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The Lacunary Polyoxoanion Synthon α-$P_2W_{15}O_{56}^{12-}$: An Investigation of the Key Variables in Its Synthesis plus Multiple Control Reactions Leading to a Reliable Synthesis

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A reliable way to determine the purity of the kinetically precipitated, noncrystalline lacunary polyoxoanion α-$P_2W_{15}O_{56}^{12-}$ has been developed, namely, the conversion of α-$P_2W_{15}O_{56}^{12-}$ into the tri-Nb^{5+}- and V^{5+}-containing polyoxoanions $P_2W_{15}Nb_3O_{62}^{9-}$ and $P_2W_{15}V_3O_{62}^{9-}$, respectively, followed by quantitative analysis of their purity by ^{31}P-NMR *prior* to recrystallization. With this previously unappreciated, straightforward α-$P_2W_{15}O_{56}^{12-}$ purity-assessment methodology in hand, the five reported literature syntheses of α-$P_2W_{15}O_{56}^{12-}$ are investigated with an emphasis on understanding the effects of the five differing variables within these syntheses (the amount of Na_2CO_3 base, the rate of addition of the base, the reaction temperature, the reaction scale, and the product drying method). Two methods of Nb^{5+} addition ($Nb_6O_{19}^{8-}$ and $NbCl_5$) to yield $P_2W_{15}Nb_3O_{62}^{9-}$ are also evaluated, as is the issue of whether any purification is provided by the normally optimum strategy of first preparing a water-soluble salt and its crystallization from water (here the $(CH_3)_4N^+$ salt of the Nb–O–Nb bridged anhydride, $P_4W_{30}Nb_6O_{123}^{16-}$), followed by its conversion to the organic-solvent soluble, but noncrystalline, $(n\text{-}C_4H_9)_4N^+$ salt, $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$. The results yield five previously unavailable and unequivocal insights: (1) Only the amount of added Na_2CO_3 base affects the purity or yield of the desired α-$P_2W_{15}O_{56}^{12-}$; the amount of added base is key, however. (2) Contant's 1990 *Inorganic Syntheses* procedure provides the highest-purity α-$P_2W_{15}O_{56}^{12-}$ presently available. (3) All prior syntheses calling for the addition of base to $P_2W_{18}O_{62}^{6-}$ until pH 9 must be abandoned. (4) The purity of even Contant's α-$P_2W_{15}O_{56}^{12-}$ is only 90%. (5) An identifiable impurity is the 16 tungsten polyoxoanion, α-$P_2W_{\mathbf{16}}O_{59}^{12-}$. Also identified and summarized are multiple compounding errors in the observation of, reporting on, and thinking about the synthesis of α-$P_2W_{15}O_{56}^{12-}$ historically, errors which delayed the most reliable synthesis of α-$P_2W_{15}O_{56}^{12-}$ from being identified for 18 years (from the 1983 discovery of α-$P_2W_{15}O_{56}^{12-}$). However, these errors yield valuable take-home lessons for anyone interested in working in this demanding area of inorganic synthetic chemistry, where direct structural methods for identifying the products and their purity, such as the lacunary polyoxoanion synthon α-$P_2W_{15}O_{56}^{12-}$, sometimes simply do not exist.

Introduction

The α-$P_2W_{15}O_{56}^{12-}$ polyoxoanion was first reported in 1983,[1−4] when it was recognized that what was previously believed to be the ditungsten vacant "$P_2W_{\mathbf{16}}O_{59}^{12-}$", derived from base degradation of the parent Wells−Dawson α-$P_2W_{18}O_{62}^{6-}$, was actually primarily the tritungsten vacant α-$P_2W_{15}O_{56}^{12-}$.[5] Since this time, α-$P_2W_{15}O_{56}^{12-}$ has proven to be an important lacunary polyoxoanion synthon for the preparation of the then novel $P_4W_{30}M_4O_{112}^{16-}$ (M = Co(II), Cu(II), Zn(II), and Mn(II),[1,2,4,6] and more recently[7] M = Fe(III)), $P_2W_{15}V_3O_{62}^{9-}$,[8,9] the multipurpose $P_2W_{15}Nb_3O_{62}^{9-}$,[10−12] and more recently[13] $(P_2W_{15}Ti_3O_{60.5})_4^{36-}$ and $Fe_2(NaOH_2)_2$-$(P_2W_{15}O_{56})_2^{16-}$.[14] In short, α-$P_2W_{15}O_{56}^{12-}$ is the prototype multitungsten vacant lacunary polyoxoanion of the Wells−Dawson structural type.[15]

However, despite its importance, the summary of the five reported syntheses of α-$P_2W_{15}O_{56}^{12-}$ in Table 1 reveals that there is little uniformity among the syntheses and no preferred synthesis. Significantly, the data in Table 1 identify

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(1) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006−1007.
(2) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886−3896.
(3) Contant, R. *Inorg. Synth.* **1990**, *27*, 106−111.
(4) Randall, J. W.; Droege, M. W.; Mizuno, N.; Nomiya, K.; Weakley, T. J. R.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 167−185.

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Table 1. The History of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ Synthesis and the Key Differences between Them

ref	amount of 1 M Na_2CO_3 added ($CO_3^{2-}/[P_2W_{18}O_{62}]^{6-}$ ratio)	rate of Na_2CO_3 addition (rxn time)	temperature of the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ solution	scale, g (based on $K_6[\alpha\text{-}P_2W_{18}O_{62}]$)	drying method	% yield of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$	direct evidence of purity	comments
5b	to pH 9 (not provided)	fast (~10 min)	room temp	400	over H_2SO_4	60	not provided	the product was thought to be $\alpha\text{-}P_2W_{\mathbf{16}}O_{59}^{12-}$
2	to pH 9, maintained for 1 hour (not provided)	slow (>1 h)	room temp	20	over H_2SO_4 for 2 days	85	not provided[a]	discovery that "$\alpha\text{-}P_2W_{\mathbf{16}}O_{59}^{12-}$" is predominantly $\alpha\text{-}P_2W_{15}O_{56}^{12-}$
10	to pH 9, maintained for 1 h (>12.9/1)	not provided (>1 h)	room temp	75	60 °C oven, overnight	83	>90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ by ^{31}P-NMR	the authors state, "the present literature synthesis probably produces impure material." (i.e., $Na_{12}\alpha\text{-}P_2W_{15}O_{56}$)
3	100 mL (12.6/1)	fast (~10 min)	ice bath	38.5	air dry for 3 days	62	not provided	
4	to pH 9, maintained for 1 h (44.3/1)	not provided (>1 h)	ice bath	186	50 °C oven, overnight	78	not provided[a]	

[a] The $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ product was used to make crystalline compounds of the form $Na_{16}[(P_2W_{15}O_{56})_2M_4]$ ($M = Co^{2+}, Cu^{2+}, Zn^{2+}$) which have been fully characterized.[2]

a previously unrecognized, large discrepancy *in the amount of Na_2CO_3 base* added to degrade the parent $\alpha\text{-}P_2W_{18}O_{62}^{6-}$, with the molar ratios of $Na_2CO_3/\alpha\text{-}P_2W_{18}O_{62}^{6-}$ varying from 11.2−44.3. The variation in the amount of base is traceable to the original synthesis which called for base to be added until pH 9 was achieved.[5a] The present work will show for the first time that all prior syntheses following this pH 9 recipe yield at best $P_2W_{15}O_{56}^{12-}$ with $\geq 20\%$ impurity.

