

Triniobium, Wells–Dawson-Type Polyoxoanion, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$: Improvements in the Synthesis, Its Reliability, the Purity of the Product, and the Detailed Synthetic Procedure

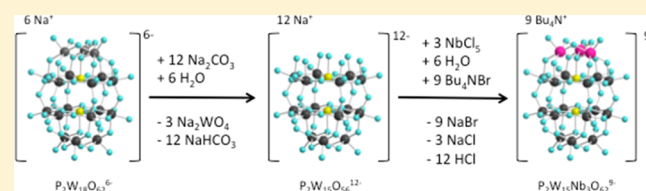
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S Supporting Information

ABSTRACT: Reproducible syntheses of high-purity $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ and, therefore, also the supported $[(1,5\text{-COD})\text{Ir}^{\text{I}}]^+$ organometallic precatalyst, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{Na}_3(1,5\text{-COD})\text{Ir}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})$, have historically proven quite challenging. In 2002, Hornstein et al. published an improved synthesis reporting 90% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ in their hands. Unfortunately, 36 subsequent attempts to replicate that 2002 synthesis by four researchers in our laboratories produced material with an average purity of $82 \pm 7\%$, albeit as judged by the improved S/N ^{31}P NMR now more routinely possible. Herein we (1) verify problems in reproducing $\geq 90\%$ purity $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, (2) determine three critical variables for the successful production of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, (3) optimize the synthesis to achieve 91–94% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, and (4) successfully reproduce and verify the synthesis via another researcher (Dr. Saim Özkar) working only from the written procedure. The key variables underlying previously irreproducible syntheses are (i) a too-short and incomplete, insufficient volume washing step for $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ that (previously) failed to remove the WO_4^{2-} byproduct present, (ii) inadequate reaction time and the need for a slight excess of niobium(V) during the incorporation of three niobium(V) ions into $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$, and (iii) incomplete removal of protons from the resultant $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ intermediate. These three insights have allowed improvement of the synthesis to a 91–94% final purity $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product by high S/N ^{31}P NMR. Moreover, the synthesis provided both is very detailed and has been independently checked (by Dr. Özkar) using only the written procedures. The finding that prior syntheses of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ are contaminated with WO_4^{2-} is one of the seemingly simple, but previously confounding, findings of the present work. An explicit check of the procedure is the second most important, more general feature of the present paper, namely, recognizing, discussing, and hopefully achieving a level of written reporting necessary to make such challenging polyoxometalate inorganic syntheses reproducible in the hands of others.



INTRODUCTION

The polyoxoanion $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ and the supported $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{Na}_3(1,5\text{-COD})\text{Ir}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})$ organometallic precatalyst are precursors to one of the best-studied¹ transition-metal nanoparticle nucleation and growth systems. Upon reduction with H_2 , $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{Na}_3(1,5\text{-COD})\text{Ir}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})$ yields now classic $\text{Ir}_{\sim 300} \cdot (\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-})_n$ nanoparticles² in which the $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ polyoxoanion serves as an excellent “Gold Standard”¹ nanoparticle stabilizer. The ability of $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ to provide a high level of kinetic control and to produce isolable, redissolvable, near-mono-disperse ($\pm 15\%$ diameter) and highly catalytically active polyoxoanion-stabilized $\text{Ir}_{\sim 300} \cdot (\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-})_n$ nanoparticles spawned the subdiscipline in polyoxometalate (POM) chemistry of POM-stabilized nanoparticles. The $\text{Ir}_{\sim 300} \cdot (\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-})_n$ nanoparticle system has also proven invaluable for investigations into the kinetics of nanoparticle nucleation and growth,^{3–7} comprising presently the most thoroughly studied and probably mechanistically best-studied

and best-understood transition-metal nucleation and growth system.⁸

Unfortunately, however, difficulty in reproducing⁹ high-purity $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ and thus the $(1,5\text{-COD})\text{Ir}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})^{8-}$ precursor has once again⁹ stymied ongoing investigations—this time into the currently important question of the precise nuclearity of the kinetically effective nucleus formed from $(1,5\text{-COD})\text{Ir}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})^{8-}$ en route to the polyoxoanion-stabilized iridium nanocluster product, $\text{Ir}_{\sim 300} \cdot (\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-})_n$. This, in turn, has necessitated the present work, an additional⁹ in-depth reexamination of the $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ synthesis and its $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ precursor, with the goal of providing a truly reliable synthesis to the highest achievable purity $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ product.

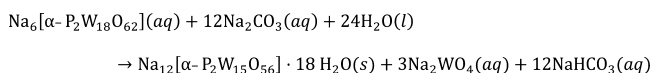
The triniobium-substituted Dawson heteropolyoxoanion $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$, which is key to the aforementioned chemistry,

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is prepared from the self-assembled Wells–Dawson POM $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$. A crucial initial step in its synthesis is the hydroxide-assisted removal of three “[W^{IV}O]” units as WO_4^{2-} to form $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ —the kinetically precipitated lacunary trivacant heteropolytungstate—upon the addition of 12 equiv of base via the balanced reaction shown in Scheme 1.

Scheme 1



Despite the apparent simplicity of this reaction, base degradation of $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$ has the potential to produce multiple POMs (Scheme 2). As a result of the many potential side products, the desired, kinetically precipitated powder $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ is metastable^{9,10} when placed back into an aqueous solution. Furthermore, directly characterizing the purity of the precipitated $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ product is a significant problem because it degrades rapidly when dissolved at low pH, thereby preventing its direct analysis by solution ³¹P NMR, the otherwise sensitive and hence preferred technique for determining the purity of polytungstates containing phosphorus.¹¹ The solution instability of the lacunary synthon $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ also means that it cannot be crystallized or, therefore, purified by crystallization, at least to date.

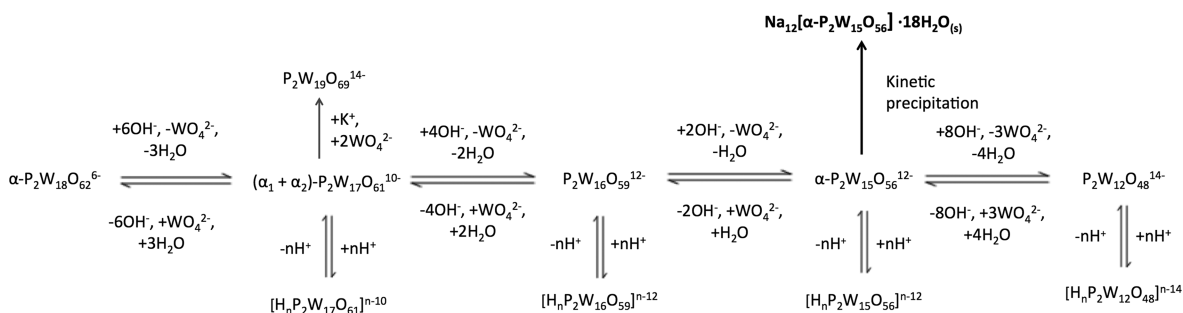
The difficulty in reliably producing the metastable, kinetically precipitated $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ powder has been addressed previously: in 2000, our research laboratory found that the synthesis of the triniobium(V)-containing $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ compound (Scheme 3) often produced a persistent ~10–35% impurity, as determined by ³¹P NMR. Around that time, we were contacted by another laboratory experiencing similar difficulties, as reported elsewhere.⁹ Hornstein examined the issue of reproducibility and correctly concluded that the problems in the synthesis originated in the production of the $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ precursor. He then investigated the five literature syntheses^{10,12–16} of $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ (Table 1a) in search of a preferred, reliable synthesis that also gives the highest-purity final $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product^{15,17,18} (Table 1b), as judged by ³¹P NMR.⁹ One important point for that work, in comparison to the present studies, is that better S/N ³¹P NMR is routinely available presently as, therefore, exploited in the current work (impurities $\geq 1\%$ can be routinely detected, vs $\geq ca.$ 5–8% in prior work; Table 1a). Also noteworthy here is

that the 1988 Edlund et al. synthesis¹⁵ of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ leads to an experimentally checked 1997 *Inorganic Syntheses* procedure¹⁸—one that was rechecked and discarded by Hornstein’s work⁹ and then also rechecked (and discarded) once more as part of the work herein.¹⁹

