough to produce a strong correlation peak between the Nb/Ta of the cluster and the associated Cs⁺. Moreover, based on the solid state model, the Cs⁺ forms three bonds to the cluster face, probably also contributing to the stability of the solution-phase interaction. We have surmised that the interaction is so strong between the cluster and Cs^+ that the Cs^+ does not bridge to other clusters, thereby hindering precipitation. Through ongoing experiments and calculations, we hope to quantify the critical feature of polyatomic anions (*i.e.*, charge density, size, type of ion-pairing) that drives the turning point from anomalous solubility behavior seen in the current system of study to normal solubility behavior. Through these investigations, we will ultimately ascertain a more general and complete set of rules by which the solubility of any given ion pair can be predicted based on the nature of both coulombic and covalent interactions in water.

6.5 Acknowledgements

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Chapter 7: Messed-up Decaniobate

Or: How We Learned To Stop Worrying And Love Countercations

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7.0 Abstract

Counterions are often overlooked in aqueous solutions. While pH and concentration are typically adequate to explain speciation of metal-oxo clusters in solution, the importance of counterions is being increasingly recognized. Group V polyoxometalates constitute such a system in which alkali cations can also exert unique effects that result in otherwise unattainable speciation processes. Here, we trace the aqueous speciation of $[Nb_{10}O_{28}]^{6-}$ into oligomers of $[HxNb_{24}O_{72}]^{(24-x)-}$ upon adding only alkali chloride salts. NMR measurements showed noticeable Li⁺ ion-association to clusters in solution, while confirming the absence of ion-association with isostructural and isoelectronic $[V_{10}O_{28}]^{6-}$. Raman reveals that the rate of cluster conversion increases with alkali cation radius and the presence of cation-bridged oligomers of $[HxNb_{24}O_{72}]^{(24-x)-}$ is confirmed by comparison of experimental small-angle x-ray scattering and x-ray total scattering spectra to simulations.

7.1 Introduction

The aqueous speciation of transition metal oxoanions arises from a number of complex, interrelated phenomena. Oxo ligands efficiently stabilize high metal oxidation states in both the solid and aqueous states. The well-characterized "oxo wall" between groups 8 and 9 on the periodic table constitutes a threshold at which terminal oxo complexes can form, as greater numbers of d-electrons result in lower capacities for ligation.²¹⁵ However, d-electron counts alone are not adequate to explain the full range of transition metal speciation in aqueous solutions. Polyoxometalates (POMs) are a group of molecular metal oxides of Group 5 and 6 transition metals in their d^0 oxidation state

with a wide variety of formation mechanisms. Isopolymetalates of V, Mo, and W form upon acidification of solutions of their monomeric, tetrahedrally-coordinated orthometalates – the oxo ligands are protonated, promoting condensation, forming M-O-M linkages and water molecules^{216,217} – a mechanism often referred to as "bottom-up". However, the formation mechanism of Nb and Ta POMs is far less certain. The Lindqvist ion $([M_6O_{19}]^{8-}; M = Nb, Ta)$, the most common Nb and Ta POM geometry, forms in highly alkaline solutions from their oxides – referred to as a "top-down" mechanism since it is formed from an extended solid.¹⁵² This is far less straightforward because tetrahedrally-coordinated monomeric Nb and Ta are unfavorable due to the larger size and lower charge-densities of the Nb^{5+} and Ta^{5+} ions compared to Mo^{6+} and W^{6+} .¹⁵⁴ The uncertainty of the formation mechanism of Nb and Ta POMs is mirrored by the incompleteness of the metals' speciation diagrams with respect to solution pH and concentration compared to those of vanadium, molybdenum, and tungsten which are very well-characterized.²¹⁸ The formation of larger Nb POMs is even more complicated, as their speciation is often driven by alkali counter-cations that not only balance charge, but can also act as structure-directing and stabilizing framework materials.^{219–221} Thus, in order to understand niobium speciation in solution, it is crucial to understand the effect of counter-cations in solution as well.

Decaniobate $([Nb_{10}O_{28}]^{6-}; \{Nb_{10}\})$ is the other isopolyniobate that can form in solution, albeit by hydrothermal synthesis in organic solvent. The $\{Nb_{10}\}$ and decavanadate $([V_{10}O_{28}]^{6-}; \{V_{10}\})$ ions are isovalent and isostructural, but their behavior in solution differ dramatically. In contrast to $\{V_{10}\}$'s rich redox chemistry and well-characterized speciation upon pH adjustment, $\{Nb_{10}\}$ is electrochemically inert, dissolves to form neutral solutions, and has been reported to convert to hexaniobate in response to pH increase.²²² Furthermore, unlike $\{V_{10}\}$, no alkali cation salt nor aqueous synthesis of

 ${\rm Nb_{10}}$ has ever been reported – only the tetramethylammonium (TMA; [(CH₃)₄N⁺]) salt has been isolated.²²³ One might surmise that this is due to compatibility with the organic media in which it is synthesized, but here we show that ${\rm Nb_{10}}$ is simply unstable in the presence of alkalis in water.

Previously, we studied the extent of Cs^+ ion pairing with hexaniobate $([Nb_6O_{19}]^{8-};$ $\{Nb_6\}$) and hexatantialate ($[Ta_6O_{19}]^{8-}$; $\{Ta_6\}$), confirming the presence of ion-pairs in both cases.¹⁶⁴ A natural expansion of this work is to extend the study to $\{Nb_{10}\}$. However, in stark contrast to the quickly-stabilizing contact ion-pairs that formed with the hexametalates, a more complicated, time-dependent system arose, ultimately resulting in consistent formation of larger polynuclear species that are similar to a number of prior reported clusters built of heptaniobate units, identified in the solid-state. Here, we used NMR to illustrate fundamental differences in alkali counterion behavior in association with $\{V_{10}\}$ and $\{Nb_{10}\}$. We used Raman spectroscopy to track the decomposition of $\{\mathrm{Nb}_{10}\}$ with concomitant formation of the new cluster and small angle x-ray scattering (SAXS) to determine the size of species in solution. X-ray total scattering (XRTS) supplemented other analytical techniques by comparing interatomic distances in solution to simulated scattering spectra based on existing structures. These data support a countercation-mediated evolution of niobium clusters, further supporting the noninnocence of alkali countercations in solution and the importance of their consideration in descriptions of cluster speciation and even generation of Pourbaix diagrams in which they are currently not considered.

7.2 Experimental

7.2.1 General Materials and Methods

Milli-Q water (Millipore, 18.2 M Ω cm at 25 °C) was used for all aqueous solutions. Isopropyl alcohol (ACS grade) and ethanol (ACS grade) were purchased from Macron Fine Chemicals. The pH of the reaction mixtures was measured using an OrionTM VERSA STARTM pH/ISE Benchtop Multiparameter Meter. The instrument was calibrated using three standard solutions of pH 4, 7, and 10.

7.2.2 Syntheses

7.2.2.1 $[(CH_3)_4N]_6[Nb_{10}O_{28}] \cdot 6H_2O$

We developed our own synthesis of decaniobate via hydrothermal treatment of hexaniobate. One gram of $[(CH_3)_4N]_5H_3[Nb_6O_{19}]^{83}$ was added to 10 mL of ethanol and stirred for 20 minutes, resulting in a white suspension. This suspension was loaded into a Teflon cup in a Parr Reactor and heated at 140 C for 18 hours. The brown supernatant was discarded and the resulting white powder was washed under vacuum with 50 mL of ethanol and allowed to dry in air.

Yield: 638 mg (87.9%). Supplementary characterization data is identical to other published syntheses.⁸³

7.2.2.2 $\text{Li}_6 \text{V}_{10} \text{O}_{28} \cdot 16 \text{H}_2 \text{O}$

90 mg of V_2O_5 was added to 10 mL of 1M LiOH, resulting in a slightly green solution that turned clear upon stirring for 10 minutes. Glacial acetic acid was added dropwise until the pH reached 6.0, resulting in a bright orange solution. 100 mL isopropanol was added to crash out the product and the resulting orange suspension was centrifuged for 15 minutes. The supernatant was discarded and the orange solid was washed under vacuum with 50 mL of ethanol and allowed to dry in air.

Yield: 51 mg (58.9%). Degree of hydration was taken from the literature.²²⁴ The Raman spectrum of this compound was compared to that of Na6V10O28²²⁵ and was found to be very similar (Appendix E).

7.2.3 Infrared Spectroscopy

Infrared spectra (400-3500 cm⁻¹) were collected on a Thermo Scientific Nicolet iS10 with a Smart Orbit Diamond ATR accessory and are reported in Appendix E.

7.2.4 Raman Spectroscopy

Raman spectra were collected on a Thermo Scientific DXR spectrometer with a 780 nm laser source, 400 lines per mm grating, and 50 μ m slit with eight scans at eight seconds each.

7.2.5 NMR

⁷Li spectra were recorded on a Bruker 500 MHz NMR spectrometer operating at the ⁷Li Larmor frequency (194.317 MHz) at a constant temperature of 25 °C (by means of a BCU05 temperature controller) in solutions of 90% H₂O and 10% D₂O. T₁ values were derived by inversion recovery experiments. Each value of T₁ was calculated by an exponential fit from 16 delay times of 4-8 scans each. T₁ inversion recovery was performed on 20 mM solutions of TMA-{Nb₁₀} combined with 120 mM LiCl and 20 mM solutions of Li-{V₁₀} combined with 120 mM TMACl 14 times over the span of four weeks in order to observe changes over time. Sixteen delay times of four scans each were used for each T₁ measurement.

7.2.6 SWAXS

Small and wide angle X-ray scattering was collected on an Anton Paar SAXSess with Cu-K radiation (1.54 Å) and line collimation with a q-range from 0.018-2.5 Å⁻¹. The instrument is equipped with a 2-dimensional image plate detector with a sample to image plate distance of 26.1 cm. Reaction solutions as well as neat water were sealed in 1.5 mm borosilicate glass capillaries. Data collection time was 30 minutes. SAXSquant software was used for data collection and initial processing. Igor Pro software utilizing Irena macros was used for the data analysis.²²⁶ SolX software was used for creating simulated scattering curves.¹⁸¹

7.2.7 PDF analysis of X-Ray Total Scattering

Raw X-ray scattering data were collected with a Rigaku Smartlab X-ray diffractometer with a Mo-K α source ($\lambda = 0.71073$ Å). For these solution X-ray scattering measurements, an aliquot of the solution was injected in a Kapton 1.5mm capillary, sealed and positioned in the goniometer. Transmission mode of the data collection was applied, where 2 range of 3.0-118.61° was used. Therefore, the maximum available Q-value is 15.2 Å⁻¹. The data collection time was 0.2° min⁻¹ using a 0.01 degree resolution. In order to eliminate the contribution of the solvent and the sample holder, Milli-Q water was also measured for background subtraction applying identical experimental parameters. The solution scattering curves were transformed to the reduced structure functions, then they were Fourier transformed to obtain the reduced atomic pair distribution functions (PDF, denoted as G(r) on the graph). For the mathematical transformations and background subtractions we used the PDFgetX3 software.¹⁸⁰ Simulated PDF data were obtained with the solX software¹⁸¹ using the appropriate parameters.

7.2.8 ESI-MS

ESI-MS was carried out using an Agilent 6230 ESI-MS system comprised of a Time-of-Flight (TOF) mass spectrometer coupled to an electrospray ionizer. The aged solutions were diluted to 1 mM Nb and infused into the ESI-MS system at a flow rate of 0.4 mL min⁻¹ using a syringe pump. The solutions were nebulized with the aid of heated N₂ (325 °C) flowing at 8 L min⁻¹ and a pressure of 35 psig (241 kPa). The voltages of the capillary, skimmer, and RT octopole were set at 3500, 65, and 750 V respectively, while the voltage of the fragmenter was set at 100 V. The data were collected in the negative ionization mode.

7.3 Results & Discussion

7.3.1 Contrasting Li⁺ Ion-Association with $\{Nb_{10}\}$ and $\{V_{10}\}$

The ⁷Li quadrupolar relaxation rate (R_{QR}) was measured for solutions of $\{V_{10}\}$ and $\{Nb_{10}\}$ with six equivalents of Li⁺ each (fully balancing the 6- charge on each cluster). ⁷Li is a quadrupolar nucleus $(I = \frac{3}{2})$,²²⁷ so proximity to electric field gradients in solution such as those provided by the highly-charged decametalates are chiefly responsible for its T₁ (the reciprocal of R_{QR}) relaxation.²²⁸ Thus, a "free" Li⁺ ion in solution would have a low R_{QR} , whereas a Li⁺ that is associated to a cluster would have a much larger R_{QR} . Because the R_{QR} of a solution represents the mole fraction-weighted average of free and associated ions, solutions with the same amount of Li⁺ can be directly compared to determine relative degrees of ion-association. Although R_{QR} is also dependent on viscosity, it was determined to be negligibly different between the two solutions.

Immediately after the two solutions (20 mM $\text{Li}_6[V_{10}O_{28}]$ with 120 mM TMACl and 20 mM (TMA)₆[Nb₁₀O₂₈] with 120 mM LiCl) were prepared, the R_{QR} values differed considerably (Figure 7.1). In the decavanadate solution, Li⁺ has a very low R_{QR} , indicating minimal interaction with the clusters in solution as expected. However, Li⁺ has a much higher RQR in the presence of {Nb₁₀}, indicating a nontrivial degree of ion-association despite Li⁺'s large hydration sphere. Over the course of several weeks, Li⁺ undergoes an increasing degree of ion-pairing with {Nb₁₀}, whereas the degree of ion-association remains constant and minimal in the decavanadate solution. This time dependence of cation association with {Nb₁₀} is a curious departure from ion-pairing with hexaniobate,



Figure 7.1: ⁷Li quadrupolar relaxation rates (R_{QR}) over time of 20 mM solutions of TMA-{Nb₁₀} with 120 mM LiCl and Li-{V₁₀} with 120 mM TMACl.

in which the degree of Cs^+ ion-association equilibrated rapidly. When taken alone, the increasing R_{QR} could indicate one of two possible scenarios. The first potential explanation is that the hydration sphere of Li⁺ inhibits the rapid ion-association seen with Cs⁺ and hexaniobate, resulting in a much slower, but still simple ion-pairing process. The second possibility is that the Li⁺ cation associates to {Nb₁₀} and plays an active role in a more complex Nb cluster speciation process.