The stoichiometric amount required for the degradation of $\alpha\text{-}P_2W_{18}O_{62}^{6-}$ to $\alpha\text{-}P_2W_{15}O_{56}^{12-}$ is 12 equiv of OH^- (eq 1). The actual amount of the base, Na_2CO_3, necessary to stay in the optimum pH range where $\alpha\text{-}P_2W_{15}O_{56}^{12-}$ precipitates (pH ca. 8.5; see Figure 1, vide infra) is ca. *12 equiv* (eq 2), *because HCO_3^- is the carbonate product at this pH* (pK_a of $HCO_3^- = 10.2$[16]).

$$Na_6[\alpha\text{-}P_2W_{18}O_{62}]_{(aq)} + 12NaOH + 10H_2O \rightarrow Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 16H_2O_{(ppt)} + 3Na_2WO_4 \quad (1)$$

$$Na_6[\alpha\text{-}P_2W_{18}O_{62}]_{(aq)} + 12Na_2CO_3 + 22H_2O \rightarrow Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 16H_2O_{(ppt)} + 3Na_2WO_4 + 12NaHCO_3 \quad (2)$$

Due to the lack of a way to unequivocally identify the composition and purity of the lacunary polyoxoanion product (and, therefore, the confusion created by its original misidentification as "$P_2W_{\mathbf{16}}O_{59}^{12-}$" and lack of a stoichiometry to the correct $\alpha\text{-}P_2W_{15}O_{56}^{12-}$ product[3]), the correct stoichiometries in eqs 1 and 2 did not appear in the literature until Contant's 1990 *Inorganic Syntheses*, where he used 12.6 equiv of Na_2CO_3 for his synthesis. Unfortunately, the lack of an unequivocal way to monitor the purity of the $P_2W_{15}O_{56}^{12-}$ product until the present report has also meant that there was previously no way to be certain about which $P_2W_{15}O_{56}^{12-}$ synthesis provided the best product. Until now, there was also no way to catch the previous errors in the stoichiometry for the formation of $P_2W_{15}O_{56}^{12-}$, for example, the erroneous stoichiometry of 6 equiv of Na_2CO_3 going to

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(5) (a) Despite the misidentification of $P_2W_{15}O_{56}^{12-}$ as "$P_2W_{\mathbf{16}}O_{59}^{12-}$" in 1977, and although there was, and still is, no *direct* method able to characterize and quantitate the purity of the metastable $P_2W_{15}O_{56}^{12-}$ *in solution*, credit for the original preparation of $P_2W_{15}O_{56}^{12-}$ clearly goes to Contant and Ciabrini.[5b] What is impressive is the ability of the French school to develop the chemistry of multiple metastable lacunary polyoxoanion species[5b,c,17] using primarily only polarography, IR, elemental analysis, and great intuitive insights plus careful experimental work as their main tools. Consistent with this, the present work shows unequivocally that Contant's 1990 *Inorganic Synthesis* is presently the best synthesis of $P_2W_{15}O_{56}^{12-}$. Also noteworthy is the insight from the French school of using polarography to follow the formation of lacunary polyoxoanions as the next best available method to the desired, but missing, direct structural probe, an insight that emphasizes the value of *using direct methods to monitor all chemical reactions*. (b) Contant, R.; Ciabrini, J. P. *J. Chem. Res., Synop.* **1977**, 222. Contant, R.; Ciabrini, J. P. *J. Chem. Res., Miniprint* **1977**, 2601. (c) Ciabrini, J. P.; Contant, R.; Fruchart, J. M. *Polyhedron* **1983**, *2*, 1229−1233.

(6) Gómez-García, C. J.; Borrás-Almenar, J. J.; Coronado, E.; Ouahab, L. *Inorg. Chem.* **1994**, *33*, 4016−4022.

(7) Zhang, X.; Chen, Q.; Duncan, D. C.; Campana, C. F.; Hill, C. L. *Inorg. Chem.* **1997**, *36*, 4208−4215.

(8) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286−4292.

(9) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2959.

(10) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692. This 1988 synthesis says to use >200 mL of 1.0 M Na_2CO_3 en route to pH 9. This amount is >12.9 equiv, so researchers using this preparation, who were also aware of the key stoichiometries in eqs 1 and 2, were using close to the required 12 equiv of base. Therefore, the $\alpha\text{-}P_2W_{15}O_{56}^{12-}$ from this synthesis, and then also the resultant $P_2W_{15}Nb_3O_{62}^{9-}$, were generally of acceptable purity.

(11) Weiner, H.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 7905. Note that a typo exists in footnote 20 of this reference. Rather than a "5%" H_2O_2 solution, a 0.5 M H_2O_2 solution should be used.

(12) Nomiya, K.; Pohl, M.; Mizuno, N.; Lyon, D. K.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 186.

(13) Nomiya, K.; Arai, Y.; Shimizu, Y.; Takahashi, M.; Takayama, T.; Weiner, H.; Nagata, T.; Widegren, J. A.; Finke, R. G. *Inorg. Chim. Acta* **2000**, *300−302*, 285−304.

(14) Zhang, X.; Anderson, T. M.; Chen, Q.; Hill, C. L. *Inorg. Chem.* **2001**, *40*, 418−419.

(15) More recently, derivatives of the hexatungsten vacant $P_2W_{12}O_{48}^{16-}$ have been described, but it seems likely that they will not have the range of chemistry exhibited by the derivatives of $P_2W_{15}O_{56}^{12-}$ due to problems of controlling Nb−O−Nb anhydride formation. Judd, D. A.; Chen, Q.; Campana, C. F.; Hill, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 5461−5462.

(16) Chemical Rubber Company. *Handbook of Chemistry and Physics*, 53rd ed.; Cleveland, OH, 1972.