In Hornstein’s hands, only Contant’s 1990 *Inorganic Syntheses*¹⁰ of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ could be used to produce 90% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, no matter which synthesis was used for the conversion of $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ to $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ (Table 1b). Hornstein’s synthesis adds exactly 12.6 equiv of base and contrasts with the other procedures,^{12–16} which require the addition of base continually to achieve and maintain a pH of 9 for up to 1 h. Hornstein also carefully examined four additional variables to optimize the 1990 Contant procedure including the rate of Na_2CO_3 addition, the temperature of the $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$ solution when Na_2CO_3 is added, the scale of the synthesis, and the method of drying the product. None of these additional variables (i.e., over and above the 12.6 equiv of base) produced any meaningful improvement in the ~90% purity of the resulting $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product, in Hornstein’s hands. Hornstein also reexamined the previous syntheses for converting $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ to $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, including Edlund’s 1988 procedure¹⁵ which was the basis for a checked 1997 publication¹⁸ in *Inorganic Syntheses*. He found no effect on the purity of the subsequent $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ when using that previous synthesis involving a $(\text{CH}_3)_4\text{N}^+$ salt reprecipitation step. We have corroborated herein that finding of the lack of any additional purification via the (unnecessary) $(\text{CH}_3)_4\text{N}^+$ salt reprecipitation step.¹⁹

Surprisingly and frustratingly, subsequent researchers in our group have struggled to achieve even 90% purity using Hornstein’s improved synthesis.⁹ A look back at all of the notebooks of those researchers shows that the purity attained averaged $82 \pm 7\%$ over 36 syntheses, with a range of purities between 68% and 89%, with only approximately one in four samples achieving Hornstein’s ~90% purity within experimental error. Hence, yet another, even more detailed look at the syntheses of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ was mandated: what is required to achieve the highest possible purity products in a synthesis that others can then also reproduce? The results presented herein required efforts over a 2-year period via more than 95 experiments, all despite the availability of the prior six syntheses in Table 1a and the three reports in Table 1b—again including three *Inorganic Syntheses* procedures.^{10,16,18} This by itself gives one an indication of the challenges of working with kinetically

Scheme 2. Route to $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ and the Other Known POMs along That Route (Reproduced from Hornstein et al.⁹ and References Therein with Permission)



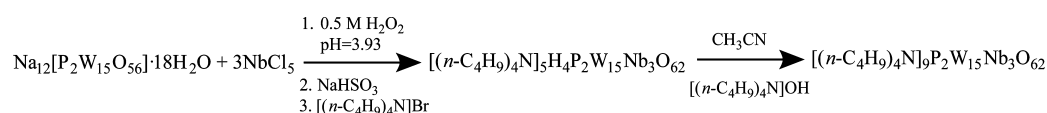
Scheme 3. Weiner's¹⁷ Synthesis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ from $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ 

Table 1. Literature Syntheses and Selected Experimental Details

(a) $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$					
author and reference	year	Na_2CO_3 addition	yield (%)	reported $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ purity	comments
Contant and Ciabrini (CC) ^{12,13}	1977	to pH 9	60	N/A	product thought to be $\text{P}_2\text{W}_{16}\text{O}_{59}^{12-}$
Finke, Droege, and Domaille (FDD) ¹⁴	1987	to pH 9 for 1 h	85	N/A	discovery that $\text{P}_2\text{W}_{16}\text{O}_{59}^{12-}$ is actually predominantly $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$
Edlund, Saxton, Lyon, and Finke (ESLF) ¹⁵	1988	to pH 9 for 1 h	83	>90	states that "probably produces impure ($\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$) material"
Contant's <i>Inorg. Synth.</i> (C-IS) ¹⁰	1990	12.6 equiv	62	N/A	states a $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ washing time of 1–2 min during workup
Randall, Droege, Mizuno, et al. (RDM) ¹⁶	1997	to pH 9 for 1 h	78	N/A	
Hornstein and Finke (HF) ⁹	2002	12.6 equiv	62	90	based on Contant's <i>Inorg. Synth.</i> , ¹⁰ Hornstein optimized five variables to find the best synthesis in his hands
This work (modified FDD)	2013	to pH 9 for 1 h	81	94–97	based on FDD ¹⁴ (above) with an improved $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ washing procedure; independently repeated and checked procedure
(b) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$					
author and reference	year	niobium(V) incorporation time	intermediate deprotonation time	reported $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ purity (%)	comments
ESLF ¹⁵	1988	until $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ dissolved (~10 min)	30 min	>98	published ³¹ P NMR S/N could have missed impurities ≤~8%
Weiner, Aiken, and Finke ¹⁷	1996	not provided	15 min	>95	published ³¹ P NMR S/N could have missed impurities ≤~5%
Nomiya, Pohl, Mizuno, Lyon, and Finke ¹⁸	1997	until $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ dissolved (~10 min)	30 min	not provided	
This work	2013	60 min	6 ± 2 h	91–94	³¹ P NMR S/N can detect impurities ≥~1%

precipitated powders of metastable intermediates such as $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ of less than 100% purity and where purification by crystallization proves unavailable.

Herein, we report the discovery that three sources of impurities in the synthesis are (i) a crucial—but previously inappropriately short and incomplete—*washing step* during the workup for $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$, a more thorough washing being required to remove all traces of Na_2WO_4 produced in the OH^- -induced degradation of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$, so that the resultant $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$ behaves as such and not like the additional tungsten-containing " $\text{P}_2\text{W}_{16}\text{O}_{59}^{12-}$ " as was first believed,^{9,12,13} (ii) insufficient time specified for the complete incorporation of niobium into the lacunary $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$, which requires at least 1 h to fully react, as well as the use of a slight excess (3.5 equiv) of niobium(V) to obtain the highest-purity final $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ product, and also (iii) not allowing a complete OH^- "titration" reaction of the protonated $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ intermediate with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$. Weiner et al.¹⁷ had reported that this titration required 15 min, but the complete reaction with OH^- can require more than 6 h to yield the purest product according to ³¹P NMR—a result that requires that there is more going on in this reaction with OH^- than a simple, facile deprotonation. With these discoveries, the present paper returns to, and solves synthetically, the now 25-year-old problem of producing high-purity $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$, a compound originally reported^{12,13} as " $\text{P}_2\text{W}_{16}\text{O}_{59}^{12-}$ " probably as a result of

the same difficulty of removing WO_4^{2-} that has continued to frustrate synthetic efforts (vide infra).

In addition, we report detailed checked procedures for both full- and $1/5$ -scale syntheses to obtain 91–94% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ by two independent researchers. We also examine a method of converting the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ to the sodium salt²⁰ $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ of the POM and find that repeated reprecipitations of this salt from acetonitrile/water can improve the purity of "failed" syntheses with purities as low as 74%, improving the purity of the resultant $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ up to ~89% purity, but at significant cost to the yield. Because the sodium salt has yielded single crystals²¹ (albeit in low yield), we also investigated the possibility of employing crystallization for further improvements in the purity of the final $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ product. Our efforts to date at bulk recrystallization of $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ have, however, proved unsuccessful.

The broader scientific and synthetic inorganic chemistry issues addressed herein include (i) how one can best and effectively work with kinetically precipitated powders of metastable intermediates such as $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$, especially when neither it nor any of the intermediates or products can be purified by recrystallization (at least to date). That is, finding each and every salient variable in the synthesis and use of such metastable, kinetically precipitated precursors has required slow, tedious, generally trial-and-error studies to bring syntheses to their highest level of purity and to make them

reproducible. The second, important issue addressed herein is (ii) the level of detailed reporting required to make such sensitive syntheses fully reproducible in others' hands *using only the written procedure*, as that is presently all that outside researchers typically can access. Indeed, the detailed experimental procedures, provided in the Supporting Information (SI), provide via underlining the additional details that proved required to make the procedure reproducible (i.e., over the prior written procedures). As such, the current contribution can perhaps serve as a training document, for beginning as well as more advanced polyoxoanion and other synthetic inorganic chemists, showing the written detail required to make a complex procedure reproducible in the hands of others—arguably one of the more important aspects of the present paper.

Finally, we dedicate this paper to the memory of Roland Contant because it is his insightful and creative 1977 work^{12,13} that led to the discovery¹⁴ of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$, the critical lacunary polyometalate precursor underpinning the syntheses that follow. Indeed, we believe Roland would have been pleased to see the understanding herein of the $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ kinetic precipitate, as well as the level of detail in the syntheses that follow, en route to striving for a truly reproducible synthesis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ in the highest purity and yield to date, reported in a highly detailed manner that proved reproducible when independently checked.