7.3.2 Observing $\{Nb_{10}\}$ Alteration

Raman spectroscopy was performed on a series of temperature-controlled (28 °C) aqueous solutions containing 20 mM {Nb₁₀} with added 120 mM ACl (A = Li, Na, K, Rb, Cs). Over the course of one week, a reaction clearly occurs and the reaction rate sharply increases with alkali cation radius (Figure 7.2). Cs⁺ begins to decompose {Nb₁₀} much more rapidly than the other alkalis, exemplified by the drastically diminished peak inten-



Figure 7.2: Raman spectra showing the decomposition of 20 mM $\{Nb_{10}\}$ in the presence 120 mM ACl (A = Li, Na, K, Rb, Cs) after (top left) three hours, (top right) one day, (bottom left) three days, and (bottom right) 1 week. The peak at 755 cm⁻¹ corresponds to tetramethylammonium and acts as an internal standard.

sity of the $\{Nb_{10}\}$ symmetric terminal-oxo stretch at 936 cm⁻¹ after three hours.^{222,229} Within a day, this peak has entirely disappeared in the presence of Cs⁺, indicating that all of the $\{Nb_{10}\}$ has been depleted. At this point, $\{Nb_{10}\}$ concentration has decreased considerably in the presence of K⁺ and Rb⁺, while the presence of Li⁺ and Na⁺ do not lead to appreciable changes. After three days, the spectra of K⁺ and Rb⁺ have also stopped changing, while Na⁺ and Li⁺ have shown noticeable but limited conversion. After a week, all alkali cations have fully decomposed $\{Nb_{10}\}$ except for Li⁺, which has only a small amount of unconverted $\{Nb_{10}\}$ remaining. The solution of TMA- $\{Nb_{10}\}$ only remained almost completely unchanged over the course of the week, confirming that no conversion takes place in the absence of the added alkali chlorides and that $\{Nb_{10}\}$ is stable in aqueous solution when only its tetramethylammonium countercations are also present.



Figure 7.3: pH measurements over time of 20 mM {Nb₁₀} with 120 mM ACl (A = Li, K, Cs) in neat water and in 1M HEPES/TMAOH buffer (pH = 7).

In neat water, solutions of $\{Nb_{10}\}$ with alkali cations undergo an initial raise in pH, which steadies out over time (Figure 7.3). Mirroring the reaction rates seen by Raman, Cs⁺ promotes the fastest change in pH, followed by K⁺, and Li⁺ drives the slowest change. However, each solution equilibrates to very nearly the same pH value over time (8.5-9) as the respective reactions go to completion. As expected, the pH of a solution containing only TMA- $\{Nb_{10}\}$ maintains a constant pH around 7, indicating that $\{Nb_{10}\}$ is not prone to protonation in the presence of only TMA⁺. Thus, alkali cations are indirectly responsible for inducing the increase in pH. When placed into a 1M HEPES buffer (buffered to pH = 7 with TMAOH), the pH change is largely suppressed and does not exceed 7.6 at any time for any alkali cation.

The effect of buffering the solution on speciation can be observed by tracing the intensity of the aforementioned $\{Nb_{10}\}$ Raman peak at 937 cm⁻¹ (Figure 7.4). The decomposition of $\{Nb_{10}\}$ is significantly slowed in buffered solutions for each alkali cation, confirming that pH has a significant role in speciation. Comparing the shapes of the curves over time reveals insight into this process. As exemplified by the shape of the



Figure 7.4: Raman peak intensity (937 cm⁻¹) over time for the decomposition of 20 mM {Nb₁₀} with 120 mM ACl (A = Li, K, Cs) in both neat water and 1 molar HEPES/TMAOH buffer (pH = 7).

curve of $\{Nb_{10}\}$ + LiCl in neat water, the reaction accelerates when the pH is allowed to increase unbuffered, indicating that the availability of free hydroxide ions in solution is significant in the speciation of the clusters. This is further confirmed by the comparatively linear curves for Li⁺ and K⁺ in HEPES – since the hydroxide ion concentration in solution is more constant, the reaction does not accelerate as it does in neat water. The speciation of $\{Nb_{10}\}$ and Cs⁺ in HEPES is also significantly slower compared to neat water, though the apparent difference is less pronounced due to the relative speed of the reaction driven by Cs⁺. However, it is important to note that despite being significantly slowed, the reaction still occurs when the pH of the solution is buffered. The Raman spectra of HEPES solutions are available in the Appendix E (Figure E.3-E.5).

A new Raman peak forms at 904 cm⁻¹ simultaneously with the disappearance of the $\{Nb_{10}\}\ peak$. The new peak is very close to those from reported spectra that were ascribed to symmetric terminal-oxo stretches of the hexaniobate structure $([Nb_6O_{19}]^{8-})^{.222}$ In the absence of other measurements, it may be concluded that alkali cations decom-



Figure 7.5: SAXS spectra of 20 mM $\{Nb_{10}\}$ in neat water and with 120 mM ACl (A = Li, Na, K, Rb, Cs). Solutions were aged for two weeks to assure full speciation.

pose $\{Nb_{10}\}$ into the more water-soluble and stable hexaniobate. However, a solution pH of 8.5-9 is significantly below hexaniobate's window of aqueous stability, ¹⁵⁴ so this conclusion is unsatisfactory.

7.3.3 Determining Cluster Sizes

After two weeks of aging in order ensure that cluster conversion was complete, the solutions previously measured by Raman were measured by SAXS (Figure 5). The TMA- $\{Nb_{10}\}$ solution retained small, approximately spherical particles (Rg = 3.4 Å) indicative of stable $\{Nb_{10}\}$. However, the alkali cation-containing solutions exhibited earlier and more sloped Guinier regions, as well as higher I[0] values, indicating significant speciation

into larger clusters, with larger cations resulting in overall larger assemblies (Table 7.1). However, the flatness of the curves at low q values and the similarity in the curves' shapes indicate that we each solution is monodisperse, aging has indeed completed within two weeks (Figure E.7-E.11), and each assembly is likely made of similar subunits, differing only in oligomer type. Thus, the hexaniobate-like stretching seen by Raman is not from single discrete $\{Nb_6\}$ clusters, but is instead from larger clusters that are constructed from $\{Nb_6\}$ -like units.

The $\{Nb_7\}$ ($[Nb_7O_{22}]^{9-}$, the Lindqvist unit with an additional edge-sharing $[NbO_6]$ octahedron) unit has been reported as the building block of a multitude of larger polyniobates $^{230-232}$ and even suggested as an intermediate between $\{Nb_{10}\}$ and $\{Nb_6\}$ conversion in base. 233 Because the Raman stretching from an $\{Nb_7\}$ unit is very likely to be similar to that of a Lindqvist ion, these clusters provide a good starting point for predicting the identity of the alkali-restructured niobium cluster. By comparing the curve of the potassium salt (the median of the alkali-converted clusters) to those of known large polyniobates, we can arrive at the relative sizes and, by extension, nuclearity, depending on the modeled geometry.

We simulated the SAXS curves of a myriad of large polyniobates – $[Nb_{24}O_{72}]^{24-}$, $[Nb_{32}O_{96}]^{32-}$, and $[K_{12}Nb_{96}O_{288}]^{84-230}$ (Figures E.12-E.14) – and compared them to the experimental data of the TMA- $\{Nb_{10}\}$ and aged $\{Nb_{10}\}$ + KCl solutions (Figure 7.6). The K solution was chosen on account of its median size out of the alkalis, the lack of structure factor in its SAXS curve, and its prominence in the structures of the other simulated clusters. As expected, the $\{Nb_{10}\}$ solution curve indicated much smaller particles than any of the simulations of larger clusters. The relative position of the aged solution's curve, however, provides more information. The Guinier elbow is located at lower q values than $\{Nb_{24}\}$ and $\{Nb_{32}\}$, but at a significantly higher q value than $\{Nb_{96}\}$;



Figure 7.6: Experimental spectra of 20 mM TMA{Nb₁₀} in 1M TMANO3 and aged with 120 mM KCl, along with simulated spectra of {Nb₂₄}, {Nb₃₂} and {K₁₂Nb₉₆}, normalized for I[0].

where the q-value of this feature is inversely proportional to the size of the scattering species. Additionally, the shape of the experimental curve's plateau and second "dip" in the 0.4-0.9 Å⁻¹ range most closely matches those of {Nb₂₄} and {Nb₃₂}. We can initially predict that upon attack by alkali cations, {Nb₁₀} likely rearranges into larger assemblies based on oligomers of either {Nb₂₄} or {Nb₃₂} units.

7.3.4 Determining the Building Block

Comparing the curve of the lithium salt to that of a simulated $\{Nb_{24}\}$ dimer bridged by Li⁺ results in a very close fit (Figure 7.7). The R_g values of the experimental and



Figure 7.7: Experimental spectra of 20 mM TMA-{Nb₁₀} in neat water and aged with 120 mM KCl, along with a simulated scattering curve of an {Nb₂₄} dimer bridged by Li⁺. The dimer is pictured (left) showing the bridging Li⁺ and (right) the centers of the {Nb₂₄} units.

simulated curves are very close to the same (8.76 and 8.77 Å, respectively). Furthermore, the plateaus and second "dips" between 0.3 and 0.8 Å⁻¹ between the two curves line up almost perfectly, suggesting that the two species are very similar in size and geometry, if not identical. The size of each assembly indicates that the Li, Na, and K salts all most likely coordinate dimers of $\{Nb_{24}\}$ ($R_g = 8.76$, 8.78, and 9.78 Å), while Rb and Cs coordinate tetramers ($R_g = 11.8$ and 12.9 Å). The assertion that each alkali cation forms oligomers of $\{Nb_{24}\}$ is corroborated by the identicalness of the experimental Raman spectra at the end of each aging process. Furthermore, a comparison of the simulated Raman spectra of $\{Nb_{10}\}$ and $\{Nb_{24}\}$ reveals a shift of 30 cm⁻¹ between the two, perfectly matching the experimental shift (Figure E.18).



Figure 7.8: (left) Experimental scattering curve for 100 mM TMA-{Nb₁₀} with its simulated spectrum. Peak assignments: W = Nb-O, X = cis Nb-Nb, Y = trans Nb-Nb, Z = second-to-most-adjacent Nb-Nb; (right) Experimental scattering curve for evaporated-down Li-{Nb₂₄} solution with a simulated spectrum for {Nb₂₄}. Peaks A-D are labeled.

X-ray total scattering is also a powerful tool for comparing experimental data to simulated scattering curves from crystal structures by revealing interatomic distances within single clusters in solution. Comparing an experimental PDF spectrum of a solution of 100 mM TMA-{Nb₁₀} to a simulation from its crystal structure (Figure 8), we see good agreement in the peak positions (with notable Nb-Nb distances marked X through Z), as well as decent agreement in the relative peak intensities.

The Li-aged solution is ideal for comparison with simulated $\{Nb_{24}\}$, since associated Li⁺ are too small to significantly scatter x-rays, unlike the larger alkali cations. The experimental and simulated spectra of $\{Nb_{24}\}$ are very similar (Figure 8). The previously unseen shoulder (marked 'A') on the cis Nb-Nb peak (marked 'X') at 3.6 Å is ascribable to Nb-Nb distances from a corner-sharing $[NbO_6]$ octahedron to the nearest metal center on an $\{Nb_7\}$ unit, which is present in $\{Nb_{24}\}$ and absent in $\{Nb_{10}\}$. Peaks W through Y from $\{Nb_{10}\}$ are maintained in $\{Nb_7\}$ units and are also present in both experimental and simulated $\{Nb_{24}\}$. Furthermore, the relatively intense peak Z from

 $\{Nb_{10}\}\$ is significantly suppressed in $\{Nb_{24}\}\$ and also overlaps somewhat with peak B. This decrease in intensity arises from the far fewer cis-Nb-O-Nb-O-Nb distances present in $\{Nb_7\}\$ compared to in $\{Nb_{10}\}\$. At distances beyond 8 Å, the simulated $\{Nb_{24}\}\$ spectrum's peaks become significantly better-defined than the experimental peaks, which become nearly indistinguishable from noise. This is attributable to the $1/r^2$ relationship between peak intensity and inter-atomic distance that appears in experimental spectra, but is not reflected in simulation. Electrospray ionization mass spectrometry data on the Li, K, and Cs solutions further confirm that $\{Nb_{24}\}\$ is formed in each case and can be found in the Appendix E (Figures E.15-E.17, Tables E.1-E.3).

7.4 Conclusion

By combining computational and experimental results, we have characterized a speciation event from decaniobate to oligomers of a larger, 24-center niobium cluster driven by countercations. The rate of this conversion was significantly dependent on the size of the countercations, with cesium ions promoting rapid speciation and Li⁺ promoting far slower speciation. Not only does this study get to the root of why only the tetramethylammonium salt and never an alkali cation of decaniobate has been isolated, but it also illustrates a system in which pH and concentration effects alone do not adequately explain the speciation process. Thus, alkali cations have again been shown to be crucial for a full understanding of Group V polyoxometalate chemistry. However, in contrast to cesium's stable ion-association to hexaniobate and hexatantalate, alkali cation association is responsible for speciation into an entirely new cluster. Additionally, this study lends yet more credence to our conviction that covalency in ion-interactions in water is not only relevant, but often crucial for a full understanding. Furthermore, these solution processes are in stark contrast to the isovalent decvanadate ion, which remains stable and unchanged in solution with alkali countercations. This further highlights the fundamental differences between polyoxovanadates and polyoxometalates of the larger group V metals and highlights the necessity of delineating the clear distinction between them.

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Chapter 8: Conclusions

The work presented in this thesis is focused on contrasting the ion association behaviors of hexaniobate (as well as some isostructural tungsten-mixed clusters) and hexatantalate. We also endeavored to elucidate the fundamental physical causes behind these differences. The solid-state crystal stuctures of cesium $\{Nb_2W_4\}, \{Nb_4W_2\}, and \{Nb_6\}$ exhibited decreasing degrees of Cs^+ association with increasing tungsten character in the cluster, whereas the solid state structures of cesium hexaniobate and cesium hexatanalate were essentially identical. However, differences in the solid-state cesium salts, as well as other alkali salts of the hexacoltanates, arose during high-temperature calorimetry measurements. Room-temperature dissolution studies revealed a much greater slope for cesium hexaniobate than for the other alkali salts, indicating that the degree of ionpairing increased the most sharply with concentration for the cesium salt. However, both cesium and rubidium hexatantalate exhibited this anomalously steep slope, indicating that hexatanatlate also has strong ion-pairing behavior with rubidium. ¹³³Cs NMR measurements of aqueous solutions of hexacoltanates and cesium indicated a significantly greater degree of cesium ion pairing to hexatantalate than to hexaniobate at a range of concentrations and Cs⁺:{M₆} ratios. Solution-state x-ray total scattering confirmed this. Additionally, computational bond enthalpy decomposition measurements revealed that the orbital interaction term marked the difference between cesiumassociation energies of hexaniobate and hexatantlate and that this difference arose from relativistic effects in core 4f electrons present in tantalum but absent in niobium. Thus, pure electrostatics are insufficient to explain these ion-pairing behaviors and at least some degree of covalency is at play in ion-pairing. Further work on these studies will include more rigorous calorimetry, countercation quadrupolar relaxation NMR, and x-ray total scattering experiments on mixed Group V/VI clusters, as well as the Group VI Keggin ions. We hope to eventually arrive at a general set of rules from which the aqueous solubility of metal-oxo species can be reliably determined.