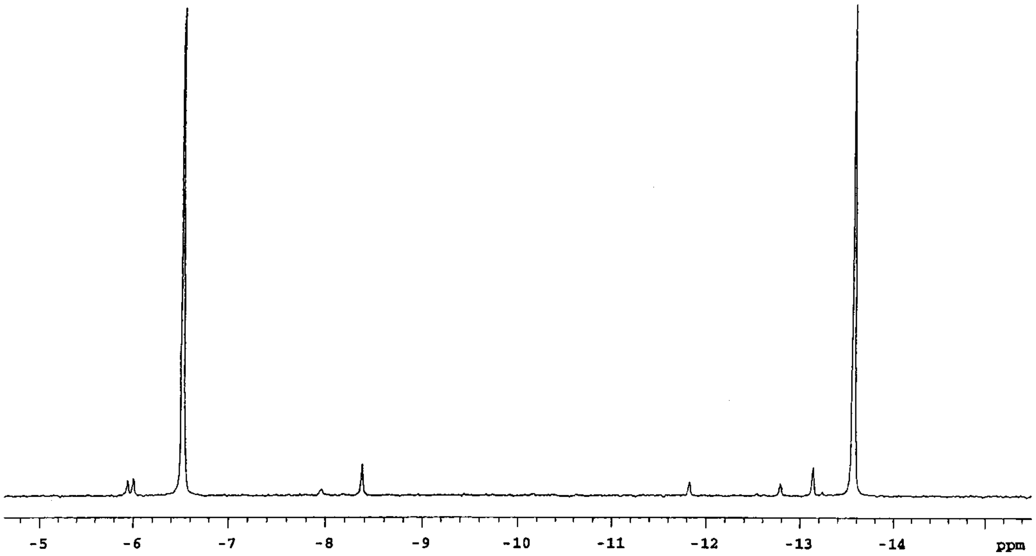
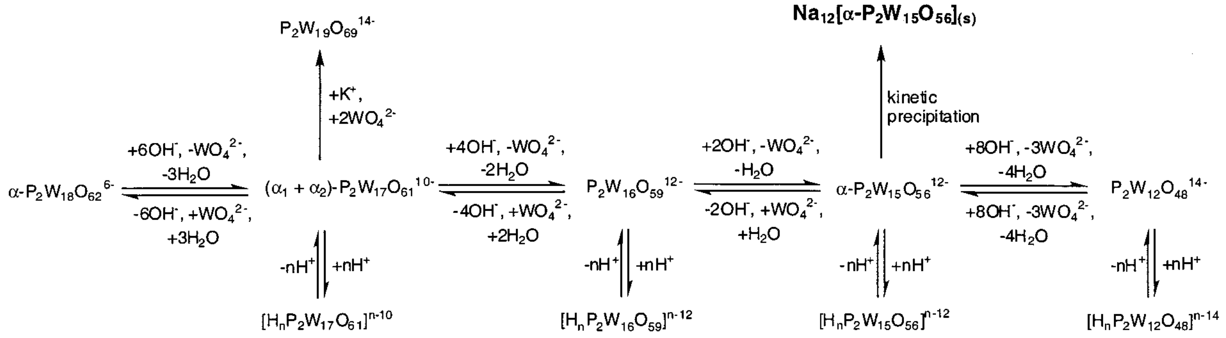


Figure 1. ^{31}P-NMR spectrum (CD_3CN) of 90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ ($\delta = -6.5$ and -13.6 ppm relative to an internal capillary of 85% H_3PO_4) made from $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ prepared by Contant's 1990 method.[3]

Scheme 1



$6CO_2$ [4,12] (without connecting the pH 9 reaction conditions to the fact that all CO_2 would be captured by HO^- as HCO_3^-), an error which we have hereby corrected via eq 2 above.

However, it is important to note that the synthesis of α-$P_2W_{15}O_{56}^{12-}$ is not expected to be anything near as simple as eq 1 or 2 implies. As Scheme 1 illustrates, *at least* five other polyoxoanion species are possible (see the scheme on p 69 in ref 17) en route to α-$P_2W_{15}O_{56}^{12-}$: $(\alpha_1 + \alpha_2)$-$P_2W_{17}O_{61}^{10-}$, $P_2W_{19}O_{69}^{14-}$, the largely unknown and presumed unstable α-$P_2W_{\mathbf{16}}O_{59}^{12-}$, the desired metastable α-$P_2W_{15}O_{56}^{12-}$, and the further base-degradation product α-$P_2W_{12}O_{56}^{12-}$. Hence, *at least* five K_{eq} constants and *at least four additional* pK_a *values and associated* K_{eq} *constants* govern the reactions leading to α-$P_2W_{15}O_{56}^{12-}$ (i.e., four pK_as govern the protonation of these four species shown in Scheme 1, considering only the $n = 1$ protonation states for simplicity). The branching reaction to $P_2W_{19}O_{69}^{14-}$ shown in Scheme 1 is said to be favored by faster addition of OH^-, higher temperatures (80 °C), longer heating times, and added WO_4^{2-}.[17] To make matters worse, α-$P_2W_{15}O_{56}^{12-}$ is a *kinetically precipitated powder* (Scheme 1), a powder that degrades once redissolved in an aqueous solution.[3,18] This raises the question of whether it is possible to successfully synthesize and use kinetically precipitated powders of lacunary polyoxoanions without at least some degradation to other polyoxoanions, especially when one is without crystallization as a means to purify those powders (due to the product's instability when redissolved, vide infra) and also without a way to monitor directly the purity of the α-$P_2W_{15}O_{56}^{12-}$ product. Indeed, the exact purity of α-$P_2W_{15}O_{56}^{12-}$ from any of its syntheses in Table 1 has been unknown until the present work.

In addition to the (i) variations in the amount of added Na_2CO_3 base, there are other potentially important but previously uninvestigated and, thus, ill-understood variables in the synthesis of α-$P_2W_{15}O_{56}^{12-}$: (ii) the effects of atmospheric CO_2 on the measured pH and as a function of the reaction time, as well as any possible effects of precipitation of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ on the pH electrode; (iii) the rate of the addition of base and the total reaction time at pH 9; (iv) the temperature of the synthesis; (v) any effects of the scale on the synthesis and, therefore, on the kinetic precipitation of the desired $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$; (vi) how the

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(17) Tourné, C. M.; Tourné, G. F. Progress in Polytungstophosphate and -arsenate(V) Chemistry. In *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity;* Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Norwell, MA, 1994; pp 59−70.

(18) Pohl, M.; Lyon, D. K.; Mizuno, N.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 1413−1429.

resultant $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ is best dried (time, temperature, and desiccant); and, again, (vii) the very important issue of the indirect[5b] method used to monitor the purity of the solution unstable, resultant α-$P_2W_{15}O_{56}^{12-}$. An issue related to (vii) is (viii): is the previously used ^{31}P-NMR of α-$P_2W_{15}O_{56}^{12-}$ in solution irreproducible and, therefore, providing misleading results? Our preliminary attempts to repeat that otherwise highly desirable experiment suggest that this experiment is irreproducible (see the claim of ^{31}P-NMR peaks at +0.1 and −13.3 ppm vs 85% H_3PO_4 in 1 M HOAc/LiOAc buffer[3], as well as Figure M of the Supporting Information which uses 1.5 M HOAc/1.0 M LiCl/0.5 M NaOAc[18]). Next, two additional major issues are (ix) whether the Nb insertion methods ($Nb_6O_{19}^{8-}$ vs $NbCl_5$, both in H_2O_2) are giving poor purity $P_2W_{15}Nb_3O_{62}^{9-}$ out of otherwise good α-$P_2W_{15}O_{56}^{12-}$ and, thus, (x) whether the purity of the resultant α-$P_2W_{15}O_{56}^{12-}$ is accurately reported by the otherwise very valuable method of its conversion to $P_2W_{15}Nb_3O_{62}^{9-}$ or $P_2W_{15}V_3O_{62}^{9-}$ for ^{31}P-NMR analysis. Finally, a key point in the synthetic strategy of making polyoxoanions soluble in organic solvents is raised again by this work: (xi) is our original 1988 strategy[10] of making and purifying $P_2W_{15}Nb_3O_{62}^{9-}$ *in water* (as its $(CH_3)_4N^+$ salt)[19] and *then* converting to the (nonpurifiable) organic solvent-soluble (n-$C_4H_9)_4N^+$ salt the preferred synthetic strategy? Or, as our "Improved $P_2W_{15}Nb_3O_{62}^{9-}$ Synthesis" paper asserted,[11] can one work directly with kinetically precipitated powders of lacunary polyoxoanions and, if so, at what level of purity determined by what factors?