Construction of the Experimental Section Which Follows: Approach and Important Comments En Route to Reliable, Reproducible, Written Syntheses. It is well-known that getting 100% repeatable syntheses in written form is an enormous challenge in chemical science—witness the rise and value of *Inorganic Syntheses*, *Organic Syntheses*, and *Materials Syntheses*. Indeed, a recent editorial in *Chem. Eng. News*, titled “In Search of Good Recipes”,²² notes the general problem of obtaining and recording reliable, 100% reproducible synthetic procedures. That editorial focused on organic chemistry, where it is arguably less difficult to attain reproducible procedures than in the case of sometimes ultrasensitive POM self-assembly inorganic syntheses involving, for instance, kinetically precipitated ionic compounds, all where direct reaction monitoring (analogous to the invaluable use of ^1H NMR in organic chemistry) is not possible. Indeed, a followup letter to the editor²³ notes that “during the period 1982–2005 about 12% of the articles submitted to *Organic Syntheses* eventually had to be rejected because the results could not be reproduced”. The difficulty of, and hence the great need for, reproducible POM syntheses is why we,^{16,18} and others,^{10,24} have contributed a number of our POM syntheses to the checked procedure format of *Inorganic Syntheses*, although even those publications have not guaranteed a reliably reproducible procedure.¹⁹

Hence, we thought long and hard in the construction of this manuscript about how to obtain a *reproducible, written Experimental Procedure* all the way to the desired $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{Na}_3(1,5\text{-COD})\text{Ir}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})$. In the end, we decided on three key points for the Experimental Section that follows: (1) to make changes from the prior written procedures,^{9,14,17,25} *only* in those places where changes were experimentally shown to be absolutely needed (the reasoning here being that the prior wording was “checked” by many subsequent researchers attempting to repeat the synthesis; hence, introducing any *unneeded* wording changes to the

synthesis would, only and inevitably, tend to introduce errors into the procedure). We also decided then and therefore (2) to *copy exactly* the prior working of procedures (with references), but then use underlining to indicate any new procedures and changes, and importantly (3) to have the procedure *independently checked from the written procedure only* (in the same way that procedures for *Inorganic, Organic, and Materials Syntheses* are checked before publication, at least to start from the written procedure only). Additionally, and while not done herein, (4) we expect that producing truly 100% reliable chemical synthesis procedures in the future will best be accomplished by adding detailed videos, for example, in addition to the written procedures, for complicated syntheses (“a picture being worth a thousand words”). The reader interested in the problem of providing reproducible syntheses in general, and in inorganic POM chemistry in particular, will also want to see our earlier papers in the area,⁹ especially footnote 20 therein in light of the continued efforts needed herein to improve the synthesis even after that publication.⁹

■ EXPERIMENTAL SECTION

The reader using the syntheses and other procedures below will want to pay strict attention to every detail, reproducing the syntheses *exactly as written* to achieve the purest product in the highest yield. Because of their length and the (somewhat distracting) underlining, the fully detailed procedures are provided in the SI. However, the general descriptions of the syntheses, and importantly the general changes made, are described below so that the reader can focus on those key parts of the paper and its conclusions.

Materials. All compounds were ACS reagent grade and used as received. NaHSO_3 , HCl (35%), H_3PO_4 (85%), $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$, $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, NaClO_4 , LiClO_4 , KCl , NaVO_3 , Na_2CO_3 , NbCl_5 (stored in a Vacuum Atmospheres glovebox under a nitrogen atmosphere; ≤ 2 ppm O_2), H_2O_2 (30%, <6 months old, stored at 5 °C), Et_2O , NaOH , phenolphthalein (0.5 wt % in $\text{EtOH}/\text{H}_2\text{O}$), a $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ solution (40% in H_2O , <6 months old, stored at 5 °C, warmed to room temperature overnight before use), and absolute ethanol were used as received. D_2O and CD_3CN were obtained from Cambridge Isotope Laboratories in 1 g sealed glass ampules and transferred into a drybox before use. All aqueous solutions were prepared using 18 M Ω deionized water from a Nanopure filtration system.

Instrumentation. All pH measurements were made with a Beckman Coulter pH electrode attached to a Beckman Coulter PHI 510 pH meter. Prior to each experiment, the electrode was calibrated with two buffer solutions from HM Digital that spanned the range of pH being monitored: neutral, acidic, or basic (pH 4.01, 7.00, and 10.01, respectively). NMR spectra were obtained in CD_3CN or D_2O in 5.0-mm-o.d. NMR tubes. ^{31}P NMR spectra were collected on a Varian Inova 300 or 400 spectrometer and externally referenced to 85% H_3PO_4 (0 ppm). Thermogravimetric analysis (TGA) was performed on a TA Instruments 2950 thermogravimetric analyzer to determine the equivalents of H_2O present (ramp rate 20 °C/min to 250 °C and then isothermal for 10 min). Elemental analyses were obtained from Galbraith Laboratories.

Syntheses for the Production of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. 1. *Synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$.* This synthesis was performed according to the Nadjo method,²⁶ at the larger 300 g scale described by Graham.²⁵ An exact copy of that procedure is deliberately reproduced in the SI of this paper for the convenience of the interested reader. Worth noting is that this relatively simple synthesis was, itself, optimized only more recently from six prior syntheses that span an 88 year period—that is, the details of that synthesis should be followed exactly. The purity of recrystallized $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ was verified by ^{31}P NMR (12.1 ppm, >99%). Yield: 193.4 g (79%). Note that after formation of the Wells–Dawson $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ POM, all transfers and

procedures should be performed with nonmetal tools such as plastic or ceramic spatulas, as previously advised,²⁷ to avoid production of reduced, tungsten(V)-containing heteropolyblues.²⁸ TGA on the product revealed 14 equiv of H₂O except in cases of drying times longer than ~12 h at 50 °C and ambient pressure, which produce the less solvated, and thus slightly hygroscopic, product with 9–12 equiv of H₂O.

II. Modified Hornstein et al. (Modified-HF) Synthesis of Na₁₂[α-P₂W₁₅O₅₆]·18H₂O Involving More Extensive Washing. This procedure was reproduced as reported by Hornstein,⁹ except that to obtain the 90% or better purity in subsequent steps, a more extensive washing procedure was added, which involved mixing each wash with a plastic spatula for at least 10 min until the product was fully suspended. Additionally, two washes with 50 mL of deionized water were added to the washing procedure after washing with NaCl and before washing with ethanol. The full detailed procedure is provided in the SI, with the changes in the procedure deliberately underlined. Yield: 13.7 g, 41%. The crumbly white Na₁₂[α-P₂W₁₅O₅₆]·18H₂O has a purity of 97%, as determined by conversion to K₈H[P₂W₁₅V₃O₆₂]·9H₂O (procedure IV herein, vide infra) or 93% by conversion to [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ by our optimized synthesis (procedure VI herein, vide infra).

III. Modified Droege et al. (Modified-FDD) Synthesis of Na₁₂[α-P₂W₁₅O₅₆]·18H₂O Involving More Extensive Washing. The Na₁₂[α-P₂W₁₅O₅₆]·18H₂O synthesis was carried out exactly as reported by Droege et al.¹⁴ except for changes in the scale of the reaction, the washing procedure, and the drying method, all as detailed in the SI. The synthesis was run at 6 times the reported scale, using 120 g of K₆[α-P₂W₁₈O₆₂]·14H₂O, and was dried in an oven because Hornstein showed that the scale and drying method do not affect the purity of the product.⁹ A more intensive washing procedure was used, involving mixing the product and wash solutions for 10 min with a plastic spatula to fully suspend the precipitate and allow removal of Na₂WO₄. Additionally, two washes with 300 mL of deionized water were added to the procedure using the same 10 min washing procedure cited directly above. The full and detailed procedure is presented in the SI, with the changes in the procedure deliberately underlined. The yield was 87.1 g of crumbly white solid (81% yield vs 85% before¹⁴ the enhanced washing procedure) and produced Na₁₂[α-P₂W₁₅O₅₆]·18H₂O with a purity of up to 96%, as determined by conversion to K₈H[P₂W₁₅V₃O₆₂]·9H₂O (procedure IV herein, vide infra) or up to 94% by conversion to [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ by our optimized synthesis (i.e., by procedure VI herein, vide infra), meaning that the conversion of the Droege Na₁₂[α-P₂W₁₅O₅₆]·18H₂O to [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ was accomplished by the Weiner method¹⁷ with the improvements discovered and described herein (i.e., and *not* by the conversion to [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ reported by Droege et al.¹⁴).