Finally, an attempt to perform these studies with decaniobate resulted instead in largely counter-cation driven speciation into larger niobium oxo clusters. This speciation occurred more rapidly with increasing alkali cation radius. Despite not being able to isolate single crystals of the resulting cluster, experimental measurements of small-angle x-ray scattering and x-ray total scattering were compared to simulations of a number of existing large niobium clusters. The smaller alkali salt solutions matched closely with oligomers of a 24-centered niobium cluster. Larger alkali cations templated greater numbers of units, again demonstrating that counter-cationic behavior has the potential to be not purely electrostatic. In the future, we plan to utilize DFT to find the energetic differences between cations in their association to decaniobate in an attempt to arrive at a mechanism for the cluster's speciation and, hopefully, track the speciation of decatantalate upon the addition of alkali cations.

Although the high solubility of cesium salts of polycoltanates would make their use for ¹³⁷Cs sequestration counterproductive, the fundamental science gleaned from their study is nonetheless applicable to determine optimal sequestration techniques, in particular when considering sorption of cesium onto metal oxide surfaces. By comparing its unusual behavior with hexacoltanates to its more typical behavior in other solution environments (as well as considering intermediate cases), we can arrive at a number of interrelated trends including, but not limited to, solubility, ion-pairing, and degree of covalent bonding character with anions. When considered in tandem, these trends will provide guidelines to design chemistries and to optimize technologies for cesium remediation in contained wastes and in uncontrolled contamination scenarios. The relationship between ion association and solubility of Cs-anion or Cs-complexant pairs is important to consider for the design of solvent extraction or precipitation chemistries for Cs removal. The type of ion-pair that Cs forms with an anionic surface (*i.e.* directly bonded or mediated by a hydration sphere) dictates how strongly it will bind to that surface. Our studies of Cs-POM association have yielded fundamental knowledge that is applicable to optimal design of a myriad of Cs sequestration technologies. This is because POMs, as anionic, molecular and soluble metal oxides, possess characteristics that typify both soluble anions and metal oxide surfaces that are exploited in Cs remediation technologies.

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APPENDICES

Appendix A: Supporting Information for Chapter 3

A.1 Materials and Methods

A.1.1 Starting Materials

All reagents starting materials were purchased from VWR and used without further purification: NbCl 5 (99 %), Na₂WO₄ · 2 H₂O (95 %), CsCl (99 %), KOH (85-100 %), CsOH (99.9 %), hydrogen peroxide (30 wt%), isopropyl alcohol, and methanol. Literature procedures were used in the syntheses of K₃[Nb(O₂)₄] and Cs₃[Nb(O₂)₄]⁶⁸ and their identities were confirmed by FTIR and UV-Vis spectroscopies.

A.1.2 X-Ray Crystallography

Diffraction intensities were collected at 150 K (CsNa{Nb₄W₂}) and 173 K (Cs and CsNa{Nb₂W₄}) on a Bruker Apex2 CCD diffractometer using Mo-K radiation, $\lambda = 0.71073$ Å. Space groups were determined based on systematic absences. Absorption corrections were applied by SADABS.²³⁴ Structures were solved by direct methods and Fourier techniques and refined on F² using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in solvent water molecules in CsNa{Nb₄W₂} were located and refined with isotropic thermal parameters, but with restrictions. An O-H distance of 1.0Å was used in the refinement as a target for all O-H bonds. H atoms in Cs{Nb₂W₄} and CsNa{Nb₂W₄} were not found and not

taken into consideration. Occupation factor refinements showed that in all investigated structures, W and Nb atoms share the same positions in the (W/Nb)₆O₁₉-unit, but the W/Nb ratio at different positions is varied. In $CsNa\{Nb_4W_2\}$ and $Cs\{Nb_2W_4\}$, the $(W/Nb)_6O_{19}$ -unit is centro-symmetric and there are three W/Nb positions. Refinement shows that W and Nb atoms share these positions in ratios 0.498/0.502; 0.319/0.681; 0.235/0.765 (CsNa{Nb₄W₂}) and 0.871/0.129; 0.623/0377; 0.523/0.477 (Cs{Nb₂W₄}). These ratios provide formulae of $Cs_4Na_2Nb_{3.89}W_{2.11}O_{19}$ and $Cs_4Nb_{1.97}W_{4.03}O_{19}$ for the $(W/Nb)_6O_{19}$ -units in CsNa{Nb₄W₂}, Cs{Nb₂W₄}, respectively. In CsNa{Nb₂W₄}, the (W/Nb)₆O₁₉-unit has C₃-symmetry with two symmetrically independent positions. Refinement shows that W and Nb atoms share both these positions with different ratios -0.756/0.244 and 0.532/0.468, providing a formula of $Cs_3NaNb_{2.14}W_{3.86}O_{19}$ for $CsNa{Nb_2W_4}$. Two Cs atoms in $Cs{Nb_2W_4}$ and two Cs and one Na atoms in $CsNa{Nb_4W_2}$ are located in a general positions. The Na atom in $CsNa{Nb_2W_4}$ is located on a three-fold axis and the Cs atom is in a general position. In all structures Cs and Na atoms are joined by solvent water molecules. The $\mathrm{CsNa}\{\mathrm{Nb}_2\mathrm{W}_4\}$ structure is a racemic twin consisting of two blocks in the ratio 0.65/0.35. All calculations were performed by the Bruker SHELXTL (v. 6.10)²³⁵ and SHELXL-2013 packages.²³⁶

A.1.3 Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDX)

Micrographs and spectra of the crystalline materials were obtained from a Quanta 600F instrument (FEI).

A.1.4 Electrospray Ionization Mass Spectroscopy (ESI-MS)

Mass spectra were obtained from an Agilent 6230 ESI-MS system comprised of a Timeof-Flight (TOF) mass spectrometer coupled to an electrospray ioniser. 100 µL volumes of compound solutions (0.1 mM in $\rm H_2O$) were first mixed with a water mobile phase and then infused into the ESIMS system at a flow rate of 0.5 mL min⁻¹ using an Agilent 1260 Infinity quaternary pump. The solutions were nebulized with the aid of heated N₂ (325 °C) flowing at 8 L min⁻¹ and a pressure of 35 psi (241 kPa). The voltages of the capillary, skimmer and RT octopole were set at 3500, 65 and 750 V respectively, while the voltage of the fragmentor was set at 100 V.

A.1.5 Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded in attenuated reflectance mode (ATR) using a NicoletTM iS^{TM} 10 spectrometer (Thermo Scientific).

A.1.6 Ultraviolet-Visible Spectroscopy (UV-Vis)

Electronic absorption spectra were recorded on an EvolutionTM 220 spectrophotometer (Thermo Scientific).

A.1.7 Thermogravimetric Analysis (TGA)

Crystalline samples (10-20 mg) were placed in alumina crucibles and the corresponding thermograms were recorded under air flow (100 mL min⁻¹ on a SDT Q600 instrument (TA).

A.1.8 pH measurements

The pH of the reaction mixtures was measured using an OrionTM VERSA STARTM pH/ISE Benchtop Multiparameter Meter. The instrument was calibrated using standard solutions before each round of measurements.

A.2 Experimental Details

A.2.1 Crystallographic Data

\mathcal{O}	114[1192114]		
	$CsNa{Nb_4W_2}$	$Cs{Nb_2W_4}$	$CsNa{Nb_2W_4}$
Emperical Formula	$Cs_4H_{24}Na_2O_3Nb_{3.89}W_{2.11}$	$Cs_4H_8O_{31}Nb_{1.97}W_{4.03}$	$Cs_3H_{20}NaO_3Nb_{2.14}W_{3.86}$
$FW g mol^{-1}$	1846.70	1832.11	1814.67
T (K)	150(2)	173(2)	173(2)
Crystal System	Monoclinic	Monoclinic	Trigonal
Space Group	$P2_1/n$	$P2_1/n$	R3
a (Å)	9.5760(3)	9.6119(8)	11.6452(15)
b (Å)	13.5844(4)	11.8087(10)	11.6472(15)
c (Å)	12.3503(4)	11.2532(9)	11.2532(9)
α (°)	90	90	90
β (°)	90.0790(12)	90.929(18)	90
γ (°)	90	90	120
$V (Å^3)$	1606.58(9)	1277.12(18)	2245.9(6)
Z	2	2	3
$\mu \ (\mathrm{mm}^{-1})$	13.446	24.655	19.280
F(000)	1659	1582	2404
Crystal Size (mm^3)	$0.16 \times 0.14 \times 0.08$	$0.16 \times 0.14 \times 0.08$	$0.09 \times 0.07 \times 0.04$
Reflections collected	45150	42881	12477
Unique / $[R(int)]$	$9955 \ [0.0299]$	$9627 \ [0.0744]$	$2686 \ [0.0566]$
GOF (F^2)	1.260	1.016	1.008
Final R indices	R1 = 0.0310	R1 = 0.0468	R1 = 0.0325
$(I > 2\sigma(I))$	wR2 = 0.0917	wR2 = 0.869	wR2 = 0.0520
R indices (all data)	R1 = 0.0310	R1 = 0.0468	R1 = 0.0496
	wR2 = 0.0921	wR2 = 0.0869	wR2 = 0.563
Peak/hole diff. $(e/Å^3)$	2.644/-1.995	5.933/-4.251	1.211/-1.167

Table A.1: Summary of the crystallographic refinement data for $CsNa\{Nb_4W_2\}$, $Cs\{Nb_2W_4\}$, and $CsNa\{Nb_2W_4\}$



Figure A.1: Thermogravimetric analysis for $\mathrm{CsNa}\{\mathrm{Nb}_4\mathrm{W}_2\}$ under air.



Figure A.2: Thermogravimetric analysis for $\rm Cs\{Nb_2W_4\}$ under air.



Figure A.3: Thermogravimetric analysis for $\mathrm{Cs}\{\mathrm{Nb}_2\mathrm{W}_4\}$ under air.



Figure A.4: Full FTIR spectra of the studied species. The POM fingerprint region is located at $<1000~{\rm cm^{-1}}.$

A.3 Group Theory Analysis

An irreducible representation of stretching modes for the terminal-oxo bonds in the $\{Nb_4W_2\}$ ion is obtained. The cis- (C_{2v}) and trans- (D_{4h}) isomers are considered. The irreducible representations for $\{Nb_2W_4\}$ are identical, albeit with tungsten and niobium interchanged.

Table A.2: Solving the irreducible representation of cis- and trans- isomers (C_{2v} and D_{4h} considering symmetry operations on terminal-oxo bonds.

C_{2v}	Е	$2C_2$	$\sigma_{\rm v}({\rm xz})$	$\sigma_{\rm v}({\rm yz})$
$W-O_t$	2	0	2	0
$\mathrm{Nb}\text{-}\mathrm{O}_{\mathrm{t}}$	4	0	2	2

 $\begin{array}{l} \Gamma_{W=O} \colon A_1 + B_1 \ (both \ IR \ active) \\ \Gamma_{Nb=O} \colon 2A_1 + B_1 + B_2 \ (all \ IR \ active) \\ \mathbf{Six} \ IR \ active \ modes. \end{array}$

D_{4h}	Е	$2C_4$	C_2	$2C_2$	$2C_2$ "	i	$2S_4$	$\sigma_{ m h}$	$2\sigma_{\rm v}$	$2\sigma_{\rm d}$
$W-O_t$	2	2	2	0	0	0	0	0	2	2
$\mathrm{Nb-O_{t}}$	4	0	0	2	0	0	0	4	2	0

 $\begin{array}{l} \Gamma_{W=O} \colon A_{1g} \mbox{(inactive)} + A_{2u} \mbox{(IR active)} \\ \Gamma_{Nb=O} \colon A_{1g} \mbox{(inactive)} + B_{1g} \mbox{(inactive)} + E_u \mbox{(IR active)} \\ {\bf Two \mbox{ IR-active modes.}} \end{array}$

Due to the existence of more than two terminal oxo stretching peaks in the 850-1000 cm^{-1} region of each IR spectrum (Figure 3.2, A.4), the D_{4h} trans-isomer is ruled out.

A.4 Crystallographic Cesium Environments



Figure A.5: Representations of the crystal structures of (left) $CsNa\{Nb_4W_2\}$, (middle) $Cs\{Nb_2W_4\}$, and (right) $CsNa\{Nb_4W_2\}$, highlighting the coordination environment of crystal structures. Solvent water molecules act as bridges between Cs^+ (pink) and Na^+ (tan) counter-cations. Na⁺ ions are coordinated solely by waters of hydration. Unit cell edges are shown in green.

A.5 SEM/EDX Micrographs and Spectra



Figure A.6: SEM micrographs and EDX spectrum for CsNa{Nb}_4W_2\}. Crystals are well-formed and block-like.



Figure A.7: SEM micrographs and EDX spectrum for $CsNa{Nb_2W_4}$, indicating the existence of sodium in the lattice.



Figure A.8: SEM micrographs and EDX spectrum for $\rm Cs\{Nb_2W_4\}$, indicating the lack of Na⁺ in the lattice. Crystals are hexagonal in shape.

Appendix B: Supporting Information for Chapter 4

B.1 Drop Solution Enthalpies

Drop solution enthalpies were measured in a custom-made isoperibol Tian-Calvet twin microcalorimeter.^{237,238} Pellets of about 5 mg were loosely pressed, weighed, and dropped from room temperature into $3Na_2O\cdot4MoO_3$ molten solvent at 702 °C. The calorimeter assembly was washed with oxygen at 43 mL min^{-1} . Oxygen was bubbled through the solvent at 4.5 mL min^{-1} to aid dissolution, evolve water vapor, and to maintain oxidizing conditions. The calorimeter was calibrated against the heat content of 5 mg pellets of high-purity Al_2O_3 (99.997%, Alfa Aesar) dropped into an empty crucible.

Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
3.961	2329.54
4.997	2337.22
4.397	2384.57
4.677	2345.47
4.753	2362.28
4.857	2401.55
4.181	2380.88
4.073	2379.58
Average:	2365.13 ± 18.13
-23.5 $\mathrm{H_2O}$	-1621.50
Final:	$\textbf{743.63} \pm \textbf{18.13}$

Table B.1: Drop solution enthalpy of $Li\{Nb_6\}$

Final:	592.30 ± 11.52
-16.0 $\mathrm{H_2O}$	-1104.00
Average	1696.30 ± 11.52
6.703	1688.89
8.214	1692.57
4.923	1687.22
6.918	1669.54
7.137	1701.78
6.863	1726.15
5.340	1701.07
4.992	1703.17
Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$

Table B.2: Drop solution enthalpy of $K\{Nb_6\}$

Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
5.745	1616.96
6.927	1618.01
5.718	1606.60
5.366	1597.92
5.908	1594.62
5.234	1606.34
5.563	1580.90
5.344	1580.31
Average:	1600.21 ± 10.28
-14.1 $\mathrm{H_2O}$	-927.90
Final:	$\textbf{627.31} \pm \textbf{10.28}$

Table B.3: Drop solution enthalpy of $Rb\{Nb_6\}$

$\begin{array}{ccccc} 5.316 & 1693.16 \\ 6.698 & 1707.05 \\ 5.132 & 1700.20 \\ 5.039 & 1703.34 \\ 6.210 & 1700.20 \\ \hline \text{Average:} & 1700.43 \pm 3.93 \\ -14.8 \ \text{H}_2\text{O} & -1021.20 \\ \end{array}$
$\begin{array}{cccccc} 5.316 & 1693.16 \\ 6.698 & 1707.05 \\ 5.132 & 1700.20 \\ 5.039 & 1703.34 \\ 6.210 & 1700.20 \end{array}$
$\begin{array}{ccccc} 5.316 & 1693.16 \\ 6.698 & 1707.05 \\ 5.132 & 1700.20 \\ 5.039 & 1703.34 \end{array}$
$\begin{array}{cccc} 5.316 & 1693.16 \\ 6.698 & 1707.05 \\ 5.132 & 1700.20 \end{array}$
$\begin{array}{cccc} 5.316 & 1693.16 \\ 6.698 & 1707.05 \end{array}$
5.316 1693.16
8.326 1699.83
4.847 1700.79
5.304 1698.86
Mass (mg) $\Delta H_{ds} (\text{kJ}\text{mol}^{-1})$

Table B.4: Drop solution enthalpy of Cs{Nb₆}

B.2 Thermochemical Cycles

Lithium Hexaniobate

The formation enthalpy of $Li_8Nb_6O_{19}$ from constituent binary oxides is -137.2 kJ/mol Nb. The correction of 69 kJ/mol H₂O for lattice water has been applied as seen in Table B.1.

$$\frac{1}{6} \{ \text{Li}_8 \text{Nb}_6 \text{O}_{19} \} (\text{xl}, 25^{\circ}\text{C}) \rightarrow \frac{2}{3} \text{Li}_2 \text{O}(\text{soln}, 702^{\circ}\text{C}) + \frac{1}{2} \text{Nb}_2 \text{O}_5(\text{soln}, 702^{\circ}\text{C}) \qquad (B.1)$$
$$\Delta H_1 = \Delta H_{ds} = 123.94 \pm 3.02 \text{kJ/mol Nb}$$

$$Nb_2O_5(s, 25^{\circ}C) \rightarrow Nb_2O_5(soln, 702^{\circ}C)$$
(B.2)
$$\Delta H_2 = \Delta H_{ds}(Nb_2O_5) = 93.97 \pm 1.60 \text{kJ/mol Nb}$$

$$\operatorname{Li}_{2}\mathcal{O}(\mathrm{xl}, 25^{\circ}\mathrm{C}) \to \operatorname{Li}_{2}\mathcal{O}(\mathrm{soln}, 702^{\circ}\mathrm{C})$$
(B.3)
$$\Delta H_{3} = \Delta H_{ds}(\mathrm{Li}_{2}\mathrm{O}) = -90.3 \pm 2.5 \mathrm{kJ/mol\,Nb}$$

$$\frac{2}{3}\text{Li}_{2}\text{O} + \frac{1}{2}\text{Nb}_{2}\text{O}_{5} (\text{xl}, 25^{\circ}\text{C}) \rightarrow \frac{1}{6}\{\text{Li}_{8}\text{Nb}_{6}\text{O}_{19}\} (\text{xl}, 25^{\circ}\text{C})$$
(B.4)

$$\Delta H_4 = \Delta H_f^{ox}(\text{Li}_8\text{Nb}_6\text{O}_{19}) = -\Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_3 = -137.2 \pm 4.8\text{kJ/mol Nb}$$

Potassium Hexaniobate

The formation enthalpy of $K_8Nb_6O_{19}$ from constituent binary oxides is -262.7 kJ/mol Nb. The correction of 69 kJ/mol H₂O for lattice water has been applied as seen in Table B.2.

$$\frac{1}{6} \{ K_8 Nb_6 O_{19} \} (xl, 25^{\circ}C) \rightarrow \frac{2}{3} K_2 O(soln, 702^{\circ}C) + \frac{1}{2} Nb_2 O_5(soln, 702^{\circ}C)$$
(B.5)
$$\Delta H_5 = \Delta H_{ds} = 98.72 \pm 1.22 kJ/mol Nb$$

$$K_2 O(xl, 25^{\circ}C) \rightarrow K_2 O(soln, 702^{\circ}C)$$
(B.6)
$$\Delta H_6 = \Delta H_{ds}(K_2 O) = -318.0 \pm 3.1 \text{kJ/mol Nb}$$

$$\frac{2}{3}K_2O + \frac{1}{2}Nb_2O_5 (xl, 25^{\circ}C) \rightarrow \frac{1}{6}\{K_8Nb_6O_{19}\} (xl, 25^{\circ}C)$$
(B.7)

$$\Delta H_7 = \Delta H_f^{ox}(\mathbf{K}_8 Nb_6 O_{19}) = -\Delta H_5 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_6 = -262.7 \pm 5.0 \text{kJ/mol Nb}$$

Rubidium Hexaniobate

The formation enthalpy of $\rm Rb_8Nb_6O_{19}$ from binary oxides is -279.3 kJ/molNb. The correction of 69 kJ/molH₂O for lattice water has been applied as seen in Table B.3.

$$\frac{1}{6} \{ \text{Rb}_8 \text{Nb}_6 \text{O}_{19} \} (\text{xl}, 25^{\circ}\text{C}) \rightarrow \frac{2}{3} \text{Rb}_2 \text{O}(\text{soln}, 702^{\circ}\text{C}) + \frac{1}{2} \text{Nb}_2 \text{O}_5(\text{soln}, 702^{\circ}\text{C}) \qquad (B.8)$$
$$\Delta H_8 = \Delta H_{ds} = 104.55 \pm 1.71 \text{kJ/mol Nb}$$

$$Rb_2O(xl, 25^{\circ}C) \rightarrow Rb_2O(soln, 702^{\circ}C)$$
(B.9)
$$\Delta H_9 = \Delta H_{ds}(Rb_2O) = -332.6 \pm 2.2 \text{kJ/mol Nb}$$

$$\frac{2}{3}\text{Rb}_{2}\text{O} + \frac{1}{2}\text{Nb}_{2}\text{O}_{5} \text{ (xl, 25^{\circ}\text{C})} \rightarrow \frac{1}{6}\{\text{Rb}_{8}\text{Nb}_{6}\text{O}_{19}\} \text{ (xl, 25^{\circ}\text{C})}$$
(B.10)

$$\Delta H_{10} = \Delta H_f^{ox}(\text{Rb}_8\text{Nb}_6\text{O}_{19}) = -\Delta H_8 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_9 = -279.3 \pm 5.9\text{kJ/mol Nb}$$

Cesium Hexaniobate

The formation enthalpy of $Cs_8Nb_6O_{19}$ from binary oxides is -298.7 kJ/molNb. The correction of 69 kJ/molH₂O for lattice water has been applied as seen in Table B.4.

$$\frac{1}{6} \{ Cs_8 Nb_6 O_{19} \} (xl, 25^{\circ}C) \rightarrow \frac{2}{3} Cs_2 O(soln, 702^{\circ}C) + \frac{1}{2} Nb_2 O_5(soln, 702^{\circ}C) \qquad (B.11)$$
$$\Delta H_{11} = \Delta H_{ds} = 113.21 \pm 0.66 \text{kJ/mol Nb}$$

$$Cs_2O(xl, 25^{\circ}C) \rightarrow Cs_2O(soln, 702^{\circ}C)$$
(B.12)
$$\Delta H_{12} = \Delta H_{ds}(Cs_2O) = -348.9 \pm 1.7 \text{kJ/mol Nb}$$

$$\frac{2}{3}Cs_2O + \frac{1}{2}Nb_2O_5 (xl, 25^{\circ}C) \to \frac{1}{6}\{Cs_8Nb_6O_{19}\} (xl, 25^{\circ}C)$$
(B.13)

$$\Delta H_{13} = \Delta H_f^{ox}(\mathrm{Cs}_8\mathrm{Nb}_6\mathrm{O}_{19}) = -\Delta H_{11} + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_{12} = -298.7 \pm 4.2\mathrm{kJ/mol\,Nb}$$

Where ΔH_{ds} are drop solution enthalpies under oxygen bubbling.

B.3 Room Temperature Dissolution Enthalpies

 ΔH_{dis} was measured using a CSC 4400 isothermal microcalorimeter operated at 25 °C. About 5 mg of each sample was hand pressed into a pellet and dropped one at a time into 25.0 g of H₂O. Each experiment was repeated in 1M AOH (A = K, Rb, Cs, TMA) for the respective clusters.

Dissolution enthalpies of hydrated hexaniobate clusters in water

$$\begin{split} \mathrm{Li}_8\mathrm{Nb}_6\mathrm{O}_{19} \cdot 23.5\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Li}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (23.5\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{K}_8\mathrm{Nb}_6\mathrm{O}_{19} \cdot 16.0\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{K}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (16.0\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{Rb}_8\mathrm{Nb}_6\mathrm{O}_{19} \cdot 14.1\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Rb}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (14.1\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{Cs}_8\mathrm{Nb}_6\mathrm{O}_{19} \cdot 14.8\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Cs}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (14.8\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ (\mathrm{TMA})_5\mathrm{H}_3\mathrm{Nb}_6\mathrm{O}_{19} \cdot 20\mathrm{H}_2\mathrm{O} &\longrightarrow 5\,\mathrm{TMA}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + (3-\mathrm{x})\mathrm{H}_3\mathrm{O}^+ + (17+\mathrm{x})\mathrm{H}_2\mathrm{O} \end{split}$$

Dissolution enthalpies of anhydrous hexaniobate clusters in water

$$\begin{split} \mathrm{Li}_8\mathrm{Nb}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Li}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ \mathrm{K}_8\mathrm{Nb}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{K}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ \mathrm{Rb}_8\mathrm{Nb}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Rb}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ \mathrm{Cs}_8\mathrm{Nb}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Cs}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ (\mathrm{TMA})_5\mathrm{H}_3\mathrm{Nb}_6\mathrm{O}_{19} + 3\mathrm{OH}^- &\longrightarrow 5\,\mathrm{TMA}^+ + [\mathrm{H}_{3-\mathrm{x}}\mathrm{Nb}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xH}_2\mathrm{O} + (3-\mathrm{x})\mathrm{OH}^- \end{split}$$

Enthalpies of anhydrous clusters were found by subtracting the enthalpy of dissolu-

tion of lattice water $(0.4 \text{ kJ mol}^{-1})^{239}$ and then adjusting for the relative molar weights of the hydrated and anhydrous clusters, namely:

$$\Delta H_{dis,anhydrous} = (\Delta H_{dis,hydrated} - (0.4 \,\mathrm{kJ \,mol^{-1}})(n_{\mathrm{H_2O}})) \frac{\mathrm{MW}(\mathrm{Anhydrous \, Cluster})}{\mathrm{MW}(\mathrm{Hydrated \, Cluster})}$$
(B.14)

The calorimeter was calibrated by dissolving 15 mg pellets of KCl in water with stirring at 25 °C. Hydrous and anhydrous cluster dissolution enthalpy values in water are reported in Tables S5-S9.

B.3.1 Tables of Aqueous Dissolution Enthalpies

Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
100.12	59.12
95.53	55.97
93.49	54.58
83.98	48.07
81.83	47.02
100.81	59.58
96.32	56.51
91.71	53.36
85.74	49.27
81.28	46.22
	Dissolution Enthalpy $(\Delta H_{dis} / \text{kJ mol}^{-1})$ 100.12 95.53 93.49 83.98 81.83 100.81 96.32 91.71 85.74 81.28

Table B.5: Lithium Hexaniobate Dissolution Enthalpies in Water

Table B.6: Potassium Hexaniobate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
Run #1		
10.40	125.61	91.47
28.06	119.77	86.78
43.67	115.34	83.22
65.46	111.28	79.96
87.03	108.11	77.42
106.97	106.42	76.06
Run #2		
3.90	127.91	96.315
20.15	119.57	89.62
41.92	117.67	88.09
59.68	111.06	82.79
75.02	106.82	79.38

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
Run #1		
8.05	111.89	90.04
34.08	105.07	84.19
65.08	101.49	81.11
89.90	101.75	81.33
120.13	94.32	74.95
159.55	91.41	72.45
Run $#2$		
12.50	112.57	91.19
43.61	108.54	87.72
76.37	101.64	81.79
105.65	95.08	76.15
135.25	93.17	74.51

Table B.7: Rubidium Hexaniobate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Annydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$
Run #1		
3.99	118.38	98.07
12.27	114.30	94.48
24.09	106.55	87.67
37.78	104.16	85.57
47.58	97.25	79.51
55.81	93.22	75.96
64.28	87.48	70.92
87.62	87.03	69.19
101.64	80.36	63.33
113.91	75.75	59.28
135.96	75.14	58.75
Run $#2$		
7.25	117.19	97.03
25.52	104.55	85.92
58.66	90.88	73.91
76.24	82.71	66.73
134.52	74.00	59.09

 Table B.9: TMA Hexaniobate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$\Delta H_{dis} / \text{kJ} \text{mol}^{-1}$	ΔH_{dis} / kJ mol ⁻¹
Run #1		
4.88	-47.16	-44.52
33.72	-44.74	-42.65
61.103	-43.68	-41.82
82.60	-43.04	-41.33
106.62	-41.15	-39.86
126.62	-40.17	-39.11
Run #2		
7.93	-46.68	-44.15
38.11	-43.72	-41.85
81.43	-42.37	-40.91

B.3.2 Tables of 1M Parent Hydroxide Dissolution Enthalpies

Each experiment was repeated in 1M AOH, (A = K, Rb, Cs, TMA) for the respective clusters. Enthalpies are reported in Tables B.10-13. Lithium was omitted due to insolubility.