The problems addressed in this paper came to a head when our research group simply lost the ability to prepare ≥90% pure $P_2W_{15}Nb_3O_{62}^{9-}$. This was a rather puzzling result, because we had prepared this polyoxoanion without significant problems at least 50 times since our 1988 report[10] first describing $P_2W_{15}Nb_3O_{62}^{9-}$.[20] As the studies reported herein were nearing completion, we were contacted by another group that was also having problems in making high-purity $P_2W_{15}Nb_3O_{62}^{9-}$;[21] hence, it seemed likely that there was a problem in one or more of the published syntheses[4,11] of α-$P_2W_{15}O_{56}^{12-}$, its conversion to $P_2W_{15}Nb_3O_{62}^{9-}$, or both. We were forced to stop and reinvestigate the variables and issues (i)−(xi) listed above and our most recent syntheses[4,11] until we found the answer(s). It occurred to us that neither we nor others had previously stopped and taken time to fully investigate *and report in detail* the synthesis of the key synthon α-$P_2W_{15}O_{56}^{12-}$, a "mistake" according to our experience in polyoxoanion syntheses: it is generally not possible to "skip over a step," yet have reproducible and reliable syntheses in this demanding area of synthetic inorganic chemistry, an area where the details matter.

Therefore, herein we have investigated all of the key variables and issues raised in (i)−(xi) above. Our findings have lead to the discovery that, as we suspected from the start of these studies, the *exact amount of base*, and not the attainment of pH 9, is the only, but *crucial*, variable in the synthesis of ≥90% pure α-$P_2W_{15}O_{62}^{12-}$. We also report a host of control and other experiments that investigate each conceivably important variable and detail in the syntheses of α-$P_2W_{15}O_{56}^{12-}$ and $P_2W_{15}Nb_3O_{62}^{9-}$. We have written the results with an eye to the needed details, in order to finally make this prototype lacunary ion available to others. We also emphasize the hindsight-discovered mistakes in observation, reporting, and thinking[19,20,22,23] which led to the confusion over the previously preferred α-$P_2W_{15}O_{62}^{12-}$ synthesis. It is our hope that this report will assist others in avoiding similar errors in future polyoxoanion chemistry.

Results and Discussion

The following are the results of 23 experiments testing 6 synthetic variables and 10 control experiments. Key points include the demonstration that the conversion of α-$P_2W_{15}O_{56}^{12-}$ to $P_2W_{15}Nb_3O_{62}^{9-}$ or $P_2W_{15}V_3O_{62}^{9-}$ coupled with ^{31}P-NMR analysis of the products is the method of choice for determining the purity of the lacunary precursor. The amount of Na_2CO_3 base added is then experimentally demonstrated to be the key variable in the synthesis of the best $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ which, in turn, is identified to be Contant's 1990 *Inorganic Syntheses* procedure.[3]

Determining the Purity of Noncrystalline $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. A widely used and effective diagnostic

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(19) Experiments carried out herein show that the desired "purification" step reported in both the 1988 *Organometallics* and in the 1997 *Inorganic Synthesis* papers is, in fact, *not* a purification but, rather, a product yield diminishing reprecipitation.

(20) Regarding the need for accurate experimental observing and reporting: (a) The problems in obtaining pure $P_2W_{15}Nb_3O_{62}^{9-}$ caused us to go back and tabulate all of the *more recent*, ca. 13, preparations of $P_2W_{15}Nb_3O_{62}^{9-}$ by 6 different researchers in our group to see if we could discover what the problem(s) might be. The first problem in experimental reporting was that the researchers involved tended not to report syntheses that failed and, thereby, covered up the crucial data indicating that the synthesis had problems. The tabulation of the 13 most recent preparations revealed that the problems arose when we began preparing $P_2W_{15}O_{56}^{12-}$ according to our "Improved $P_2W_{15}Nb_3O_{62}^{9-}$ Synthesis" paper. As it turns out, that paper miscited our 1997 *Inorganic Syntheses* procedure for the source of the α-$P_2W_{15}O_{56}^{12-}$ used by stating, "The $Na_{12}[P_2W_{15}O_{56}]\cdot 18H_2O$ was prepared and characterized as previously reported[7h,i]". The key references therein (7h,i) lead back to our 1997 *Inorganic Syntheses*. We now can state with certainty that the synthesis that was actually being used to make α-$P_2W_{15}O_{56}^{12-}$ could not have been that provided in the cited 1997 *Inorganic Syntheses* (i.e., with its 44 equiv of base, Table 1); instead, a synthesis closer to our 1988 preparation, with its 12.6 equiv of base, must have been used. This miscitation of what was actually done in the lab to prepare the crucial $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ precursor had the very unfortunate effect of coupling the synthesis of $P_2W_{15}Nb_3O_{62}^{9-}$ to what turns out to be *the worst* synthesis of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ in Table 1. This error in experimental reporting, and its magnification by happenstance, emphasizes the need *for accurate and detailed experimental reporting* in all synthetic chemistry, and certainly in areas as complex as polyoxoanion chemistry.
Another error in reporting was the failure to write the number of equivalents of Na_2CO_3 being added (44 equiv) in the *Inorganic Syntheses* procedure (only a volume, 1700 mL, is given), which meant that the key piece of information, that too much base was being added, was obscured from all the authors, as well as the checkers, of that work. Yet another error in reporting is in what is omitted in the too brief report of what has proved to be the best $P_2W_{15}O_{56}^{12-}$ synthesis. It was not mentioned or corrected that the earlier "pH 9" directive[5b] was incorrect, nor was there any reference to, or comparison of, the 1990 synthesis to the other three α-$P_2W_{15}O_{56}^{12-}$ syntheses that existed at that time (the first three entries in Table 1). (b) The question also arises of how the checked *Inorganic Syntheses* procedure "failed". The answer is that it does not fail for the specific syntheses it describes, the α-$P_2W_{15}O_{56}^{12-}$ made therein being of sufficient (but lower, ca. 82 ± 3%) purity to allow pure $P_4W_{30}M_4O_{112}^{16-}$ type polyoxoanions to be made *following recrystallization* of the $P_4W_{30}M_4O_{112}^{16-}$ products that are part of the *Inorganic Syntheses* procedure.

(21) Private communication from Prof. Anna Proust, cited with permission.

spectral method for the analysis of phosphorus-containing polyoxoanions is ^{31}P-NMR.[18,24−26] Attempts were made to directly measure the purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ using this relatively simple method. NMR experiments were carried out with the fresh solutions prepared in 1.5 M HOAc/0.5 M NaOAc/1.0 M LiCl buffer (suggested in ref 18, Figure M)[18] and in 1.0 M LiOAc/1.0 M HOAc buffer (suggested by ref 3 herein). Multiline spectra were obtained in both experiments (see Figures A and B in the Supporting Information). These results were expected given the documented decomposition of $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$ under these conditions.[3,18] Hence, the use of ^{31}P-NMR to quantitatively assess the purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ is not reliable and, therefore, should be abandoned.