IV. Synthesis of K₈H[P₂W₁₅V₃O₆₂]·9H₂O. Starting with Na₁₂[α-P₂W₁₅O₅₆]·18H₂O obtained using both the modified-HF and modified-FDD syntheses (procedures II and III, vide supra), the water-soluble K₈H[P₂W₁₅V₃O₆₂]·9H₂O vanadium adduct was produced as an additional method for checking the purity of Na₁₂[α-P₂W₁₅O₅₆]·18H₂O. K₈H[P₂W₁₅V₃O₆₂]·9H₂O was produced by the literature procedure as described by Hornstein⁹ and in 96–97% purity by ³¹P NMR for Na₁₂[α-P₂W₁₅O₅₆]·18H₂O starting materials prepared by both the modified-HF and modified-FDD procedures.

V. Weiner's Synthesis¹⁷ of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂. Starting with Na₁₂[α-P₂W₁₅O₅₆]·18H₂O obtained using both the modified-HF and modified-FDD syntheses (Table 1a and procedures II and III, vide supra), the synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ was performed using the improved methods described by Weiner et al.¹⁷ with the exception of correcting a typo⁹ for the concentration of H₂O₂ and allowing 1 h for niobium(V) incorporation (Weiner's published procedure¹⁷ does not suggest a time for this reaction). The full details of the synthesis, including additional observations and details, are presented in the SI with any changes in the procedure underlined. Yield: 25–29.6 g, 55–66%. The purity is 90 ± 1% based on conversion to [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ (procedure IX herein, vide infra)

using Na₁₂[α-P₂W₁₅O₅₆]·18H₂O from both the modified-HF and modified-FDD, procedures II and III, respectively.

VI. Optimized Syntheses of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ for 91–94% Purity. This synthesis employed Na₁₂[α-P₂W₁₅O₅₆]·18H₂O obtained by the modified-FDD method (Table 1a and procedure III, vide supra). The procedure is identical with Weiner's improved synthesis¹⁷ (procedure V, vide supra) except that 8.00 g of NbCl₅ (30 mmol, 3.50 equiv, vs Na₁₂[α-P₂W₁₅O₅₆]·18H₂O) was added to 650 mL of 1.63 M H₂O₂ (rather than 0.5 M H₂O₂⁹). Additionally, extra NaHSO₃ was required to destroy the excess hydrogen peroxide, so 121.4 g (1.16 mol, 1.1 equiv, vs H₂O₂) was added over 60 min as quickly as possible while monitoring the temperature of the solution to ensure it never exceeded 65 °C. The solution was then allowed to stir for 30 min before [(n-C₄H₉)₄N]₉Br was added, and the rest of the procedure was carried out as in the literature synthesis in procedure V. The yield is 65%, and the purity of the titrated [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ product (as performed in procedure IX) is 91–94%, as determined by ³¹P NMR. Elem anal. Calcd (found) for [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂: C, 27.57 (27.19); H, 5.21 (5.24); N, 2.01 (1.98); P, 0.99 (0.77); W, 43.96, (41.40, reanalyzed 42.25); Nb, 4.45 (4.55). Full detailed experimental procedures are presented in the SI with the exact changes from previous methods denoted by underlining.

VII. Small-Scale ¹/₅ Synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ with the Optimized Method for 92% Purity. This synthesis employed Na₁₂[α-P₂W₁₅O₅₆]·18H₂O obtained by the modified-FDD method (Table 1a and procedure III, vide supra). The ¹/₅-scale synthesis follows the procedure for the optimized synthesis with every reagent and solution scaled to 20% of its value. The checked procedure produces 92% pure [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ in a similar 66% yield. The full and detailed procedure is available in the SI.

VIII. Control Experiments Testing Other Variables in the Synthesis of [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂. VIII-A. Control Synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ in Which Na₁₂[α-P₂W₁₅O₅₆]·18H₂O Is Allowed to Dissolve Completely but Is Not Stirred for 1 h (as Discovered and Recommended in the Improved Synthesis Herein). The Weiner synthesis,¹⁷ with the refined procedures herein that achieve up to 94% purity [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂, was carried out as described in procedures V and VI, but Na₁₂[α-P₂W₁₅O₅₆]·18H₂O (prepared by the modified-FDD, procedure III, vide supra) was deliberately allowed to stir for only 5 min after it had fully dissolved (10 min total stirring after the addition of Na₁₂[α-P₂W₁₅O₅₆]·18H₂O) and before beginning the addition of NaHSO₃. With 10 min for niobium(V) incorporation, [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ produced using procedure V was 85% pure (vs 90% for when stirring for 1 h). When using the optimized procedure VI but with 10 min for niobium(V) incorporation, the purity was 89% (vs 91–94% pure when stirring for 1 h).

VIII-B. Control Synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ with 1 equiv of Added Na₂WO₄. To determine if Na₂WO₄ could affect the synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂, 2.4 g of Na₂WO₄ (8 mmol, 1 equiv) was mixed with 36 g (8 mmol) of well-washed (vide supra) Na₁₂[α-P₂W₁₅O₅₆]·18H₂O (prepared by the modified-FDD, procedure III, vide supra) that had previously been used to synthesize >90% pure [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂. That mixture of 1:1 Na₂WO₄:Na₁₂[α-P₂W₁₅O₅₆]·18H₂O was then used in the synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ by procedure V. The purity of the resulting [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ was <75%, as determined by ³¹P NMR.

VIII-C. Control Synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ with a Deliberate Deficit of Niobium(V). To test what impurities are formed if one deliberately uses less than the literature reported 3.05 equiv of niobium(V), the Weiner et al.¹⁷ [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ synthesis was completed as described in procedure V (and using Na₁₂[α-P₂W₁₅O₅₆]·18H₂O prepared by the modified-FDD, procedure III, vide supra) but now using 4.56 g of NbCl₅ (2.00 equiv rather than 3.05 equiv vs P₂W₁₅O₅₆^{12–9}). This produced [(n-C₄H₉)₄N]₉P₂W₁₅Nb₃O₆₂ with a purity of <27% by ³¹P NMR.

VIII-D. Control Synthesis of [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ with Both Added Na₂WO₄ and a Deficit of Niobium(V). The literature [(n-C₄H₉)₄N]₅H₄P₂W₁₅Nb₃O₆₂ synthesis¹⁷ (procedure V, using

$\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ prepared by the modified-FDD, procedure III, vide supra) was carried out except with 2.4 g of Na_2WO_4 (8 mmol, 1 equiv) added to the well-washed $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ powder and with only 4.56 g of NbCl_5 (2.00 equiv vs $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$). This experiment produces almost no $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ (<7%), as determined by ^{31}P NMR.

IX. Deprotonation of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ to $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. **IX-A. Literature Titration of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$.** Deprotonation of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ (prepared by procedure V, using $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ prepared by the modified-FDD, procedure III, vide supra) was performed by titration with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ against a phenolphthalein indicator. The literature procedure¹⁷ was followed exactly except for the following details: (i) The solution was allowed to equilibrate until no “titration peaks” (vide infra) were visible in the ^{31}P NMR spectra, which required 6 ± 2 h. (ii) The titration was carried out in a Vacuum Atmospheres drybox with a nitrogen atmosphere in a 100 mL round-bottomed flask sealed with a rubber stopper to avoid wasting argon during this lengthened procedure. (iii) $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ was added through the stopper with a 1 mL gastight syringe while the solution was stirred. After the titration end point, where the solution remained pink for at least 6 h, the sample was dried at room temperature under vacuum at <640 mmHg overnight and the purity of the product was checked by ^{31}P NMR to ensure that there were no titration impurities (vide infra). Then, a large-scale deprotonation of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ from the same synthesis as that used for the titration was carried out in the absence of phenolphthalein, using the experimentally determined ratio of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ to $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ derived from the small-scale titration. Deprotonated $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ (actually $[(n\text{-C}_4\text{H}_9)_4\text{N}]_{9-x}\text{H}_x\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ where “x” is determined by the equivalents of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ required to deprotonate the sample) was dried overnight at room temperature under a vacuum of <640 mmHg to produce the solid white $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product. Syntheses of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ should be used within 2 weeks or regularly checked by ^{31}P NMR because it can degrade even when stored in air-free or low-temperature conditions, as previously reported.¹⁷ A detailed experimental description is provided in the SI with changes in the synthesis underlined to indicate any differences in wording or the procedure from the prior literature.