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$
Run #1		
9.31	10.29	-1.14
36.41	8.95	-2.21
62.19	12.78	0.86
80.68	11.63	-0.06
98.17	13.16	1.16
Run #2		
14.09	9.84	-1.15
60.42	9.31	-1.92

 Table B.10: Potassium Hexaniobate Dissolution Enthalpies in 1M KOH

 Concentration
 Dissolution Enthalpy
 Anhydrous Dissolution Enthalpy

Table B.11: Rubidium Hexaniobate Dissolution Enthalpies in 1M RbOH

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$	$(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$
Run #1		
15.27	56.97	43.38
49.98	57.79	44.09
84.87	57.77	44.07
122.68	53.41	40.32
Run #2		
15.19	55.43	49.83
59.00	53.67	48.07
131.79	59.10	50.62

Concentration Dissolution Enthalpy Anhydrous Dissolution Enthalpy $(M \times 10^5)$ $(\Delta H_{dis} / \text{kJ} \text{mol}^{-1})$ $(\Delta H_{dis} / \text{kJ mol}^{-1})$ Run #1 5.7335.62 25.3726.0837.3726.9057.4124.0634.1373.4532.2822.4396.2430.3520.74Run #2 12.6634.7124.5748.3433.9023.86106.0531.9422.14

Table B.12: Cesium Hexaniobate Dissolution Enthalpies in 1M CsOH

Table B.13: TMA Hexaniobate Dissolution Enthalpies in 1M TMAOH

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta H_{dis} \ / \ \mathrm{kJ \ mol}^{-1}$
Run #1		
8.52	-196.79	-160.31
36.08	-191.05	-155.93
69.96	-188.11	-153.66
96.52	-186.23	-152.20
118.58	-182.55	-149.35
Run $#2$		
40.97	-191.50	-156.28
82.99	-185.48	-151.62
137.76	-180.05	-147.42





Figure B.1: Enthalpies of dissolution for hydrated alkali metal salts of hexaniobate in water and in 1M solutions of their parent hydroxide, uncorrected for lattice water.



Figure B.2: Enthalpies of dissolution for hydrated TMA hexaniobate in water and in 1M solutions of their parent hydroxide, uncorrected for lattice water.

B.4 Supplementary Characterization

B.4.1 Synthesis

Potassium Hexaniobate $(K_8Nb_6O_{19} \cdot 16.0H_2O)$

 $2.13 \text{ g of Nb}_2\text{O}_5 \cdot \text{xH}_2\text{O}$ were slowly added to 10 mL of 3M KOH at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After the all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula: $K_8Nb_6O_{35}H_{32}$. $M_W = 1461.86 \text{ g mol}^{-1}$. Atomic ratios, calculated (found): K/Nb: 1.33 (1.39). Water content (%), crystallographic (TGA 22-600°C in air): 16.0 (19.76).⁶⁹

Rubidium Hexaniobate ($Rb_8Nb_6O_{19} \cdot 14.1H_2O$)

2.10 g of $Nb_2O_5 \cdot xH_2O$ were slowly added to 5.0 g of 50 wt% RbOH solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula: $\text{Rb}_8\text{Nb}_6\text{O}_{33.1}\text{H}_{28.2}$. $M_W = 1799.18 \,\text{g mol}^{-1}$. Atomic ratios, calculated (found): Rb/Nb: 1.33 (1.33). Water content (%), crystallographic (TGA 22-600°C in air): 14.1 (14.13).⁶⁹
Cesium Hexaniobate $(Cs_8Nb_6O_{19} \cdot 14.8H_2O)$

3.42 g of $\text{Nb}_2\text{O}_5 \cdot \text{xH}_2\text{O}$ were slowly added to 10.0 g of 50 wt% CsOH solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula: $Cs_8Nb_6O_{33.8}H_{29.6}$. $M_W = 2191.29 \text{ g mol}^{-1}$. Atomic ratios, calculated (found): Cs/Nb: 1.33 (1.34). Water content (%), crystallographic (TGA 22-600°C in air): 14.8 (12.19).⁶⁹

Lithium Hexaniobate $(Li_8Nb_6O_{19} \cdot 23.5H_2O)$

1.00 g of $\text{Cs}_8\text{Nb}_6\text{O}_{19} \cdot 14 \text{ H}_2\text{O}$ was dissolved in 1.0 mL of H_2O at room temperature. This solution was then added dropwise to 25.0 mL of 1M LiOH| solution and stirred. A precipitate began to form almost immediately. The solution was further stirred for 30 minutes to allow for more precipitate to form. The solution was then filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula: $\text{Li}_8\text{Nb}_6\text{O}_{42.5}\text{H}_{47}$. $M_W = 1340.32 \,\text{g mol}^{-1}$. Water content (%), crystallographic (TGA 22-600°C in air): 23.5 (31.59).⁶⁹

Tetramethylammonium Hexaniobate ([(CH_3)_4N]_5H_3Nb_6O_{19}\cdot 20H_2O)

2.0 g of $\text{Nb}_2\text{O}_5 \cdot \text{xH}_2\text{O}$ were slowly added to 10.0 mL of 25 wt% tetramethylammonium hydroxide (TMAOH) solution at 90 °C and stirred such that the solution was allowed

to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered. 40 mL of 2-propanol was added to the microfiltered solution. The resultant suspension was centrifuged, the supernatant was removed, and 40 mL of 2-propanol was again added. The solution was then filtered under vacuum, and dried at 60 °C under vacuum.

Full formula: $C_{20}N_5Nb_6O_{39}H_{100}$. $M_W = 1595.48 \text{ g mol}^{-1}$. Water content, 20.0 (from crystal structure).⁶⁸



Figure B.3: Thermogravimetric Analysis curve for ${\rm LiNb}_6$



Figure B.4: Thermogravimetric Analysis curve for ${\rm K_8Nb_6O_{19}}.$



Figure B.5: Thermogravimetric Analysis curve for ${\rm RbNb}_6$



Figure B.6: Thermogravimetric Analysis curve for $\rm Cs_8Nb_6O_{19}$

Thermogravimetric analysis could not be performed for $\rm TMANb_6,$ due to $\rm TMA^+$ being unstable at 600 $^{\circ}\rm C$

B.4.3 Elemental Analysis

Elemental analysis was not performed on tetramethylammonium hexaniobate, due to the lack of reliability in measuring the lighter elements in the TMA⁺ counter-cations.



Figure B.7: Sample Elemental Analysis spectrum for $Li\{Nb_6\}$. Due to Li being too small for reliable measurement, it is instead demonstrated that the amount of remaining Cs from the starting material is indistinguishable from the background (P/B = 0.54).



1.84 2.14

Bkgd Inte. Inte. Error

4.72 4.86

0.7230

1.0000

P/B

43.97 32.26

ΚK

NbL ΚK

36.62

Total 100.00 100.00 Element Net Inte.

207.62 156.69

Figure B.8: Sample Elemental Analysis spectrum for $K\{Nb_6\}.$



Figure B.9: Sample Elemental Analysis spectrum for $Rb\{Nb_6\}$.

1.80

2.55

9.21

RbL

NbL

156.26

16.96



Figure B.10: Sample Elemental Analysis spectrum for $Cs\{Nb_6\}$.

Appendix C: Supporting Information for Chapter 5

C.1 Drop Solution Enthalpies

 ΔH_{ds} was measured in a custom-made isoperibol Tian-Calvet twin microcalorimeter. Pellets of about 5 mg were loosely pressed, weighed, and dropped from room temperature into $3Na_2O.4MoO_3$ molten solvent at 702 °C. The calorimeter assembly was washed with oxygen at 43 mL min⁻¹. Oxygen was bubbled through the solvent at 4.5 mL min⁻¹ to aid dissolution, evolve water vapor, and to maintain oxidizing conditions. The calorimeter was calibrated against the heat content of 5 mg pellets of high-purity Al₂O₃ (99.997%, Alfa Aesar) dropped into an empty crucible.

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Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
4.73	1860.21
3.85	1853.85
3.75	1839.61
3.47	1856.16
3.00	1855.44
3.69	1859.97
2.31	1862.38
3.22	1856.14
Average:	1855.47 ± 4.97
$-18 \text{ H}_2\text{O}$	-1242.00
Final:	613.47 ± 4.97

Table C.1: Drop solution enthalpy of Li_8 Ta₆O₁₉

	10 0 10
Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
4.65	1586.34
4.91	1672.26
5.41	1603.25
5.13	1586.34
7.87	1647.62
4.29	1635.12
5.39	1665.30
6.97	1627.86
Average	1628.01 ± 23.71
-16 H_2O	-1104.00
Final:	$\textbf{514.01} \pm \textbf{23.71}$
C.3: Drop solu	tion enthalpy of $Rb_8Ta_6O_{19}$
Mass (mg)	ΔH_{d_0} (kJ mol ⁻¹)

Table C.2: Drop solution enthalpy of K_8 Ta₆O₁₉

Table C.	3: Drop solut	ion enthalpy of Rb ₈ 7
-	Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
-	3.92	1406.56
	5.74	1403.56
	4.31	1388.76
	5.38	1389.67
	5.33	1379.51
	7.61	1427.34
	6.88	1401.91
	4.40	1401.85
-	Average:	1399.89 ± 10.22
	-14 H_2O	-966.00
-	Final:	$\textbf{433.89} \pm \textbf{10.22}$

Table C	2.4:	Drop	solutio	on entha	alpy of	f Cs_8	Ta ₆ C	$)_{19}$
					-	4		

-	· I. · · · ·	
	Mass (mg)	$\Delta H_{ds} \; (\mathrm{kJ} \mathrm{mol}^{-1})$
	4.95	1415.26
	5.69	1421.01
	4.58	1409.12
	4.35	1427.62
	5.70	1426.25
	7.83	1413.61
	4.20	1423.81
	4.02	1422.82
	Average:	1419.94 ± 4.65
	$-14~\mathrm{H_2O}$	-966.00
	Final:	$\textbf{453.94} \pm \textbf{4.65}$

C.2 Thermochemical Cycles

Lithium Hexatantalate

The formation enthalpy of $Li_8Ta_6O_{19}$ from constituent binary oxides is -117.2 kJ/mol Ta. The correction of 69 kJ/mol H₂O for lattice water has been applied as seen in Table C.1.

$$\frac{1}{6} \{ \text{Li}_8 \text{Ta}_6 \text{O}_{19} \} (\text{xl}, 25^{\circ}\text{C}) \rightarrow \frac{2}{3} \text{Li}_2 \text{O}(\text{soln}, 702^{\circ}\text{C}) + \frac{1}{2} \text{Ta}_2 \text{O}_5(\text{soln}, 702^{\circ}\text{C})$$
(C.1)

$$\Delta H_1 = \Delta H_{ds} = 102.25 \pm 0.83 \text{kJ/mol Ta}$$

$$Ta_2O_5(s, 25^{\circ}C) \to Ta_2O_5(soln, 702^{\circ}C)^{240}$$
 (C.2)

$$\Delta H_2 = \Delta H_{ds}(\mathrm{Ta}_2\mathrm{O}_5) = 90.41 \pm 2.50 \mathrm{kJ/mol\,Ta}$$

$$\text{Li}_2\text{O}(\text{xl}, 25^\circ\text{C}) \to \text{Li}_2\text{O}(\text{soln}, 702^\circ\text{C})$$
 (C.3)

$$\Delta H_3 = \Delta H_{ds}(\text{Li}_2\text{O}) = -90.3 \pm 2.5 \text{kJ/mol Ta}$$

$$\frac{2}{3}\text{Li}_{2}\text{O} + \frac{1}{2}\text{Ta}_{2}\text{O}_{5} (\text{xl}, 25^{\circ}\text{C}) \rightarrow \frac{1}{6}\{\text{Li}_{8}\text{Nb}_{6}\text{O}_{19}\} (\text{xl}, 25^{\circ}\text{C})$$
(C.4)

$$\Delta H_4 = \Delta H_f^{ox}(\text{Li}_8\text{Ta}_6\text{O}_{19}) = -\Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_3 = -117.2 \pm 2.1\text{kJ/mol Ta}$$

Potassium Hexatantalate

The formation enthalpy of $K_8Ta_6O_{19}$ from constituent binary oxides is -253.7 kJ/mol Ta. The correction of 69 kJ/mol H₂O for lattice water has been applied as seen in Table C.2.

$$\frac{1}{6} \{ K_8 Ta_6 O_{19} \} (xl, 25^{\circ}C) \rightarrow \frac{2}{3} K_2 O(soln, 702^{\circ}C) + \frac{1}{2} Ta_2 O_5(soln, 702^{\circ}C)$$
(C.5)

$$\Delta H_5 = \Delta H_{ds} = 72.32 \pm 3.95 \mathrm{kJ/mol\,Ta}$$

$$K_2O(xl, 25^{\circ}C) \rightarrow K_2O(soln, 702^{\circ}C)$$
 (C.6)

$$\Delta H_6 = \Delta H_{ds}(\mathrm{K_2O}) = -318.0 \pm 3.1 \mathrm{kJ/mol\,Ta}$$

$$\frac{2}{3}K_{2}O + \frac{1}{2}Ta_{2}O_{5} (xl, 25^{\circ}C) \rightarrow \frac{1}{6}\{K_{8}Ta_{6}O_{19}\} (xl, 25^{\circ}C)$$
(C.7)

$$\Delta H_7 = \Delta H_f^{ox}(\mathbf{K}_8 \mathrm{Ta}_6 \mathbf{O}_{19}) = -\Delta H_5 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_6 = -253.7 \pm 4.4 \mathrm{kJ/mol} \, \mathrm{Ta}_{19} + \frac{1}{2}\Delta H_{19} + \frac{1}{2}\Delta H_{$$

Rubidium Hexatantalate

The formation enthalpy of $Rb_8Ta_6O_{19}$ from constituent binary oxides is -248.9 kJ/mol Ta. The correction of 69 kJ/mol H₂O for lattice water has been applied as seen in Table C.3.