IR spectroscopy is another possible means of determining the purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$, and its IR spectra are commonly reported.[2−4,18] Unfortunately, we found that the spectra of 70 and 90% $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ were nearly identical between 600 and 1300 cm^{-1}; therefore, as expected, IR is an unsuitable method for quantitatively determining the purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ at even a modest ±20% precision level.

Since there is no direct method of characterization or purification for the noncrystalline $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$, the next-best option is to transform this lacunary polyoxoanion into a stable compound which can be examined by ^{31}P-NMR. The best-characterized of these transformations are the reactions of $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$ with transition metals, such as Cu^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Fe^{3+}, V^{5+}, and Nb^{5+}, which result in stable, isolable products that are well-characterized by ^{31}P-NMR.[1,2,7,8,11,14,26−28] It is important that the target compound reflect the true purity of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ precursor; therefore, only *noncrystalline* compounds should be considered.[29] The noncrystalline $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ was selected for the purity analysis used throughout this work based on our ongoing interest[30] and need for pure $P_2W_{15}Nb_3O_{62}{}^{9-}$. We also prepared the noncrystalline V^{5+} adduct, $K_8H[P_2W_{15}V_3O_{62}]$, as a control experiment.

Conversion of the samples from the identical batch of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ into uncrystallized samples of both $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ and $K_8H[P_2W_{15}V_3O_{62}]$ produced products of the same purity by ^{31}P-NMR of 83 ± 3% and 80 ± 3%, respectively (see Figures C and D of the Supporting Information). These results strongly suggest that both conversions can reliably report the purity of the parent $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ (ca. 90% based on the data which follow). The quicker and easier preparation of the V^{5+} adduct compared to the Nb^{5+} product means that uncrystallized $K_8H[P_2W_{15}V_3O_{62}]$ is probably the best compound for others to use to most quickly assay the purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. However, our interest and need for $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ makes it the compound of choice for our own work which follows.

Before we leave the V^{5+} adduct, it is noteworthy that the ^{31}P-NMR of the uncrystallized $K_8H[P_2W_{15}V_3O_{62}]$ also provides insight into an impurity present in this sample of ca. 20% $P_2W_{\mathbf{16}}V_2O_{62}{}^{8-}$ (Figure C of the Supporting Information), based on the peaks at −8.7 and −13.3 ppm (relative to 85% H_3PO_4) compared to −9.3 and −13.9 ppm in the literature (also relative to 85% H_3PO_4).[8] This, in turn, suggests the presence of $\alpha\text{-}P_2W_{\mathbf{16}}O_{59}{}^{12-}$ in the starting material, a result which brings us back nearly full circle to the 1983 issue[1] of "what is $\alpha\text{-}P_2W_{\mathbf{16}}O_{59}{}^{12-}/\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$?" It is mostly $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$, but it contains up to 20% $P_2W_{\mathbf{16}}O_{59}{}^{12-}$. This result implies that the impurity peak in the ^{31}P-NMR of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ at −8.7 and −13.2 ppm relative to 85% H_3PO_4 (ca. 8%, Figure D of the Supporting Information) is likely due to a $P_2W_{\mathbf{16}}Nb_2O_{62}{}^{8-}$ impurity, as

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(22) Regarding the need to take the time to write full, balanced, reaction stoichiometries for all reactions: in hindsight, failure to adhere rigorously to this basic principle of freshman chemistry by up to 11 investigators[1,2,4,5b,10−12] is the most important reason that convergence to a single, best, reproducible synthesis of $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$ has taken 19 years. Note also that the confusion over the identity of $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$ initially, as well as the lack of a direct method to follow the composition and purity of $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$, meant that the careful use of balanced stoichiometries was one of the few synthetic tools available, so that failure to employ it had especially costly and time-consuming consequences in this case.

(23) There is a need for students to repeat any synthesis at least three times exactly as it is written before concluding that they are incompetent or before they start thinking about changing that synthesis (i.e., in the case where the synthesis is not working). Adherence to this valuable rule, which is known to more experienced synthetic chemists, would have led each researcher that had problems with the synthesis of $P_2W_{15}Nb_3O_{62}{}^{9-}$ to report those failed syntheses, and doing so with some confidence that it was *not* a problem with their "hands". Adherence to this simple rule would also help avoid introducing well intended, but unneeded and often bad, changes into well-established syntheses that, instead, simply require the beginning researcher to repeat the synthesis multiple times in order to attain the skills needed to successfully carry out that synthesis.

(24) Nomiya, K.; Nozaki, C.; Miyazawa, K.; Shimizu, Y.; Takayama, T.; Nomura, K. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 1369−1377. Bartis, J.; Sukal, S.; Dankova, M.; Kraft, E.; Kronzon, R.; Blumenstein, M.; Francesconi, L. C. *J. Chem. Soc., Dalton Trans*. **1997**, 1937−1944. Abbessi, M.; Contant, R.; Thouvenot, R.; Hervé, G. *Inorg. Chem*. **1991**, *30*, 1695−1702. Jorris, T. L.; Kozik, M.; Casan-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc*. **1987**, *109*, 7402−7408. Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983. Massart, R.; Contant, R.; Fruchart, J.-M.; Ciabrini, J.-P.; Fournier, M. *Inorg. Chem*. **1977**, *16*, 2916−2921. O'Donnell, S. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans*. **1976**, 2290−2297.

(25) See ref 34 for further comments on the ^{31}P-NMR of polyoxoanions.

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

(27) (a) Gómez-García, C. J.; Borrás-Almenar, J. J.; Coronado, E.; Ouahab, L. *Inorg. Chem*. **1994**, *33*, 4016−4022. (b) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem*. **1990**, *29*, 1235−1241.

(28) Reactions of $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with M give $[M_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$ ($M = Cu^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}$).[2,27a] Reactions with iron produce the Fe^{3+} adducts, $[Fe_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{12-}$, and the novel $[Fe_2(NaOH_2)_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{16-}$.[7,14] The products $[P_2W_{15}M'_3O_{62}]^{9-}$ are formed with V^{5+} and Nb^{5+}.[8,9,11,12]

(29) A control experiment was carried out to determine if the measured purity was different for a crystalline product versus a noncrystalline product, as detailed in the Supporting Information. Crystalline $Na_{16}[Zn_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]$ was >95% pure by ^{31}P-NMR as compared to the noncrystalline $[(C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ which was only 75% pure by ^{31}P-NMR. Since these two compounds were made from the same sample of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$, this experiment confirms that crystallization of the Zn^{2+} product obfuscates the true purity of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ starting material; hence, only noncrystalline compounds were considered.

(30) For example, $P_2W_{15}Nb_3O_{62}{}^{9-}$ is the current "Gold Standard" anion, among all known nanocluster-stabilizing anions, for the synthesis and stability of catalytically active Ir(0) nanoclusters: Özkar, S.; Finke, R. G. Nanocluster Formation and Stabilization Fundamental Studies: Ranking Commonly Employed Anionic Stabilizers via the Development, Then Application, of Five Comparative Criteria. *J. Am. Chem. Soc*., in press, 2002.