IX-B. ^{31}P NMR Titration of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ Employed Herein. Samples of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ (150.0 mg, 28.3 mmol, prepared by procedure V, using $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ prepared by the modified-FDD, procedure III, vide supra) were placed in 5-mm-o.d. NMR tubes in the drybox. CD_3CN (0.8 mL) was added to each sample along with 2 drops of phenolphthalein. The NMR tubes were sealed with airtight rubber stoppers and removed from the drybox. $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ (0.692 M) was added to the NMR tubes dropwise at a rate of ~ 1 drop every 5 s with a 50 μL syringe by injection through the stopper. The NMR tube should be shaken after every drop because a faster addition rate or incomplete mixing produces a ^{31}P NMR impurity at 7.0 ppm relative to 85% H_3PO_4 . The titration is continued until both the pink phenolphthalein end point remains for 6 ± 2 h and there are no remaining “undertitration peaks/impurities” visible by ^{31}P NMR (defined as the -8.15 and -13.2 ppm peaks; Figure 1, vide infra). To demonstrate the commensurate end point by phenolphthalein and ^{31}P NMR, as well as the time to reach the “true” end point, a series of samples were slightly under- or over-titrated by this method and examined for color and by ^{31}P NMR. Five samples of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ with an end point of 3.30 equiv of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$, carefully determined in a prior independent experiment, were titrated with 3.15, 3.20, 3.25, 3.30, and 3.35 equiv of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$, respectively, chosen to bracket the previously determined true end point. The samples were each examined by ^{31}P NMR after 15 min, 2 h, and 6 h to quantitatively determine the amount of impurity resulting from undertitration; each sample was also photographed at these three times to demonstrate when the phenolphthalein indicator remained pink and when it turned clear,

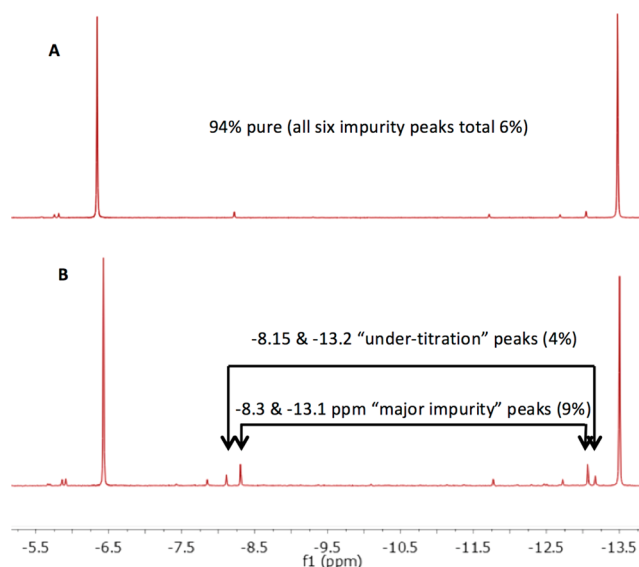


Figure 1. ^{31}P NMR spectra ($S/N = 17$ for the small peaks): (A) best 94% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ currently available from procedure VI in the Experimental Section. The six small peaks make up a total of 6% impurity. (B) Example of an 81% purity sample obtained from the Hornstein and Weiner literature syntheses^{9,17} without any of the improvements described herein. Each impurity produces a pair of peaks as expected for POMs containing two distinct phosphorus atoms. Two identifiable sets of impurity peaks here are the “major impurity” peaks at -8.3 and -13.1 ppm (9% impurity) and the “undertitration” peaks at -8.15 and -13.2 ppm (4% impurity). The remaining five peaks account for an additional 6% impurity.

with persistent pink indicating a complete titration. The results of these experiments are reported in Table 4, and the photographs are available in the SI.

X. Synthesis of the Sodium Salt $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\cdot 23\text{H}_2\text{O}$ from Impure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. This synthesis²⁰ of $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ used the more convenient $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ from the Weiner et al.¹⁷ synthesis rather than the previously employed $[(n\text{-C}_4\text{H}_9)_4\text{N}]_{12}\text{H}_4\text{P}_4\text{W}_{30}\text{Nb}_6\text{O}_{123}$ precursor described by Edlund et al.¹⁵ Specifically, 14.9 g (2.5 mmol) of white, impure (78%) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ prepared by literature^{9,17} methods (i.e., without the washing and other improvements reported herein) was dissolved in 270 mL of CH_3CN and heated to 60°C . Next, 2.5 g of NaBF_4 (22.22 mmol, 9.3 equiv) was added to the rapidly stirring solution and allowed to stir at 60°C for 15 min while NaBF_4 dissolved and the solution turned opaque and white. The solution was allowed to cool with stirring for 10 min, and then 30 mL of deionized water was added dropwise at ~ 1 drop per 1 s to form a thick white oil, which settled to the bottom of the beaker. The solution was allowed to settle over 10 min, and the top solution was decanted off, leaving the oily, acetonitrile-insoluble $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. The oil was triturated three times with 40–50 mL of acetonitrile by mixing with a plastic spatula, and the white solid was collected on a fine frit and dried at 55°C to produce 7.7 g (73% yield) of $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\cdot 23\text{H}_2\text{O}$ (87% purity by ^{31}P NMR in D_2O). The fine white powder $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\cdot 23\text{H}_2\text{O}$ can be reprecipitated to further improve its purity up to 89% by dissolving in 15–30 mL of deionized water followed by the dropwise addition of 10–15 times more acetonitrile than the 15–30 mL of water. This again forms a thick white oil, which is triturated with 30–50 mL of acetonitrile, collected on a fine frit, and dried at 55°C to produce 5.2 g, 49% total yield. ^{31}P NMR primary peaks are at -7.2 (1.0 P) and -13.7 (1.0 P) in D_2O (purity 89%). While this procedure does improve the purity of impure samples, it does not produce a superior purity compared with the optimized direct synthesis, procedure VI described herein. Additionally, this is not a viable route to purify the organic soluble $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salt because one would then have to go to the sodium

Table 2. Purity of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ Made from $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ Produced by Methods with Different Washing Procedures

$\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ synthesis	yield of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ (%)	purity by conversion to $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\cdot 9\text{H}_2\text{O}$ (%)	purity by conversion to $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ using the nonoptimized procedure V (%)
FDD synthesis as written	85	NA	71
HD synthesis as written	65	NA	83
modified-FDD synthesis (with two extra washes) (this work)	81	96 ± 1	90 ± 1
modified-HD synthesis (with two extra washes) (this work)	41	97 ± 1	90 ± 1

salt and then back to the $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salt, adding two steps and losing material en route to a lower yield along the way. Attempts to recrystallize the sodium salt as a method of bulk purification were tried but were not successful, as discussed in the SI.

XI. Checking the Solubility of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ Product. Using $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ produced from our improved synthesis (procedure VI), we tested the solubility of the well-dried product by dissolving it in water. To repeat Weiner's experiment on the solubility,¹⁷ two samples, each from independent syntheses of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ precursor, were added in ~30 mg portions to 40 mL of nanopure deionized water while stirring with a plastic spatula. After each addition, the solution was stirred for ~2 min while the crushed white powder dissolved. After each addition, the pH of the solution was checked. Above a concentration of ~1.1 mM, the pH of both solutions had leveled off (at 9.2 and 7.25, respectively), and ~0.8 mL of each solution was pipetted to an NMR tube along with ~10% D₂O and analyzed by ³¹P NMR to produce low S/N spectra with the two distinct and expected lines. To test higher concentrations, more suitable for NMR analysis, 0.55 g (0.1 mMol) of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ was added to 10 mL of nanopure deionized water and stirred for ~10 min with a plastic spatula to produce a nearly colorless, but very slightly milky, ~8.8 mM solution. A total of ~0.8 mL of this solution was pipetted to an NMR tube, and ~10% D₂O was added. ³¹P NMR of the solution showed the expected two-line spectra with the same impurities as the starting compound. All samples had their primary peaks at -7.3 and -13.8 ppm, with the higher-concentration solution showing significantly improved S/N. These peaks are notably different from those reported by Weiner et al.¹⁷ (at -9.4 and -15.9 ppm for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ in D₂O) but closely match the solution NMR of $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ in D₂O (±0.1 ppm).