$$\frac{1}{6} \{ Rb_8 Ta_6 O_{19} \} (xl, 25^{\circ}C) \rightarrow \frac{2}{3} Rb_2 O(soln, 702^{\circ}C) + \frac{1}{2} Ta_2 O_5(soln, 702^{\circ}C)$$
(C.8)

$$\Delta H_8 = \Delta H_{ds} = 85.67 \pm 1.70 \text{kJ/mol Ta}$$

$$Rb_2O(xl, 25^{\circ}C) \rightarrow Rb_2O(soln, 702^{\circ}C)$$
 (C.9)

$$\Delta H_9 = \Delta H_{ds}(\text{Rb}_2\text{O}) = -332.6 \pm 2.2 \text{kJ/mol Ta}$$

$$\frac{2}{3}\text{Rb}_{2}\text{O} + \frac{1}{2}\text{Ta}_{2}\text{O}_{5} (\text{xl}, 25^{\circ}\text{C}) \rightarrow \frac{1}{6}\{\text{Rb}_{8}\text{Ta}_{6}\text{O}_{19}\} (\text{xl}, 25^{\circ}\text{C})$$
(C.10)

$$\Delta H_{10} = \Delta H_f^{ox} (\text{Rb}_8 \text{Ta}_6 \text{O}_{19}) = -\Delta H_8 + \frac{1}{2} \Delta H_2 + \frac{2}{3} \Delta H_9 = -248.9 \pm 2.7 \text{kJ/mol Ta}$$

Cesium Hexatantalate

The formation enthalpy of $Cs_8Ta_6O_{19}$ from constituent binary oxides is -263.1 kJ/mol Ta. The correction of 69 kJ/mol H₂O for lattice water has been applied as seen in Table C.4.

$$\frac{1}{6} \{ Cs_8 Ta_6 O_{19} \} (xl, 25^{\circ}C) \rightarrow \frac{2}{3} Cs_2 O(soln, 702^{\circ}C) + \frac{1}{2} Ta_2 O_5(soln, 702^{\circ}C)$$
(C.11)

$$\Delta H_{11} = \Delta H_{ds} = 75.66 \pm 0.81 \text{kJ/mol Ta}$$

$$Cs_2O(xl, 25^{\circ}C) \rightarrow Cs_2O(soln, 702^{\circ}C)$$
 (C.12)

$$\Delta H_{12} = \Delta H_{ds}(\mathrm{Cs}_2\mathrm{O}) = -348.9 \pm 1.7 \mathrm{kJ/mol \,Ta}$$

$$\frac{2}{3}Cs_2O + \frac{1}{2}Ta_2O_5 (xl, 25^{\circ}C) \rightarrow \frac{1}{6}\{Cs_8Ta_6O_{19}\} (xl, 25^{\circ}C)$$
(C.13)

$$\Delta H_{13} = \Delta H_f^{ox}(\text{Cs}_8\text{Ta}_6\text{O}_{19}) = -\Delta H_{11} + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_{12} = -263.1 \pm 1.9\text{kJ/mol Ta}$$

Where ΔH_{ds} are drop solution enthalpies under oxygen bubbling.

C.3 Room Temperature Dissolution Enthalpies

 ΔH_{dis} was measured using a CSC 4400 isothermal microcalorimeter operated at 25 °C. About 5 mg of each sample was hand pressed into a pellet and dropped one at a time into 25.0 g of H₂O. Each experiment was repeated in 1M AOH (A = K, Rb, Cs, TMA) for the respective clusters. Dissolution enthalpies of hydrated hexaniobate clusters in water

$$\begin{split} \mathrm{Li}_8\mathrm{Ta}_6\mathrm{O}_{19}\cdot 18\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Li}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (18\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{K}_8\mathrm{Ta}_6\mathrm{O}_{19}\cdot 16\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{K}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (16\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{Rb}_8\mathrm{Ta}_6\mathrm{O}_{19}\cdot 14\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Rb}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (14\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{Cs}_8\mathrm{Ta}_6\mathrm{O}_{19}\cdot 14\mathrm{H}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Cs}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \ (14\mathrm{-x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{(TMA)}_6\mathrm{H}_2\mathrm{Ta}_6\mathrm{O}_{19}\cdot 21\mathrm{H}_2\mathrm{O} &\longrightarrow 6\,\mathrm{TMA}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + (2-\mathrm{x})\mathrm{H}_3\mathrm{O}^+ + (19\mathrm{+x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{(TMA)}_6\mathrm{H}_2\mathrm{Ta}_6\mathrm{O}_{19}\cdot 21\mathrm{H}_2\mathrm{O} &\longrightarrow 6\,\mathrm{TMA}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + (2-\mathrm{x})\mathrm{H}_3\mathrm{O}^+ + (19\mathrm{+x})\mathrm{H}_2\mathrm{O} + \mathrm{xOH}^-\\ \mathrm{TMA}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{H}_{\mathrm{v}}\mathrm{Ta}_{\mathrm{v}}\mathrm{H}_$$

Dissolution enthalpies of anhydrous hexaniobate clusters in water

$$\begin{split} \mathrm{Li}_8\mathrm{Ta}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Li}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ \mathrm{K}_8\mathrm{Ta}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{K}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ \mathrm{Rb}_8\mathrm{Ta}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Rb}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ \mathrm{Cs}_8\mathrm{Ta}_6\mathrm{O}_{19} + \mathrm{xH}_2\mathrm{O} &\longrightarrow 8\,\mathrm{Cs}^+ + [\mathrm{H}_{\mathrm{x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xOH}^- \\ (\mathrm{TMA})_6\mathrm{H}_2\mathrm{Ta}_6\mathrm{O}_{19} + 3\mathrm{OH}^- &\longrightarrow 5\,\mathrm{TMA}^+ + [\mathrm{H}_{2\mathrm{-x}}\mathrm{Ta}_6\mathrm{O}_{19}]^{(8-\mathrm{x})-} + \mathrm{xH}_2\mathrm{O} + (2-\mathrm{x})\mathrm{OH}^- \end{split}$$

Enthalpies of anhydrous clusters were found by subtracting the enthalpy of dissolution of lattice water $(0.4 \text{ kJ mol}^{-1})^{239}$ and then adjusting for the relative molar weights of the hydrated and anhydrous clusters, namely:

$$\Delta H_{dis,anhydrous} = (\Delta H_{dis,hydrated} - (0.4 \,\mathrm{kJ \,mol^{-1}})(n_{\mathrm{H_2O}})) \frac{\mathrm{MW}(\mathrm{Anhydrous \, Cluster})}{\mathrm{MW}(\mathrm{Hydrated \, Cluster})}$$
(C.14)

The calorimeter was calibrated by dissolving 15 mg pellets of KCl in water with stirring at 25 °C. Hydrous and anhydrous cluster dissolution enthalpy values in water are reported in Tables C.5-C.9.

Table C.5: Lithium Hexatantalate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ { m kJ} { m mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
22.59	73.61	54.24
27.27	72.90	53.67
39.49	71.06	52.17
51.54	66.91	48.77
63.29	64.77	47.02
69.94	61.39	44.27

 Table C.6: Potassium Hexatantalate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ {\rm kJ \ mol^{-1}})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
16.56	130.46	106.10
35.20	122.37	99.18
50.19	118.60	95.94
55.29	110.35	88.91
79.44	111.50	89.89
95.57	106.98	86.02
104.90	106.52	85.63
122.31	104.02	83.49
126.64	101.47	81.31

C.3.1 Tables of Aqueous Dissolution Enthalpies

C.3.2 Tables of 1M Parent Hydroxide Dissolution Enthalpies

Each experiment was repeated in 1M AOH, (A = K, Rb, Cs, TMA) for the respective clusters. Enthalpies are reported in tables D.10-D.13. Lithium was omitted due to its insolubility.

Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
107.69	91.02
114.87	97.42
107.27	90.64
105.64	89.20
102.88	86.73
88.78	74.16
89.69	74.97
87.23	72.78
87.66	73.16
84.66	70.49
	Dissolution Enthalpy $(\Delta H_{dis} / \text{kJ mol}^{-1})$ 107.69 114.87 107.27 105.64 102.88 88.78 89.69 87.23 87.66 84.66

 Table C.7: Rubidium Hexatantalate Dissolution Enthalpies in Water

Table C.8: Cesium Hexatantalate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
14.14	109.64	94.34
26.14	114.21	98.48
31.09	105.95	91.00
43.84	93.33	79.56
54.10	93.60	79.79
61.43	86.61	73.46
78.12	85.84	72.76
96.32	82.94	70.13
122.55	79.77	67.25

Table C.9: Tetramethylammonium Hexatantalate Dissolution Enthalpies in Water

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ {\rm kJ \ mol^{-1}})$	$(\Delta H_{dis} \ / \ \mathrm{kJ mol^{-1}})$
30.32	-5.02	-12.04
59.36	-4.17	-11.20
93.65	-2.53	-9.55
117.01	-5.87	-12.89
139.70	-3.65	-10.68

Table C.10: Potassium Hexatantalate Dissolution Enthalpies in 1M KOH

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
16.34	56.329	42.70
45.57	61.43	47.06
72.78	56.17	42.56
105.07	59.23	45.18
133.24	61.68	47.28

Table C.11: Rubidium Hexatantalate Dissolution Enthalpies in 1M RbOH

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
13.57	41.31	31.84
38.66	40.82	31.40
64.17	40.81	35.41
92.30	46.66	31.39
121.00	46.02	36.61

 Table C.12: Cesium Hexatantalate Dissolution Enthalpies in 1M CsOH

Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$(\Delta H_{dis} \ / \ { m kJ} { m mol}^{-1})$	$(\Delta H_{dis} \ / \ \mathrm{kJ} \mathrm{mol}^{-1})$
11.99	24.82	17.43
31.28	27.32	19.70
49.15	30.80	22.85
68.96	25.71	18.24
93.97	29.01	21.23
110.76	21.05	14.01
123.02	30.99	23.02
136.68	31.66	23.63

Table C.13: TMA Hexaniobate Dissolution Enthalpies in 1M TMAOE	ł
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Concentration	Dissolution Enthalpy	Anhydrous Dissolution Enthalpy
$(M \times 10^5)$	$\Delta H_{dis} \ / \ {\rm kJ \ mol}^{-1}$	$\Delta H_{dis} \ / \ { m kJ \ mol}^{-1}$
12.62	-40.39	-38.37
43.26	-38.26	-36.69
74.52	-33.63	-33.05
101.71	-35.31	-34.37
130.60	-40.72	-38.63

C.4 Supplementary Characterization

C.4.1 Energy Dispersive X-ray Analysis (EDX)



Figure C.1: Sample EDX spectrum of $\text{Li}_8\text{Ta}_6\text{O}_{19}$, indicating the complete replacement of K⁺ countercations (indistinguishable from background) by metathesis in 1M LiOH.



Figure C.2: Sample EDX spectrum of $\mathrm{K}_{8}\mathrm{Ta}_{6}\mathrm{O}_{19}.$

M	-+07 IZ	-+07 T-
Measurement $\#$	at% K	at% 1a
1	59.97	40.03
2	55.59	44.41
3	60.14	39.86
4	52.85	47.15
5	58.72	41.28
Average	57.45	42.55
Expected	57.14	42.86

Table C.14: Atom % values for K and Ta in $K_8Ta_6O_{19}$



Figure C.3: Sample EDX spectrum of $\rm Rb_8Ta_6O_{19}.$

Measurement $\#$	at $\%$ Rb	at% Ta
1	58.42	41.58
2	56.38	43.62
3	56.82	43.18
4	57.93	42.07
5	56.39	43.61
Average	57.19	42.81
Expected	57.14	42.86

Table C.15: Atom % values for Rb and Ta in $\rm Rb_8Ta_6O_{19}$



Figure C.4: Sample EDX spectrum of $\rm Cs_8Ta_6O_{19}.$

Measurement $\#$	at% Cs $$	at% Ta
1	58.56	41.44
2	56.82	43.18
3	59.72	40.28
4	59.65	40.35
5	59.71	40.29
Average	58.89	41.11
Expected	57.14	42.86

Table C.16: Atom % values for Cs and Ta in $\rm Cs_8Ta_6O_{19}$



Figure C.5: Thermogravimetric analysis of $\text{Li}_8\text{Ta}_6\text{O}_{19}$. All mass loss is due to lattice water, corresponding to 18 H₂O molecules per formula unit.



Figure C.6: Thermogravimetric analysis of $K_8Ta_6O_{19}$. All mass loss is due to lattice water, corresponding to 16 H₂O molecules per formula unit.



Figure C.7: Thermogravimetric analysis of $Rb_8Ta_6O_{19}$. All mass loss is due to lattice water, corresponding to 14 H₂O molecules per formula unit.

C.4.3 Syntheses

C.4.3.1 Alkali Salts

The larger alkali salts of $[Ta_6O_{19}]^{8-}$ were synthesized by refluxing a ≈ 40 mM solution of their peroxotantalate analogues $(A_3Ta(O_2)_4; A = K, Rb, Cs)$ in concentrated parent alkali hydroxide solution for 4 hours, except for the lithium salt, which was formed by metathesis of the potassium salt in 1M LiOH solution. The peroxotantalates were formed by adding 4.6 g TaCl₅ to 40 mL of cold 30% (w/w) H₂O₂ solution, adding concentrated AOH solutions (A = K, Rb, Cs), and precipitating with ethanol. Full syntheses can be found in a prior publication.²⁴¹



Figure C.8: Thermogravimetric analysis of $Cs_8Ta_6O_{19}$. All mass loss is due to lattice water, corresponding to 14 H₂O molecules per formula unit.

C.4.3.2 Tetramethylammonium Salt

Tetramethylammonium hexatanatalate ([(CH₃)₄N]₆H₂Ta₆O₁₉) was synthesized by adding 1.32 g of (NH₄)₃Ta(O₂)₄ to 8.25 mL of 1.4 M tetramethylammonium hydroxide and refluxing for 5 hours. The solution was then microfiltered, 40 mL isopropyl alcohol was added, and then the resulting solution was centrifuged to yield a small denser layer containing the product. The supernatant was discarded and further addition of 30 mL isopropyl alcohol yielded a white precipitate, which was washed with more isopropyl alcohol and oven-dried under vacuum at 60 °C.⁸³

Appendix D: Supporting Information for Chapter 6

D.1 T_1 Relaxation Fits



Figure D.1: Sample 1D 133 Cs sprectrum (60 mM Cs₈Nb₆O₁₉). The single peak arises from rapid exchange of free and bound Cs⁺.

Each reported T_1 value was obtained from a fit from a 16-membered variable delay (τ) list. Delay time (d_1) values were at least five times longer than the T_1 for each solution to ensure complete relaxation before proceeding to the next 180° pulse. Each

species is reported as the set of parameters I[0], P, and R_{QR} , along with the standard deviation of the fit (Tables S1-S3).