Table 2. Variables Identified in the Synthesis of Pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ and Pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$

1. The $Na_2CO_3/[\alpha\text{-}P_2W_{18}O_{62}]$ Ratio in Solution

experiment number	mass $K_6[\alpha\text{-}P_2W_{18}O_{62}]$, g	volume of 1 M Na_2CO_3, mL	$Na_2CO_3/[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ molar ratio	purity of the resulting $[P_2W_{15}Nb_3O_{62}]^{9-}$ by ^{31}P-NMR, %
		Best Product Purity Syntheses		
1	38	100	12.6	90
2	38	100	12.6	90
3	38	100	12.6	90
4	38	100	12.6	89
5	38	100	12.6	90
6	176	458	12.6	90−92
		Lower Product Purity Syntheses		
7	74	240	14.6	73
8	37	125	16.4	68
9	74	250	16.4	65
10	186	700	18.2	83
11	19	71	18.4	67
12	19	88	22.9	70
13	186	1050	27.4	82

2. Rate of 1 M Na_2CO_3 Addition

experiment number	time over which 100 mL of base was added to $K_6[\alpha\text{-}P_2W_{18}O_{62}]$, min	purity of the resulting $[P_2W_{15}Nb_3O_{62}]^{9-}$ by ^{31}P-NMR, %
1	4	90
3	60	90

3. Temperature of the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ Solution Prior to the Addition of 1 M Na_2CO_3

experiment number	temperature of solution, °C	purity of the resulting $[P_2W_{15}Nb_3O_{62}]^{9-}$ by ^{31}P-NMR, %
4	10	89
1	22	90
5	45	90

4. Scale of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ Synthesis

experiment number	scale (based on $K_6[\alpha\text{-}P_2W_{18}O_{62}]$), g	purity of the resulting $[P_2W_{15}Nb_3O_{62}]^{9-}$ by ^{31}P-NMR, %
1	38	90
6	176	90−92

5. Method of Drying the Solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$

experiment number	drying method	purity of the resulting $[P_2W_{15}Nb_3O_{62}]^{9-}$ by ^{31}P-NMR, %
1	over H_2SO_4 for 2 days	90
2	50 °C oven overnight	90

6. Source of Nb^{5+} Used in the Formation of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ from the Same Batch of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$

experiment number	source of Nb	purity of the resulting $[P_2W_{15}Nb_3O_{62}]^{9-}$ by ^{31}P-NMR, %
6b	$NbCl_5$	92
6d	$K_8HNb_6O_{19}$	>90

suggested in our earlier paper.[10] Note that only slightly less, ca. 6%, of this same impurity is also observed in the ^{31}P-NMR of 90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ (Figure 1).

The Key Variable in the Synthesis of Pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ Is the Amount of Added 1.0 M Na_2CO_3. The key finding herein is that, of the 6 variables examined in this study, only the amount of 1.0 M Na_2CO_3 added to the $\alpha\text{-}P_2W_{18}O_{62}{}^{6-}$ solution has an effect on the purity of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. Column 4 of Table 2 shows that the molar ratios of $Na_2CO_3/\alpha\text{-}P_2W_{18}O_{62}{}^{6-}$ near 12.6 provide 90 ± 3% pure material. In contrast, higher molar ratios of base to polyoxoanion yield purities from 65 to 82%.

To learn more about the pH as the reaction proceeded and if the prior "attain pH 9" directive[2,4,5b,10] was a problem, the pH of an $\alpha\text{-}P_2W_{18}O_{62}{}^{6-}$ solution was recorded as a function of added Na_2CO_3 base by suspending a pH electrode in solution and recording the pH after preselected volumes of base were added. A plot of pH as a function of the amount of Na_2CO_3 added is shown in Figure 2. Although there is considerable scatter in the pH profiles, presumably due to

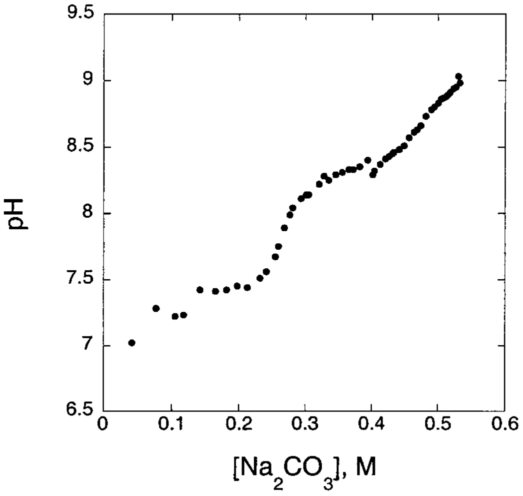

Figure 2. Plot of the pH versus Na_2CO_3 added for the conversion of α-$P_2W_{18}O_{62}^{6-}$ to α-$P_2W_{15}O_{56}^{12-}$ as measured by a pH electrode suspended in the well-stirred solution. Reaction conditions: 18.6 g of $K_6[\alpha$-$P_2W_{18}O_{62}]$ dissolved in 62 mL of H_2O and 70.6 mL of 1.0 M Na_2CO_3 (18.4 equiv) added over a period of 45 min. This synthesis resulted in 67% pure $[(n$-$C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ (experiment 11, Table 2).

the slow phosphotungstate equilibria,[31] the general shape of the plot is reproducible, including the small dips it exhibits.

One can see from the plot that a plateau of sorts is reached at approximately pH 8.2; further addition of the base causes a slow increase in pH to 9. It is interesting to note that the first visible sign of a precipitate corresponds to the beginning of this plateau near pH 8.2. Another interesting observation is that the end of this plateau (ca. 40 mL of Na_2CO_3; 10.4 equiv) qualitatively correlates with the amount of base used in Contant's 1990 synthesis.[3] These observations suggest one or more of the following: (1) pH 9 is too high for the formation and precipitation of pure product, so at this pH impurities such as $P_2W_{12}O_{48}^{14-}$ and $P_8W_{48}O_{184}^{40-}$ [32] are coprecipitated. (2) Accurate monitoring of the pH of the reaction solution is problematic due to the suspended fine product particles (the manual for the Corning pH electrode used in these experiments states, "Some samples can cause the junction to become blocked" which, of course, could lead to inaccurate pH measurements). (3) Alternatively, the pH is not crucial; rather, it is only the *amount* of base that affects the production and coprecipitation of impurities.

Each of these possibilities was addressed experimentally. To avoid coprecipitation of impurities with $Na_{12}[\alpha$-$P_2W_{15}O_{56}]$ due to high pH, our 1997 synthesis was carried out at 22 °C, but the pH was only allowed to reach 8.1 (experiment 8 in Table 2), as suggested by the pH versus volume plot of 1.0 M Na_2CO_3 in Figure 2. Even though this is well below the reported pH 9.0, the measured purity (after the addition of 16.4 equiv of Na_2CO_3) was still only 68%. Despite the shape of the pH versus Na_2CO_3 volume plot, this experiment strongly suggests that the exact *amount* of base is more important for a reproducible synthesis than the time-dependent solution pH.

Possible inaccuracies associated with the pH electrode were explored by comparing the pH value of the electrode suspended in solution with an electrode used intermittently throughout the reaction. In all cases the values agreed within ± 0.02 pH unit. Hence, any pH measurement error is likely both small and *not* the cause of the impure α-$P_2W_{15}O_{56}^{9-}$.