Independent Checking of the Procedures by a Second Researcher. A key part of the experimental procedures in this paper is that they have been checked by another researcher (Dr. Özkär) working solely from the written methods, as is typical, for example, for publications in *Inorganic Syntheses*. Even when the draft procedure provided at the time was followed, oversight on a few key details meant that it took two attempts for a collaborating researcher to repeat these results at the full scale—with the needed additional details now being provided as part of the detailed procedures provided in the SI. Details that were added as a result of that checking included items such as the exact volume of the wash solution for $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$, using a mixture of 95% ethanol and 5% water for the wash, ensuring that $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ is fully suspended in the wash solutions (so that no portion of the precipitate settles out faster than the rest), and the exact times required for each step. Once the finalized written directions were then followed to the letter, a second researcher (Dr. Özkär) was also able to produce $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ with 91–92% purity on both the small, 1/5-scale and “full-scale” syntheses detailed herein.

RESULTS AND DISCUSSION

Careful Washing of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ Is Essential to the Production of 91–94% Pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. Hornstein⁹ followed Contant's synthesis¹⁰ and recommendation of 1–2 min of washing for

each of three sequential washes on the collected $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$, washing once with 25 mL of a saline solution and then twice with 25 mL of ethanol. However, the thick claylike material that remains on the glass frit after collection takes substantially longer to be properly mixed during washing. Washing for only 1–2 min leaves small chunks of material that are not easily broken up in that time. If the reaction product Na_2WO_4 (see Scheme 1) does not get washed out in the single 1–2 min wash with a saline solution, it remains in $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ and is then carried through the synthesis because it is largely insoluble in the ethanol wash. The 1–2 min saline wash originates from the desire to prevent decomposition of the metastable product (recall Scheme 2), but prevents full dispersal of the product during washing because up to 10 min of vigorous stirring with a plastic spatula is required to fully break up the claylike chunks of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$, thereby fully suspending it in solution for a more efficient and more complete washing. Hence, two extra washes with deionized water were added to the workup of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$, in addition to a longer suggested washing time. In short, the 1990 *Inorganic Syntheses*¹⁰ and then repeated 2002⁹ recommendations for just 1–2 min washings of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ have proven to be pretty much 180° off-path of the best synthesis, misdirections that have taken an additional 14 years to correct.

Interestingly, despite concerns about decomposition of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ in solution, we find that the precipitated $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ solid can be subjected to two additional 10 min washes with deionized water, where it is fully suspended, and then collected on a medium frit, to completely remove the unwanted reaction products at a small cost to yield (81% vs 85%). No new impurities are introduced, at least as detectable by ³¹P NMR of the subsequent $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ or $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]\cdot 9\text{H}_2\text{O}$. Also noteworthy here is that, when first discovered, a high tungsten elemental analysis led world-class POM experts to conclude at the time^{12,13} that the product was the ditungsten-vacant “ $\text{P}_2\text{W}_{16}\text{O}_{59}^{12-}$ ”. Subsequent investigations later²⁹ showed that the product is best formulated as mostly $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$, but we can now add that the simplest/best explanation of all of the data³⁰ available to date is that the poorly washed product is $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ contaminated with WO_4^{2-} .

A washing procedure that fails to fully remove interfering compounds from $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ can also explain why Hornstein found⁹ that limiting the amount of Na_2CO_3 to 12 equiv produced the best-quality material in his hands. Hornstein's preferred method produces a significantly lower yield than the modified-Droege synthesis developed and recommended herein, procedure III (65% vs 81% yields, respectively). As a result of the lower yield, the reaction is expected to produce less Na_2WO_4 byproduct (recall Scheme 1)

and, perhaps most importantly, less material that needs to be washed for the volume of saline that was employed. The combination of these effects would, in turn, make the Na_2WO_4 product easier to remove during a shorter washing period.

While investigating the importance of washing, we reexamined a previous $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ synthesis, namely, the Droegge et al. synthesis¹⁴ (FDD in Table 1a) with its superior 85% yield, which Hornstein discarded⁹ because it only produced 65–83% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ in his hands. The original FDD synthesis employs the addition of carbonate to pH 9 without regarding the exact amount (usually requiring 15–20 equiv of carbonate per $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$). We now find that when the $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ solid is fully suspended in the NaCl washing solution for 10 min by vigorous stirring with a plastic spatula, followed by two similar washes with deionized water, the resultant modified-FDD and modified-HF syntheses produce equally pure $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ by conversion to both $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ and $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \cdot 9\text{H}_2\text{O}$. This is only true when both procedures use the reformulated intensive washing procedure (as shown in Table 2 herein). Furthermore, the production of 96–97% pure $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}] \cdot 9\text{H}_2\text{O}$ (as judged by ³¹P NMR) from well-washed $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ strongly suggests that there is little or no decomposition when *solid* $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ is washed in deionized water. With adequate washing steps, both the modified-HF and modified-FDD syntheses produce equally pure products within experimental error. However, the modified-FDD synthesis gives the highest yield of 81% even when two extra washes with deionized water are included, making the modified-FDD synthesis the preferred synthesis for the production of $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$, at least in our hands.

Impurities in the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ Product.

Figure 1A displays the ³¹P NMR spectrum of the best 94% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ produced by the best optimized synthesis described by procedure VI in the Experimental Section using 1.63 M H_2O_2 and 3.5 equiv of niobium(V). This is contrasted with Figure 1B to show the location of impurities in a typical “impure” sample of 81% purity, produced via the previous literature synthetic method¹⁷ (i.e., without any of the washing or other insights provided herein).

Impurity Detected at –8.3 and –13.1 ppm Resulting from Residual WO_4^{2-} , Inadequate Niobium(V), or Too Little Time for Niobium(V) Incorporation. The twin-height ³¹P NMR peaks at –8.3 and –13.1 ppm (Figure 1) historically represent the largest impurity in the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ synthesis. These two peaks have averaged $11 \pm 6\%$ across 36 syntheses by four researchers in our group. Determining the identity of this impurity, its origin, and how to prevent its formation proved critical to producing the purest $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$.

Table 3 presents the results of control experiments on the variables that affect this impurity. The first two entries are reference points of experiments already presented (in Figure 1A and Table 2, respectively). In entry 3, the time allowed for the step in which niobium(V) is incorporated into the lacunary $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ polyoxoanion is deliberately limited. When only 10 min is allowed for the niobium(V) incorporation step, as explicitly described in several of the literature syntheses^{15,17,18} (and as reproduced in procedure VIII-A of the Experimental Section of the present paper), the impurity detected at –8.3 and –13.1 ppm is increased from 6% in the equivalent synthesis to 9% when insufficient time for niobium(V) incorporation is used.

Table 3. Experimental Tests of the Sensitivity of the Impurity Detected at –8.3 and –13.1 ppm to the Conditions of Niobium(V) Incorporation

experimental test	impurities at –8.3 and –13.1 ppm (%)	all impurities (%)
(1) procedure VI: optimized synthesis using 3.5 equiv of niobium(V)	3	6
(2) procedure V: literature synthesis ¹⁷ using 3.05 equiv of niobium(V)	6	11
(3) procedure VIII-A: literature synthesis ¹⁷ with only 10 min for niobium(V) incorporation	9	15
(4) procedure VIII-B: extra 1 equiv of Na_2WO_4	17	25
(5) procedure VIII-C: only 2 equiv of niobium(V)	47	75
(6) procedure VIII-D: extra 1 equiv of Na_2WO_4 and only 2 equiv of niobium(V)	61	93

A second variable that affects the impurity at –8.3 and –13.1 ppm is the presence of residual WO_4^{2-} . This is demonstrated in entry 4 of Table 3, where we deliberately added 1 equiv (6.4% by mass) of Na_2WO_4 (procedure VIII-B in the Experimental Section) to well-washed $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$, which had previously been used to make ~90% pure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. The resulting $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ was, as anticipated, contaminated with the –8.3 and –13.1 ppm detected, “major impurity” at nearly triple the amount, 17% compared to 6% in the equivalent synthesis without the added WO_4^{2-} (Table 3, entry 4 and its comparison to entry 2). These data offer further support the hypothesis that inadequately washed $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ contains Na_2WO_4 as a byproduct of the synthesis of $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ from $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ (Scheme 1, vide supra).