Table D.1: Fitting parameters for 133 Cs T_1 Inversion-Recovery NMR for 5 mM solutions of mixed metal clusters

Species	I[0]	Р	$R_{QR} ({\rm s}^{-1})$	St. Dev
$Cs_5NbW_9O_{32}$	1.014	1.873	0.1087	3.229×10^{-3}
$Cs_5TaW_9O_{32}$	1.003	1.894	0.2414	3.784×10^{-3}
$Cs_4Nb_2W_4O_{19}$	1.001	1.874	0.1257	2.792×10^{-3}
$\rm Cs_5NbW_9O_{32}$	0.9983	1.932	0.5708	4.666×10^{-3}

Table D.2: Fitting parameters for $^{133}\mathrm{Cs}~T_1$ Inversion-Recovery NMR for solutions of $\mathrm{Cs_8M_6O_{19}}$

Species/Concentration	I[0]	Р	$R_{QR} ({\rm s}^{-1})$	St. Dev.
$Cs_8Nb_6O_{19}$				
0.5 mM	0.7400	1.687	0.2939	2.479×10^{-2}
$1 \mathrm{mM}$	0.8659	1.849	0.4268	1.372×10^{-2}
2 mM	1.001	1.919	0.5308	5.344×10^{-3}
5 mM	0.9962	1.886	0.7289	3.368×10^{-3}
10 mM	0.9985	1.889	0.9515	2.477×10^{-3}
20 mM	0.9985	1.876	1.205	8.623×10^{-4}
60 mM	0.9987	1.877	1.939	9.025×10^{-4}
100 mM	0.9990	1.874	2.312	8.962×10^{-4}
$Cs_8Ta_6O_{19}$				
0.5 mM	0.8209	1.785	0.5473	2.080×10^{-2}
1 mM	0.9981	1.962	0.8354	8.080×10^{-3}
2 mM	0.9993	1.988	1.197	5.965×10^{-3}
5 mM	0.9959	1.895	1.486	1.982×10^{-3}
10 mM	1.000	1.904	1.714	2.724×10^{-3}
$20 \mathrm{~mM}$	0.9986	1.887	2.125	3.523×10^{-3}
60 mM	1.001	1.895	3.078	1.014×10^{-3}
100 mM	0.9994	1.877	3.689	1.324×10^{-3}

Species/Concentration	I[0]	Р	$R_{QR} ({\rm s}^{-1})$	St. Dev.
$20 \text{mMTMA}\{\text{Nb}_6\}$				
+10 mM CsCl	0.9954	1.881	3.499	1.364×10^{-2}
+20 mM CsCl	0.9912	1.840	3.438	4.559×10^{-3}
+40 mM CsCl	0.9953	1.839	3.124	4.833×10^{-3}
+80 mM CsCl	0.9993	1.867	2.555	2.365×10^{-3}
+120 mM CsCl	0.9970	1.857	2.100	2.565×10^{-3}
+160 mM CsCl	0.9996	1.873	1.766	2.253×10^{-3}
+200 mM CsCl	0.9996	1.869	1.544	4.823×10^{-4}
+240 mM CsCl	0.9991	1.874	1.332	1.030×10^{-3}
$20 \text{mMTMA}\{\text{Ta}_6\}$				
+10 mM CsCl	1.001	1.785	4.434	1.257×10^{-2}
+20 mM CsCl	0.9904	1.913	4.381	7.615×10^{-3}
+40 mM CsCl	0.9957	1.888	4.170	2.603×10^{-3}
+80 mM CsCl	0.9974	1.885	3.836	2.094×10^{-3}
+120 mM CsCl	0.9973	1.883	3.436	2.148×10^{-3}
+160 mM CsCl	0.9995	1.880	3.011	9.399×10^{-4}
+200 mM CsCl	0.9988	1.886	2.684	3.463×10^{-3}
+240 mM CsCl	0.9996	1.877	2.381	1.624×10^{-3}

Table D.3: Fitting parameters for ¹³³Cs T_1 Inversion-Recovery NMR for solutions of 20 mM TMA{M₆} with added CsCl. All solutions are in 200 mM TMAOH.

D.2 Viscometry

In order to normalize between solutions, we define an adjusted quadrupolar relaxation rate:

$$R_{adj} = \frac{R_{QR}}{\eta_{rel}} \tag{D.1}$$

The viscosity of each solution was found relative to that of 10% $D_2O/90\%$ H₂O and are expressed as η_{rel} , such that:

$$\eta_{rel} = \frac{t_{soln} d_{soln}}{t_0 d_0} \tag{D.2}$$

where t_{soln} is the efflux time of the solution in an Ostwald Viscosity Tube, d_{soln} is the

density of the solution, and t_0 and d_0 are the efflux time and density of 10% D₂O/90% H₂O.

Viscosity measurements were taken with an Ostwald Viscosity Tube and a stopwatch at a constant temperature of 25 °C. A constant sample volume of 5.00 mL was held for each experiment. Five efflux times were recorded for each sample and the averages of these times are reported (Table D.4) along with solution density and relative viscosity to 10% $D_2O/90\%$ H₂O.

Table D.4: Relative viscosities of solutions found by Ostwald Viscometer. All solutions are in $10\% D_2O/90\% H_2O$

Solution	Density $(g m L^{-1})$	Mean Efflux Time (s)	η_{rel}
D_2O/H_2O	1.016	58.52	1.000
$5 \text{ mM Cs}\{Nb_6\}$	1.023	58.94	1.014
$20 \text{ mM Cs}\{Nb_6\}$	1.040	58.86	1.030
$100 \text{ mM Cs}\{Nb_6\}$	1.161	58.50	1.112
$5 \text{ mM Cs}\{\text{Ta}_6\}$	1.025	58.93	1.016
$20 \text{ mM Cs}\{\text{Ta}_6\}$	1.048	58.66	1.034
$100 \text{ mM Cs}\{\text{Ta}_6\}$	1.206	57.19	1.160
$20 \text{ mM TMA}{Nb_6} + 200 \text{ mM TMAOH}$	1.030	64.74	1.122
+ 80 mM CsCl	1.036	62.36	1.087
+ 240 mM CsCl	1.051	61.02	1.079
$20 \text{ mM TMA}{Ta_6} + 200 \text{ mM TMAOH}$	1.044	63.03	1.107
+ 80 mM CsCl	1.057	62.54	1.112
+ 240 mM CsCl	1.073	62.45	1.127

Remaining values of η_{rel} were generated by linear approximations between the two nearest concentrations. *i.e.*, for the following set of solutions:

(A) 20 mM TMA{Nb₆} + 200 mM TMAOH + 80 mM CsCl ($\eta_{rel} = 1.087$)

(B) 20 mM TMA{Nb₆} + 200 mM TMAOH + 120 mM CsCl

(C) 20 mM TMA{Nb₆} + 200 mM TMAOH + 240 mM CsCl (
$$\eta_{rel} = 1.079$$
)

we can obtain the approximate viscosity of (B) from the known values of (A) and (C)

$$\eta_B = \eta_A - \frac{120 - 80}{240 - 80} (\eta_A - \eta_C) = 1.085$$
(D.3)

D.3 Syntheses

D.3.1 $Cs_8Nb_6O_{19}$

3.42 g of $\text{Nb}_2\text{O}_5 \cdot \text{xH}_2\text{O}$ were slowly added to 10.0 g of 50 wt% CsOH solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

D.3.2 $Cs_8Ta_6O_{19}$

5.5 g of $\text{Cs}_3 \text{TaO}_8$ was added to 50 g of 50 wt% CsOH solution and heated to reflux until complete dissolution was observed. The solution was cooled and microfiltered with a 0.45 µm syringe filter. The solution was allowed to evaporate and after several days, a large crop of colorless well-formed crystals is observed.

D.3.3 $Cs_5NbW_9O_{32}$

 $K_3[Nb(O_2)_4]$ (1.1 g, 3.3 mmol) was dissolved in 25 mL of H2O at 70 degreeCelsius. In a separate beaker, $Na_2WO_4 \cdot 2H_2O$ (3.6 g, 11 mmol) was dissolved in a mixture of H_2O (11.9 mL) and aqueous H_2O_2 (0.65 mL, 30% v/v). The contents of the two beakers were then combined and stirred for 30 min at 70°C to afford a clear solution. The pH of this solution was adjusted to 2.0 (3M H_2SO_4) and the resulting mixture was first refluxed for 2 h and then centrifuged at room temperature. CsCl (5.6 g, 33 mmol) was added to the supernatant under vigorous stirring and the thick yellow suspension thus obtained was stirred for 3 min and filtrated under vacuum. The isolated yellow precipitate was finally washed with cold water (2 mL) and dried under suction. Analytically pure crystals of Cs{NbW₉} were obtained by recrystallizing this crude product twice from the minimum amount of boiling water.

D.3.4 $Cs_5TaW_9O_{32}$

 $K_3[Ta(O_2)_4]$ (2.0 g, 4.7 mmol) was added to a stirred solution of $Na_2WO_4 \cdot 2H_2O$ (6.6 g, 20.0 mmol) in 40 mL of hot (60 degreeCelsius) H₂O. The pH of the resulting mixture was carefully adjusted to 2.0 by the dropwise addition of HCl (37% w/w). The yellow suspension was refluxed for 2 h and centrifuged at room temperature. CsCl (10.0 g, 59.4 mmol) was added to the isolated bright yellow supernatant and a mass of light orange solids was isolated from the resulting suspension by centrifugation, washed twice with 5 mL of water, twice with 20 mL of 2-propanol and finally dried under vacuum. This crude product was dissolved in 30 mL of boiling H2O and yellow crystal plates formed overnight at 4 °C.

D.3.5 $[(CH_3)_4N]_5H_3Nb_6O_{19}$

A 150 mL beaker was charged with tetramethylammonium hydroxide solution (2.8 M, 100 mL) and heated to 90 °C. Hydrous Nb_2O_5 (20 g) was added in small aliquots, allowing

full dissolution before addition of new aliquots. After addition of all the niobium oxide, the solution was allowed to cool to room temperature. Isopropyl alcohol was added to precipitate the final product. After excessive washing with isopropyl alcohol, a white crystalline powder is obtained through vacuum filtration.

D.3.6 $[(CH_3)_4N]_6H_2Ta_6O_{19}$

A 125 mL flask was charged with $(NH_4)_3 Ta(O_2)_4$ (1.32 g) and 1.4 M tetramethylammonium hydroxide (8.25 mL). The solution was refluxed for 5 h with the condensing column chilled to approximately 5°C. The resulting solution was filtered with a 0.45 µm nylon syringe filter. The filtered solution was agitated with isopropyl alcohol (~40 mL) and centrifuged to yield a small denser layer containing the product. Further agitation of the bottom layer with isopropyl alcohol (30 mL) yielded a white precipitate. The precipitate was washed with isopropyl alcohol and oven-dried under vacuum (60 °C).

Syntheses for $Cs_4Na_2Nb_4W_2O_{19}$ and $Cs_4Nb_2W_4O_{19}$ are reported in Section 3.2.

D.4 Hexaniobate Total X-Ray Scattering Spectrum



Figure D.2: PDF analysis of X-ray total scattering on solutions of 100 mM TMA{Nb₆} in 200 mM TMAOH with added CsCl (0 to 12 molar equivalents), with a growing Ta-Cs peak at 4.1 Å providing structural information and atomic-level resolution of the ion-pair in solution.



Figure D.3: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 5 mM $\rm Cs_8Nb_6O_{19}.$

Measurement $\#$	$\mathrm{Br}\%$	Nb%	Cs%	$Cs/\{Nb_6\}$
1	56.65	36.37	6.97	1.15
2	59.15	35.38	5.47	0.93
3	58.93	34.60	6.47	1.12
4	65.38	29.10	5.52	1.14
5	49.03	42.02	8.95	1.28
6	47.30	43.84	8.86	1.21
Avg.				1.14
St. Dev				0.12

Table D.5: At% values of the precipitate upon adding CTAB to 5 mM $\rm Cs_8Nb_6O_{19}.$



Figure D.4: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 5 mM $\rm Cs_8Ta_6O_{19}.$

Table D.6: At% values of the precipitate upon adding CTAB to 5 mM $\rm Cs_8Ta_6O_{19}.$ Br was not measured.

Measurement $\#$	Ta%	$\mathrm{Cs}\%$	$Cs/{Ta_6}$
1	70.61	29.39	2.50
2	71.34	28.66	2.40
3	70.55	29.45	2.50
4	73.20	26.80	2.17
5	73.43	26.57	2.15
Avg.			2.36
St. Dev			0.16


Figure D.5: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 10 mM $\rm Cs_8Nb_6O_{19}.$

Measurement $\#$	$\mathrm{Br}\%$	Nb%	Cs%	$Cs/{Nb_6}$
1	48.13	43.07	8.80	1.23
2	42.99	46.32	10.69	1.38
3	55.15	34.91	9.94	1.71
4	56.52	35.66	7.82	1.32
5	50.83	38.72	10.44	1.62
6	51.42	37.85	10.62	1.68
Avg.				1.49
St. Dev				0.21

Table D.7: At% values of the precipitate upon adding CTAB to $10~{\rm mM}~{\rm Cs_8Nb_6O_{19}}.$



Figure D.6: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 10 mM $\rm Cs_8Ta_6O_{19}.$

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Measurement $\#$	${ m Br}\%$	Ta%	$\mathrm{Cs}\%$	$Cs/{Ta_6}$
1	50.19	33.83	15.98	2.83
2	43.67	37.95	18.38	2.91
3	43.93	36.95	19.13	3.11
4	42.79	38.95	18.25	2.81
5	62.43	24.63	12.94	3.15
Avg.				2.96
St. Dev				0.16

Table D.8: At% values of the precipitate upon adding CTAB to 10 mM $\rm Cs_8Ta_6O_{19}.$



Figure D.7: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 20 mM $\rm Cs_8Nb_6O_{19}.$

Table D.9: At% values of the precipitate upon adding CTAB to 20 mM $Cs_8Nb_6O_{19}$. Br was not measured.

Measurement $\#$	Nb%	Cs%	$Cs/{Nb_6}$
1	73.05	26.95	2.21
2	73.39	26.61	2.18
3	75.11	24.89	1.99
4	74.01	25.99	2.11
5	74.44	25.56	2.06
Avg.			2.11
St. Dev			0.09



Figure D.8: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 20 mM $\rm Cs_8Ta_6O_{19}.$

Measurement $\#$	Ta%	Cs%	$Cs/{Ta_6}$
1	62.21	37.39	3.58
2	64.83	35.17	3.25
3	61.38	38.62	3.76
4	60.99	39.01	3.84
5	63.07	36.93	3.51
6	62.41	37.59	3.61
Avg.			3.60
St. Dev			0.21

Table D.10: At% values of the precipitate upon adding CTAB to 20 mM $Cs_8Ta_6O_{19}$. Br was not measured.