The only identifiable factor which influences the purity of the $Na_{12}[\alpha$-$P_2W_{15}O_{56}]$ and subsequent formation of $[(n$-$C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ is the amount of 1.0 M Na_2CO_3 added to α-$P_2W_{18}O_{62}^{6-}$. When a molar ratio of $Na_2CO_3/K_6[\alpha$-$P_2W_{18}O_{62}]$ of ca. 12.6 is used, the formation of $\geq 90\%$ pure product is observed (section 1, Table 2). Excess base leads to an impure product, a finding that had not been realized until now, despite the prediction that this might be true given the stoichiometric requirement for 12 equiv of base in eqs 1 and 2. In fairness to earlier researchers, not only was there no way to distinguish between 80 and 90% pure $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$, but doing so was not necessary for the cases where *crystalline* products in good yields were synthesized.[1,2,7,8,26,27]

The Best Synthesis Is Contant's 1990 *Inorganic Syntheses* Procedure Which Yields 90 ± 3% Pure $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$. An examination of Table 1 demonstrates that only Contant's 1990 synthesis[3] provides an exact volume of 1.0 M Na_2CO_3 solution to be added to the reaction mixture, which is very close to the stoichiometrically required 12 equiv. Hence, Contant's 1990 synthesis[3] is recommended as the best current synthesis of $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$. This synthesis was successfully scaled up 4.6 times to yield 106 g of $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$ (see the Experimental Section for details). However, the purity of the resultant $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$ is ca. 90% as judged by its conversion to $[(n$-$C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ (see section 1 of Table 2 and Figure 1), an important but previously unavailable finding.

Control Experiments Testing Other Variables

With a reproducible 90% pure $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$ synthesis in hand, we systematically probed the other variables that could have had an effect on either its purity or yield. Remarkably, none of the variables examined below showed any measurable effect by ^{31}P-NMR ($\pm 3\%$) on the synthesis of $Na_{12}[\alpha$-$P_2W_{15}O_{56}]\cdot 18H_2O$ made according to Contant's 1990 preparation. The key results are shown in Table 2 and briefly discussed below.

The Rate of 1.0 M Na_2CO_3 Addition. Since $Na_{12}[\alpha$-$P_2W_{15}O_{56}]$ is kinetically precipitated from solution and given that relatively slow phosphotungstate equilibria are involved,[31] one would have anticipated that the rate at which sodium carbonate was added to the α-$P_2W_{18}O_{62}^{6-}$ solution could have been critical to the formation of a pure product. To test this, the Contant synthesis was carried out as described in the Experimental Section, except the base was added over 1 h rather than a few minutes. The conversion to $[(n$-$C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$ was carried out, and a purity of 90% was found by ^{31}P-NMR (section 2 of Table 2). This value is the same within experimental error as the purity

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(31) Pettersson, L. Equilibria of Polyoxometalates in Aqueous Solution. In *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Norwell, MA, 1994; pp 27−40.

(32) Contant, R.; Tézé, A. *Inorg. Chem.* **1985**, *24*, 4610.

obtained following the addition of base more than an order of magnitude faster (90%). The yield also seems to be unaffected by the rate of addition of base. (Contant's synthesis[3] resulted in a yield of 62%, whereas our 1997 synthesis[4] reports a 76% yield; the 10−15% "higher yield" difference corresponds rather closely to the additional level of impurity present in the 1997 synthesis.) These results also suggest that the *precipitated solid* $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ is stable in its reaction solution for up to 1 h, with little decomposition to α-$P_2W_{17}O_{61}^{10-}$ occurring under the conditions of its synthesis.[3,18] (Contant reports that the conversion of α-$P_2W_{15}O_{56}^{12-}$ to α-$P_2W_{17}O_{61}^{10-}$ is "complete after several hours"; we surmise that this conversion is a function of the concentration, that is, of how much is in solution and other unspecified conditions.)

The Temperature of the [α-$P_2W_{18}O_{62}$]$^{6-}$ Solution Prior to the Addition of 1.0 M Na_2CO_3. In all the syntheses of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$, the sodium salt of α-$P_2W_{18}O_{62}^{6-}$ is generated in situ by the addition of $NaClO_4$. To completely precipitate the metathesis product $KClO_4$, the solution is stirred in an ice bath for 3 h, and the solid is filtered from the solution. Control experiments suggest that the temperature post ice-bath treatment can range from 5 to 22 °C, depending on the amount of time elapsed between the filtration and the base-addition steps; that is, none of the published procedures specify an exact temperature for this filtrate prior to the addition of base.

To test for any possible effects of temperature on the purity and yield of the resultant $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$, the Contant synthesis was carried out at 10, 22, and 45 °C. The results of these experiments are summarized in section 3 of Table 2, and show that when sodium carbonate is added to aqueous $Na_6[\alpha\text{-}P_2W_{18}O_{62}]$ at 10, 22, and 45 °C, the purity of the final product is not affected so long as the reaction is allowed to sit for 10 min, as described in the Experimental Section. It is surprising that these changes in temperature did not affect the formation of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ (i.e., the aforementioned relatively slow phosphotungstate equilibria[31]) or its kinetic precipitation.

The Scale of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ Synthesis. Contant's 1990 synthesis was scaled up from 38.5 to 176 g of $K_6[\alpha\text{-}P_2W_{18}O_{62}]$ with no change in the 90% purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ (see section 4 of Table 2). These results demonstrate that the purity of the final product is independent of the scale over a 38−176 g range of the starting material.

The Method of Drying Solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. Another subtle difference between the syntheses in Table 1 is the method used to dry the final product. Since lacunary polyoxoanion isomerization is known to occur at elevated temperatures,[2] the method of drying solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ samples was briefly examined. Two identical syntheses of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ were carried out via the Contant method, except that one of the samples was dried in a 50 °C oven overnight, and the other dried in a desiccator over concentrated H_2SO_4 for 2 days (see section 5 of Table 2). Each sample was then converted into $[(n\text{-}C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$, and the ^{31}P-NMR spectra were obtained. The spectra show 90% pure product in both cases, showing that no isomerization (or other temperature-dependent degradation reaction) of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ occurs in a 50 °C oven for up to 24 h. More importantly, these experiments show that oven drying at 50 °C overnight is a viable alternative to the more time-consuming method of storage over H_2SO_4 for 2 days for this metastable polyoxoanion.

Controls Testing the Source of Nb^{5+} Used in the Formation of $[(n\text{-}C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$. Since the purity of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ has only been assessed by the conversion to the niobium incorporated product $[(n\text{-}C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$, factors associated with its synthesis were also considered. The major variable in this step is the source of niobium. In our most recently published procedure either $K_8HNb_6O_{19}$ or $NbCl_5$ can be used;[11] however, all syntheses performed herein to this point were carried out with $NbCl_5$ as the Nb^{5+} source. To rule out the Nb source as a variable in the observed purity of $P_2W_{15}Nb_3O_{62}^{9-}$, a synthesis was carried out with freshly prepared $K_8HNb_6O_{19}$. This experiment also resulted in ≥90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$. Since no significant improvements in the product's purity or yield were observed, the use of $NbCl_5$ is recommended based on its commercial availability.