Furthermore, if niobium(V) is deliberately restricted to only 2 equiv, Table 3, entry 5, shows that 47% of the product is formed as the impurity at –8.3 and –13.1 ppm. Using 2 equiv of niobium and adding 1 equiv of Na_2WO_4 produce 61% impurity and just 7% of the desired $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$. It was these observations which provided the insight of using 3.5 equiv of niobium and a more concentrated H_2O_2 solution (procedure VI), which reduces the peaks at –8.3 and –13.1 ppm to only 3%, as shown in entry 1 of Table 3.

These results demonstrate that the impurity detected at –8.3 and –13.2 ppm arises when excess tungsten(VI), a lack of niobium(V), or insufficient time for niobium incorporation is present. A combination of two of these can misdirect the synthesis to produce only 7% of the desired $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ product and 93% impurities! The presence of three factors, each of which individually can give rise to the impurity detected by the –8.3 and –13.2 ppm peaks, helps to further explain why the optimized synthesis has been so difficult to pin down—especially when combined in earlier syntheses with residual, variable WO_4^{2-} due to an incorrect 1–2 min washing procedure with minimal volumes of wash solution.

Incomplete Titration of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ Giving Rise to the NMR Peaks Detected at –8.15 and –13.2 ppm (“Undertitration Impurities”). Upon examination of 36 previous syntheses of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ within our group, it was found that ca. 60% have a set of ³¹P NMR peaks at –8.15 and –13.2 ppm referenced to 85% H_3PO_4 . These variable peaks average 7% when present and range from 0% to 14% of the integrated area. Unlike other

impurity peaks in the spectrum, these peaks change upon retitration of the same sample of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. Furthermore, once a sample is retitrated completely, the primary NMR signals for the desired $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ product increase, suggesting that the -8.15 and -13.2 peaks represent a protonated (or otherwise hydroxide-sensitive) intermediate.

In his improved synthesis for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, Weiner¹⁷ gave his procedure for deprotonation of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ by titration with 4 equiv of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ to a phenolphthalein end point. Weiner stressed that reproducible titrations require ensuring that the titration end point remained visible for at least 15 min. Furthermore, he stressed caution when approaching the end point of the titration because¹⁷ “Each drop of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ solution (0.02 mL) added beyond the true end point results in an approximately 8% excess of OH. As shown, this is a sufficient excess to affect significantly the support of organometallic cations; hence, we urge that care be taken when approaching the end point in the titration.”

Herein, we find that these peaks at -8.15 and -13.2 ppm can take up to 8 h to be fully removed during a careful phenolphthalein titration. We used periodic direct monitoring of these impurity peaks by ^{31}P NMR while titrating to a phenolphthalein end point in an NMR tube and discovered that reaching the end point of the titration takes significantly more time than the previously reported “at least 15 min”. In fact, it can require more than 6–8 h for the pink color of the phenolphthalein end point to persist, indicating a stable pH—one that coincides with the complete removal of the peaks at -8.15 and -13.2 ppm in the ^{31}P NMR spectra. Note that we presume that such a long equilibration time indicates that the underlying chemistry is not just an unprecedentedly slow H^+ -transfer reaction. Rather, we presume that OH^- -dependent polyoxoanion chemistry is occurring, which, in the end, gives purer $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ product, at least by ^{31}P NMR.

As part of the key experiments in this section (procedure IX-B of the Experimental Section), 150 mg samples of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ were added to NMR tubes with acetonitrile and phenolphthalein. Enough $(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ was added to each sample to reach 95.5%, 97.0%, 98.5%, 100%, or 101.5%, respectively, of a carefully predetermined end point on that sample in an independent experiment (see procedure IX-B). Each sample was observed visibly (i.e., to record the color of the indicator) after 15 min, 2 h, and 6 h. Each sample was also observed by ^{31}P NMR starting at 15 min, 2 h, and 6 h. However, because it takes ca. ~ 30 min to obtain a ^{31}P NMR spectrum with a high enough S/N ratio to see peaks of $>1\%$, the reported undertitration peak amounts at -8.15 and -13.2 ppm in the ^{31}P NMR are unavoidably lower limits to what is being observed at 15 min, 2 h, and 6 h by the phenolphthalein end point.

The results in Table 4 show that even samples apparently remaining at a phenolphthalein end point for over 2 h (and after ~ 2.5 h including the ^{31}P NMR analysis time) still have peaks at -8.15 and -13.2 ppm of up to 6%. The data show that following the literature procedure¹⁷ of waiting for the titration end point to remain pink for 15 min results in samples containing up to 12% of these “undertitration” peaks. The discrepancy between the literature procedure (~ 15 min), and the 6 ± 2 h required to reach the true end point in at least two of our hands (WWL and SÖ), can explain why $>60\%$ of past

Table 4. ^{31}P NMR Peaks at -8.15 and -13.2 ppm after 15 min, 2 h, and 6 h^a

	amount of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ added as a percentage of the “true” end point (as determined by a previous titration)				
	95.5%	97.0%	98.5%	100.0%	101.5%
after 15 min (color)	dark pink	dark pink	dark pink	dark pink	dark pink
after ~ 45 min, % of undertitration peaks by ^{31}P NMR	12	7	6	6	0
after 2 h (color)	clear	light pink	light pink	light pink	pink
after ~ 2.5 h, % of undertitration peaks by ^{31}P NMR	8	6	5	3	0
after 6 h (color)	clear	clear	clear	slightly pink	pink
after ~ 6.5 h, % of undertitration peaks by ^{31}P NMR	8	5	3	0	0

^aNote that, after 2 h, samples titrated to 97% and 98.5% of the end point appear to be at the pink phenolphthalein end point, but still contain significant undertitration peaks at -8.15 and -13.2 ppm even after coming to equilibrium after 6 h.

samples retain peaks at -8.15 and -13.2 ppm—chronic undertitration of the samples was present.

The solutions that are slightly pink after 6 h show no detectable peaks at -8.15 and -13.2 ppm by ^{31}P NMR—and will stay slightly pink for days. Because of the long equilibration time, performing the titration under an argon stream, as recommended in the literature,¹⁷ is less practical. Hence, the recommended titration method provided herein involves keeping the samples in a nitrogen-filled drybox (procedure IX-A) or using a small sample of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ (~ 150 mg) in an airtight NMR tube and titrating it with a microsyringe, all as detailed in the Experimental Section (procedure IX-B). Titrating the sample in an NMR tube also allows the sample to be immediately checked by ^{31}P NMR, and samples can be left overnight to equilibrate without any detectable degradation. Furthermore, these techniques provide better isolation from atmospheric carbon dioxide, which, if present, will interfere with the titration’s end point.

Note that when NMR is run on samples directly titrated in the NMR tube (and not dried and redissolved in acetonitrile), the presence of water from phenolphthalein and aqueous $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ shifts all of the peaks in the spectrum relative to the positions obtained when a thoroughly dried product dissolved in neat acetonitrile is used. These shifts are given in the SI, Table S1.

Check of the Water Solubility of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. Weiner et al. reported that $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ is soluble in 25 °C water,¹⁷ reporting aqueous solutions with concentrations of up to 48.4 mM. A reviewer commented that material that they had made by prior procedures was not soluble in water, so we reexamined the solubility of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ produced by our optimized synthesis herein (procedure VI) in 25 °C nanopure deionized water. We were able to dissolve $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ from two independent syntheses to produce at least 8.8 mM aqueous solutions with ~ 5 – 10 min of stirring with a plastic spatula; hence, we can confirm Weiner et

al.'s report that $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ is reasonably soluble in room temperature water. ^{31}P NMR analysis confirms that these solutions produce the characteristic two-line spectra and are stable in solution for at least 3 h.³¹

CONCLUSION

The results of our further investigations into the syntheses of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ reveal that, despite concerns about the stability of the metastable intermediate $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$, thoroughly washing the solid product at least twice with deionized water is required for a reproducible 91–94% purity synthesis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. Residual WO_4^{2-} in inadequately washed $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ is implicated as the single most important, previously confounding, factor in providing reproducible, higher-purity $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. This, in turn, provided the insight that using a slightly larger amount of NbCl_5 (3.5 vs 3.05 equiv originally) yields a small, but detectable, 1–4% increase in the maximum purity of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ as well as a more reliable and demonstrably repeatable synthesis. Evidence was also presented for chronic undertitration of tetraprotonated $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. The end result is a synthesis reported in a very high level of detail, which has been independently checked to ensure its repeatability and which yields 91–92% purity $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ for the reported $1/5$ scale and 91–94% purity for the full-scale, ~ 29 g syntheses.