Figure D.9: Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CsCl to 160 mM CsCl. Cs and Cl content was negligible (P/B < 0.6 in all cases).

D.6 Computational Details

D.6.1 Frontier MO energies

IUII IIOMO-L	UNIO gaps.			
Molecular	${\rm Nb}_6$	$Cs{Nb_6}$	$Cs_4\{Nb_6\}$	$Cs_8\{Nb_6\}$
Orbital	OE (eV)	OE (eV)	OE (eV)	OE (eV)
HOMO-2	-5.633	-5.742	-6.041	-6.449
HOMO-1	-5.225	-5.361	-5.687	-6.150
HOMO	-4.844	-4.980	-5.442	-6.068
LUMO	0.544	0.054	-0.136	-0.354
LUMO+1	0.735	0.544	0.082	-0.109
LUMO+2	1.088	0.626	0.544	0.027
LUMO+3	1.197	0.898	0.571	0.163
H-L gap	5.388	5.034	5.306	5.714

Table D.11: Frontier molecular orbital energies of $\{Nb_6\}$ with 0, 1, 4, and 8 associated Cs⁺, along with HOMO-LUMO gaps.

Table D.12: Frontier molecular orbital energies of $\{Ta_6\}$ with 0, 1, 4, and 8 associated Cs⁺, along with HOMO-LUMO gaps

	01			
Molecular	${Ta_6}$	$Cs{Ta_6}$	$Cs_4{Ta_6}$	$Cs_8{Ta_6}$
Orbital	OE (eV)	OE (eV)	OE (eV)	OE (eV)
HOMO-2	-5.578	-5.687	-6.014	-6.422
HOMO-1	-5.361	-5.497	-5.823	-6.286
HOMO	-4.925	-5.061	-5.551	-6.177
LUMO	1.361	0.054	-0.136	-0.381
LUMO+1	1.469	0.789	0.082	-0.136
LUMO+2	1.796	0.898	0.599	0.163
LUMO+3	1.905	1.116	0.626	0.381
H-L gap	6.286	5.116	5.415	5.796

D.6.2 Graphical Orbital Renderings

D.6.2.1 Oxo-Based MOs



Figure D.10: Graphical renderings of the participating orbitals in the main charge transfer band (HOMO and LUMO+2) of $\{Nb_6\}$ and $\{Ta_6\}$. The bridging oxygen O_{2p} contribution to the $\{Ta_6\}$ LUMO+2 is slightly smaller than it is for $\{Nb_6\}$. Red spheres are oxygen, blue spheres are Nb/Ta.

D.6.3 Calculated Electronic Excitations

We also derived the theoretical UV-Vis spectra of the Cs-associated $\{M_6\}$ structures by calculating the oscillator strengths of their component electronic transitions. The significant reduction of the HOMO-LUMO gap due to stabilization of the LUMOs, especially



Figure D.11: Simulated UV-Vis spectra of $\{Nb_6\}$ with 0, 1, 4, and 8 associated Cs⁺.

seen in Cs{Ta₆} (but also in Cs{Nb₆} to a lesser extent), is evidently reflected in the spectra. In Cs{Nb₆} (Figure D.11) a charge transfer (CT) band prominently appears at 258 nm as an extra "hump" on the existing $n(O_{2p}) \rightarrow \pi^*(Nb_{4d}-O_{2p})$ peak (247 nm). Remaining CT bands – always arising due to transitions from nonbonding $n(O_{2p})$ orbitals to Cs⁺-mixed Nb_{4d}, Nb_{5s}, and Nb_{5p} – are "covered" by bands already present in {Nb₆}.

In Cs{Ta₆}, on the other hand (Figure D.12), a greater degree of Cs⁺-orbital admixture with Ta_{5d}, Ta_{6s}, and Ta_{6p} gives rise to a larger number of low-lying LUMOs



Figure D.12: Simulated UV-Vis spectra of $\{Ta_6\}$ with 0, 1, 4, and 8 associated Cs⁺.

compared to Cs{Nb₆}, and produces a visibly altered situation. In this case, CT transitions give rise to two well-distinguishable peaks at 251 nm and 239 nm. Since metal-oxo $\pi^*(Ta_{5d}-O_{2p})$ orbitals are higher in energy compared to their $\pi^*(Nb_{4d}-O_{2p})$ counterparts, absorption of the $n(O_{2p}) \rightarrow \pi^*(Ta_{5d}-O_{2p})$ is blueshifted (214 nm), and it is thanks to this that less interference occurs. There is, nonetheless, a third CT transition that, at 211 nm, overlaps with the $n \rightarrow \pi^*$ band at 214 nm. Turning to the spectra of Cs₄{M₆} and Cs₈{M₆}, it is also evident that, upon association of additional Cs⁺ and steady re-increase of the HOMO-LUMO gap (this time due to stabilization of the HOMOs), CT bands become increasingly blueshifted, and eventually re-merge with the $n \to \pi^*$ bands.

Corroborating experimental UV-Vis spectra are not available, due to signal saturation from the excess base solution necessary to fully deprotonate the clusters resulting in truncated spectra upon background subtraction.

Appendix E: Supporting Information for Chapter 7

E.1 FTIR



Figure E.1: Infrared Spectrum of TMA{Nb₁₀}. TMA⁺ symmetric stretching frequency lies at 1500 cm⁻¹, terminal oxo stretches on the cluster appear at 800-1000 cm⁻¹, other stretching and bending modes, including bridging oxo stretches, appear at 400-800 cm⁻¹.



Figure E.2: Infrared Spectrum of Na{V₁₀} and Li{V₁₀}, demonstrating that the clusters are identical. Terminal oxo stretches on the cluster appear at 800-1000 cm⁻¹, other stretching and bending modes, including bridging oxo stretches, appear at 400-800 cm⁻¹.



Figure E.3: Raman spectrum of a solution of 20 mM TMA{Nb₁₀} + 120 mM LiCl + 1M HEPES (with the HEPES background subtracted), demonstrating the slowed disappearance of the {Nb₁₀} peak (at 937 cm⁻¹) over time.



Figure E.4: Raman spectrum of a solution of 20 mM TMA{Nb₁₀} + 120 mM KCl + 1M HEPES (with the HEPES background subtracted), demonstrating the slowed disappearance of the {Nb₁₀} peak (at 937 cm⁻¹) over time.



Figure E.5: Raman spectrum of a solution of 20 mM TMA{Nb₁₀} + 120 mM CsCl + 1M HEPES (with the HEPES background subtracted), demonstrating the slowed disappearance of the {Nb₁₀} peak (at 937 cm⁻¹) over time.

E.3 Monitoring Cluster Growth Over Time By SAXS

Unlike the Raman spectra presented Chapter 7, solutions for SAXS measurements were not kept in a temperature-controlled environment.



Figure E.6: SAXS spectra of 20 mM $\{Nb_{10}\}$ taken at times between immediately after solution preparation to 1 week later, demonstrating the stability of the cluster in water over time.



Figure E.7: SAXS spectra of 20 mM $\{Nb_{10}\} + 120$ mM LiCl taken at times between immediately after solution preparation to 2 weeks later, showing that speciation has completed by 2 weeks after preparation.



Figure E.8: SAXS spectra of 20 mM $\{Nb_{10}\} + 120$ mM NaCl taken at times between immediately after solution preparation to 2 weeks later, showing that speciation has completed by 2 weeks after preparation.



Figure E.9: SAXS spectra of 20 mM $\{Nb_{10}\} + 120$ mM KCl taken at times between immediately after solution preparation to 2 weeks later, showing that speciation has completed by 4 days after preparation.



Figure E.10: SAXS spectra of 20 mM $\{Nb_{10}\} + 120$ mM RbCl taken at times between immediately after solution preparation to 1 week later, showing that speciation has completed within a day of preparation.



Figure E.11: SAXS spectra of 20 mM $\{Nb_{10}\} + 120$ mM CsCl taken at times between immediately after solution preparation to 1 week later, showing that speciation has completed within a day of preparation.

E.4 Existing Large Niobate Clusters



Figure E.12: Structure of $K[Nb_{24}O_{72}]$, as prepared by Peng Huang *et al.*. Green polyhedra are $[NbO_6]$ units, lavender sphere is K, which coordinates to cluster oxo atoms and lattice water molecules at the center of the cluster.



Figure E.13: Structure of $K[Nb_{32}O_{96}]$, as prepared by Peng Huang *et al.*. Green polyhedra are $[NbO_6]$ units, lavender sphere is K, which coordinates to oxo atoms of neighboring $\{Nb_7\}$ units.



Figure E.14: Structure of $K_{12}Nb_{96}O_{288}$, as prepared by Peng Huang *et al.*. Green polyhedra are $[NbO_6]$ units, lavender spheres are K, which coordinate to oxo atoms of neighboring $\{Nb_7\}$ units throughout the interior of the cluster.



E.5

ESI-MS

Figure E.15: ESI-MS spectrum of Li{Nb₂₄} at 1 mM Nb in solution at a fragmentation voltage of 100 V.

	Table 1.1. Feak list for $\operatorname{In}(\operatorname{ro}_{24})$						
Species	Calc. m/z	Actual m/z	Rel Int	Linkage			
$[H_6Nb_{17}O_{54}]^{17-}$	144.069	144.035	100	Full cluster minus $\{Nb_7\}$ (a)			
$[H_2Nb_7O_{22}(H_2O)]^{7-}$	146.037	146.032	63	${Nb_7}$ (b)			
$[HNb_{17}O_{50}]^{14-}$	170.012	170.058	15	Full cluster minus $\{Nb_7\}$			
$[H_4Nb_{24}O_{68}]^{12-}$	276.787	276.787	86	Full cluster minus four oxo (c)			
$[H_{12}Nb_{24}O_{72}]^{12-}$	282.790	282.789	12	Full cluster			
$[H_{13}Nb_{23}O_{69}]^{10-}$	325.360	325.184	11	Full cluster minus Nb			
$[H_5Nb_{24}O_{67}]^{9-}$	367.247	367.227	12	Full cluster minus five oxo			
$[H_6Nb_{23}O_{64}]^{7-}$	452.367	452.228	15	Full cluster minus 1 Nb			

Table E.1: Peak list for $Li\{Nb_{24}\}$



Figure E.16: ESI-MS spectrum of $K\{Nb_{24}\}$ at 1 mM Nb in solution at a fragmentation voltage of 100 V.

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Species	Calc. m/z	Actual m/z	Rel Int	Linkage
$[H_6Nb_{17}O_{54}]^{17-}$	144.069	144.036	78	Full cluster minus $\{Nb_7\}$ (a)
$[H_2Nb_7O_{22}(H_2O)]^{7-}$	146.037	146.032	47	${Nb_7}$ (b)
$[HNb_{17}O_{50}]^{14-}$	170.012	170.058	22	Full cluster minus $\{Nb_7\}$
$[H_6Nb_{15}O_{46}(H_2O)_3]^{11-}$	199.040	199.173	25	${Nb_7}-Nb-{Nb_7}$
$[H_3Nb_7O_{20}]^{2-}$	486.633	487.309	100	${Nb_7}$ minus 2 oxo (c)
$[H_{16}Nb_{17}O_{53}]^{5-}$	488.653	488.314	27	Full cluster minus {Nb ₇ }
$[H_{11}Nb_{21}O_{61}]^{6-}$	489.635	489.306	34	Full cluster minus Nb-trimer (d)
$[H_{18}Nb_{20}O_{61}]^{4-}$	712.990	713.479	50	Full cluster minus 4 Nb (e)
$[H_{14}Nb_{15}O_{46}]^{3-}$	714.490	714.479	21	$\{Nb_7\}-Nb-\{Nb_7\}$
$[H_9KNb_{15}O_{44}]^{3-1}$	715.135	715.474	20	$\{Nb_7\}-Nb-\{Nb_7\}$

Table E.2: Peak list for $K{Nb_{24}}$



Figure E.17: ESI-MS spectrum of Cs{Nb₂₄} at 1 mM Nb in solution at a fragmentation voltage of 100 V.

Table E.3: Peak list for $Cs\{Nb_{24}\}$						
Species	Calc. m/z	Actual m/z	Rel Int	Linkage		
$[H_5CsNb_{24}O_{72}]^{17-}$	207.079	207.055	68	Full cluster (a)		
$[H_6Cs_2(H_2O)_6Nb_{24}O_{72}]^{16-}$	235.082	235.050	57	Full cluster (b)		
$[H_5 CsNb_{24}O_{70}]^{14-}$	249.139	249.096	47	Full cluster (c)		
$[H_6Cs_3(H_2O)_4Nb_{24}O_{72}]^{15-}$	257.213	257.152	48	Full cluster (d)		
$[H_3Cs_2Nb_{24}O_{69}]^{13-1}$	277.095	277.134	100	Full cluster minus 3 oxo (e)		
$[H_5Cs_3Nb_{23}O_{68}]^{13-1}$	279.097	279.131	31	Full cluster minus 1 Nb		
$[H_6Cs_4(H_2O)_4Nb_{24}O_{72}]^{14-}$	285.078	285.147	55	Full cluster (f)		
$[H_8CsNb_{22}O_{65}]^{11-}$	293.143	293.127	22	Full cluster minus 2 Nb		
$[H_{11}Cs_3Nb_{17}O_{53}]^{7-}$	405.277	405.230	27	Full cluster minus {Nb ₇ }		
$[H_5 CsNb_{21}O_{59}]^{7-}$	433.240	433.224	63	Full cluster minus Nb-trimer (g)		
$[H_3Cs_5Nb_{17}O_{50}]^{7-1}$	435.224	435.223	21	Full cluster minus {Nb ₇ }		
$[H_{12}CsNb_{22}O_{65}]^{7-1}$	461.230	461.221	36	Full cluster minus 2 Nb		
$[H_9Nb_{24}O_{68}]^{7-1}$	475.211	475.308	33	Full cluster minus 4 oxo		
$[H_7Cs_2(H_2O)Nb_8O_{26}]^{3-1}$	483.332	483.321	21	$\{Nb_7\}-Nb$		
$[Cs_3Nb_8O_{23}]^{3-}$	503.283	503.303	36	{Nb ₇ }-Nb		

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Figure E.18: Calculated Raman spectra of $\{Nb_{10}\}$, $Cs_8\{Nb_{10}\}$, and $\{Nb_{24}\}$ indicating a rightward shift of 30 cm⁻¹ of the main peak between $\{Nb_{10}\}$ and $\{Nb_{24}\}$, perfectly matching the experimental shift.