Of historical interest here is that the difficulties with the synthesis and purification of $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$ and $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ validate completely our original approach^{27,29} of attempting first to use crystalline $\beta\text{-SiW}_9\text{O}_{34}^{10-}$ to prepare clean $\beta\text{-SiW}_9\text{Nb}_3\text{O}_{40}$ as an alternate system for supporting organometallics and developing their resultant catalysis. Unfortunately, support of organometallic cations occurs at the lower C_s symmetry, B site of the $\text{SiW}_9\text{Nb}_3\text{O}_{40}^{7-}$ POMs,²⁷ which led, in turn,¹⁵ to our use of B- $\alpha\text{-P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ as the still preferred, higher C_{3v} symmetry, support material.

The results herein take on added significance in that they, along with the earlier eight separate studies in Table 1a,b spanning 36 years, tell a cautionary tale of the problems—and the extensive, trial-and-error experimentation it can take to overcome those problems—of working with kinetically precipitated, metastable, often somewhat impure powders such as $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ in POM chemistry specifically, and in inorganic chemistry in general. If bulk crystallization of the key intermediates or the final products is not possible, as has proven to be the case so far for $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, then one likely has one's hands full with a challenging and protracted synthesis. In this regard, one can argue in hindsight that more effort should have gone initially into trying to find a way to crystallize $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$ or the subsequent products, even if it results in a low yield, as is the case for crystalline $\beta\text{-SiW}_9\text{O}_{34}^{10-}$. Crystalline $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, or $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ thus remain important targets of future research. The saving grace has been use of the built-in, purity-monitoring handle of ^{31}P NMR as a key component of the present work. Improvements in the syntheses then at least become possible, albeit again primarily by tedious trial-and-error.

Such are the nature and challenges of at least some POM chemistry, described once as a “black art” to the senior author

when he was first entering the POM field in the 1970s. In the end analysis, then the case of $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ and $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ serves as a classic example^{9,14,17} to the problems, and thus level of effort, we can expect if one is working with <100% pure, kinetically precipitated, metastable powders in POM/inorganic chemistry. *Caveat emptor!*

ASSOCIATED CONTENT

Supporting Information

Detailed experimental descriptions, the historical distribution of the value of “ x ” in samples of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_{9-x}\text{H}_x\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ and their purity, a discussion of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ conversion to $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, the ^{31}P NMR shifts of $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ and impurity peaks in acetonitrile/water solutions, and pictures of phenolphthalein titration end points after 0.25, 2, and 6 h. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 5796–5810.
- Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335–8353.
- Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382–10400.
- Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, *9*, 3083–3095.
- Widgren, J. A.; Aiken, J. D.; Özkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312–324.
- Finke, R. G.; Özkar, S. *Coord. Chem. Rev.* **2004**, *248*, 135–146.
- Watzky, M. A.; Finney, E. E.; Finke, R. G. *J. Am. Chem. Soc.* **2008**, *130*, 11959–11969.
- Finney, E. E.; Finke, R. G. *J. Colloid Interface Sci.* **2008**, *317*, 351–374.
- Hornstein, B. J.; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 2720–2730.
- Contant, R.; Klemperer, W. G.; Yaghi, O. *Inorganic Syntheses*; Ginsberg, A. P., Ed.; John Wiley & Sons: New York, 1990; Vol. 27, pp 104–111.
- Domaille, P. J.; Hervé, G.; Tézé, A. *Inorganic Syntheses*; Ginsberg, A. P., Ed.; John Wiley & Sons: New York, 1990; Vol. 27, pp 96–104.
- Contant, R.; Ciabrini, J. P. *J. Chem. Res., Synop.* **1977**, 222.
- Contant, R.; Ciabrini, J. P. *J. Chem. Res., Miniprint* **1977**, 2601–2617.
- Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886–3896.
- Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692–1704.
- Randall, W. J.; Droege, M. W.; Mizuno, N.; Nomiya, K.; Weakley, T. J. R.; Finke, R. G.; Isern, N.; Salta, J.; Zubieta, J. *Inorganic Syntheses*; Cowley, A. H., Ed.; John Wiley & Sons: New York, 1997; Vol. 31, pp 167–185.

(17) Weiner, H.; Aiken, J. D.; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 7905–7913.

(18) Nomiya, K.; Pohl, M.; Mizuno, N.; Lyon, D. K.; Finke, R. G.; Dickman, M. H.; Glickman, D. C.; Kortz, U.; Samonte, J. L.; Xin, F.; Pope, M. T. *Inorganic Syntheses*; Cowley, A. H., Ed.; John Wiley & Sons: New York, 1997; Vol. 31, pp 186–201.

(19) Hornstein rechecked 1997 *Inorganic Syntheses* procedure¹⁸ (based on the 1988 ELSF¹⁵ synthesis in Table 1a) and found no improvement in the purity of the final $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ made from either the ELSF¹⁵ or the related *Inorganic Syntheses*¹⁶ procedures involving a $(\text{CH}_3)_4\text{N}^+$ salt reprecipitation step (see pp 2727 and 2729 in the Weiner paper, specifically the section titled “A Reevaluation of the Water Soluble $(\text{CH}_3)_4\text{N}^+$ Salt Intermediate”⁹). As part of the work herein, we too reexamined once again the $(\text{CH}_3)_4\text{N}^+$ salt reprecipitation step in the 1997 *Inorganic Syntheses* procedure,¹⁸ to address the question of whether it provides any detectable improvement in the purity of the final $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product by ³¹P NMR. Again we found that $(\text{CH}_3)_4\text{N}^+$ reprecipitation step *does not* improve the purity of the final product: ~76% purity $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ was produced when one of us (W.W.L.) followed the *Inorganic Syntheses* procedure^{16,18} as written (i.e., without the critical $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ washing steps described herein). In short, the (unnecessary) $(\text{CH}_3)_4\text{N}^+$ reprecipitation step^{15,16} should be abandoned based on the failure to find any purification in that step by, now, three independent researchers (Weiner,¹⁷ Hornstein,⁹ and now W.W.L. via the work reported herein). These results fully support Hornstein’s finding,⁹ one also fortified by the present work, that it is the purity of the lacunary $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ synthon that is a primary determinant of the purity of the final $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product.

(20) Nomiya, K.; Kaneko, M.; Kasuga, N. C.; Finke, R. G.; Pohl, M. *Inorg. Chem.* **1994**, *33*, 1469–1472.

(21) Finke, R.; Lyon, D. K.; Nomiya, K.; Weakley, T. J. R. *Acta Crystallogr., Sect. C* **1990**, *46*, 1592–1596.

(22) Rouhi, M. *Chem. Eng. News* **2013**, *91*, 3.

(23) Danheser, D. L. *Chem. Eng. News* **2013**, *4*.

(24) Klemperer, W. G. *Inorganic Syntheses*; Ginsberg, A. P., Ed.; John Wiley & Sons: New York, 1990; Vol. 27, pp 71–76.

(25) Graham, C. R.; Finke, R. G. *Inorg. Chem.* **2008**, *47*, 3679–3686.

(26) Mbomekalle, I.-M.; Lu, Y. W.; Keita, B.; Nadjo, L. *Inorg. Chem. Commun.* **2004**, *7*, 86–90.

(27) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947–2960.

(28) Pope, M. T.; Papaconstantinou, E. *Inorg. Chem.* **1967**, *6*, 1147–1152.

(29) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006–1008.

(30) Meriting mention here is that Weiner’s synthesis¹⁷ reports a tungsten analysis for the tetraprotonated intermediate $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ that is slightly *low* (not high), along with a niobium analysis that is slightly *high* (not low)—note also the typo on p 7907 in that paper claiming the opposite situation, which is hereby corrected. The somewhat high niobium elemental analysis, but *not* the low tungsten analysis, is retained in the deprotonated $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product in Weiner’s synthesis. However, given our experience that niobium and tungsten analyses can be off by $\geq 0.6\text{--}0.8$ (see the discussion on¹⁷ p 7911), herein we have emphasized high S/N ³¹P NMR as a more direct, more reliable way to judge the purity of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ product.

(31) We also repeated Weiner’s experiment¹⁷ testing the pH of the dissolved solution. One sample’s pH rose with additional $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, leveling off at pH 9.2 with a concentration of ~1.0 mM, similar to Weiner’s report.¹⁷ However, a second sample’s pH never rose above pH 7.25 up to a concentration of 1.1 mM. Hence, it appears that the pH for an aqueous solution of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ is dependent on the individual $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ titration of the protonated $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{H}_4\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ —which itself is largely insoluble.