A Reevaluation of the Water Soluble $(CH_3)_4N^+$ Salt Intermediate. As noted in the Introduction, our original strategy, as published in our 1988 paper, was to make a water recrystallizable and, thus, purifiable salt of $P_2W_{15}Nb_3O_{62}^{9-}$ *before* its conversion to the $(n\text{-}C_4H_9)_4N^+$ salt (noncrystallizable or otherwise purifiable).[10] Although this original synthetic strategy is still generally believed to be the correct one in polyoxoanion chemistry, it remained to be demonstrated whether (a) the prior use of a $(CH_3)_4N^+$ salt reprecipitation step would actually provide any purification or (b) the use of a higher-pH solution could lead to a crystallizable salt of the $P_2W_{15}Nb_3O_{62}^{9-}$ while avoiding Nb−O−Nb bridged anhydride formation and the uncrystallizable $(P_2W_{15}Nb_3O_{61})_2O^{16-}$ (i.e., $P_4W_{30}Nb_6O_{123}^{16-}$). The availability of α-$P_2W_{15}O_{56}^{12-}$ precursors of known purity allowed us to do the experiments reported below.

The synthesis of $[(CH_3)_4N]_{12}H_4[(P_2W_{15}Nb_3O_{61})_2O]$ was carried out twice starting with two separate batches of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$. Each product was reprecipitated from hot (>80 °C) water at pH 4.6, according to the literature procedure.[4] Conversion of $[(CH_3)_4N]_{12}H_4[(P_2W_{15}Nb_3O_{61})_2O]$ to $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ followed by ^{31}P-NMR analysis indicated purities of 75 ± 3% and 88 ± 3%. Similar purities (72 ± 3% and 90 ± 3%) were obtained from the same batches of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ with syntheses that *did not* involve the formation and reprecipitation of a water soluble intermediate (i.e., when the syntheses were carried out according to ref 11). Hence, *the reprecipitation does not serve as a purification step in this case*. In addition to its failure as a purification step, the reprecipitation also consumes nearly 30% of the $(CH_3)_4N^+$ salt[4] and, therefore, should be avoided.

In an attempt to obtain a crystalline salt of the $P_2W_{15}Nb_3O_{62}^{9-}$ anion while avoiding Nb−O−Nb bridged dimer formation,[33] another synthesis of the $(CH_3)_4N^+$ salt was carried out starting with 82% pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$. However, this time the material was reprecipitated from hot water at pH 6.8. Conversion of this isolated $(CH_3)_4N^+/H^+$ salt to $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ (see the Supporting Information for details) required exactly 4 equiv of $[(n\text{-}C_4H_9)_4N]OH$, a result consistent with the isolation of $[(CH_3)_4N]_{12}H_4[P_2W_{15}Nb_3O_{62}]$ (i.e., rather than the $[(CH_3)_4N]_{12}H_4[(P_2W_{15}Nb_3O_{61})_2O]$ formed upon reprecipitation at pH 4.6).[4] Despite the apparent isolation of the monomeric $(CH_3)_4N^+$ salt, attempts to crystallize this compound from pH 6.8 water were unsuccessful. Hence, although the best general strategy for purifying polyoxoanions is still crystallization from water and then conversion to an organic solvent soluble salt, it is not applicable to the $P_2W_{15}Nb_3O_{62}{}^{9-}$ system using any of the conditions we have explored.

Summary and Conclusions

In conclusion, this study:

(a) Identifies the single most reliable synthesis of the highest-purity $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ and provides the necessary underpinning for a reliable $[(n\text{-}C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$ synthesis. Improved yields of $P_2W_{15}M_3O_{62}{}^{9-}$, $P_4W_{30}M^{n+}{}_4O_{112}{}^{4n-24}$, and all other polyoxoanions where $\alpha\text{-}P_2W_{15}O_{56}{}^{9-}$ is the key lacunary precursor are also now possible.

(b) Identifies the *amount* of 1.0 M Na_2CO_3 (12.6 equiv) as the crucial variable in the synthesis of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. This work also demonstrates that the directive in the original synthesis, to add base until pH 9 was attained, is *the* key problem in prior syntheses and, therefore, must be abandoned.

(c) Demonstrates that the other variables in the synthesis of $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$, such as the rate of base addition, the temperature of the reaction solution, the scale, the drying method, and the source of Nb^{5+}, are *not* crucial if the experimental procedures cited herein were followed exactly.

(d) Emphasizes the value of the ^{31}P-NMR handle, available in $[(n\text{-}C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$: without the ^{31}P-NMR handle, solving the current problem of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ synthesis would not have been possible.

(e) Demonstrates that it is possible to work with kinetically precipitated powders of metastable lacunary polyoxoanions at the ≥90% purity level. This study also confirms the suggestion made in our 1995 paper[18] that the purity of the lacunary precursor $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ determines the purity of the noncrystalline triniobium substitution product $[(n\text{-}C_4H_9)N]_9[P_2W_{15}Nb_3O_{62}]$.

(f) Identifies the mistakes in observing, reporting, and failure to pay sufficient attention to the balanced reaction stoichiometry (eqs 1 and 2),[19,20,22] mistakes that combined to obfuscate the preferred synthesis of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ over a 19-year period until now. The great value of repeatability, the hallmark of good science, was also emphasized:[23] only via multiple repeat experiments, first with our own and then Contant's literature, were we able to find the missing piece to the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ puzzle, the proper amount of Na_2CO_3. We have also performed the other experiments necessary to provide compelling evidence that this is, indeed, the only missing piece of the puzzle.

Experimental Section

Materials. All compounds were of reagent grade and used as received unless otherwise noted: $Na_2WO_4\cdot 2H_2O$, crystalline $NaClO_4$, $NbCl_5$ (stored in the drybox), $[(n\text{-}C_4H_9)_4N]OH$ (40% from the manufacturer, 36% by titration), $[(n\text{-}C_4H_9)_4N]Br$, $[(CH_3)_4N]Cl$ (Aldrich), KCl, Na_2CO_3, NaCl, H_2O_2 (30%, stored in the refrigerator), NaOH, acetonitrile, anhydrous diethyl ether (Fisher), $NaHSO_3$ (Baker), $ZnCl_2$, H_3PO_4 (Mallinckrodt), $NaVO_3$ (Fluka), absolute ethanol (Pharmco), CD_3CN, and D_2O (Cambridge Isotope Laboratories). Aqueous solutions were prepared with in-house deionized water.

Instrumentation. All pH measurements were made with a Corning G. P. pH electrode attached to a Corning 125 pH meter. Before each experiment, the electrode was standardized with a series of buffers (pH 4.00, 7.00, and 10.01). Nuclear magnetic resonance spectra were obtained in either CD_3CN or D_2O in 5.0 mm o.d. NMR tubes from either Spectra Tech or Wilmad. Phosphorus (^{31}P) NMR spectra (121.5 MHz) were recorded on a Varian Inova 300 spectrometer at 21 °C, and referenced to 85% H_3PO_4 (0 ppm) by an internal capillary tube containing 85% H_3PO_4.

Synthesis of $K_6[\alpha,\beta\text{-}P_2W_{18}O_{62}]\cdot xH_2O$ (for α, $x = 14$, and for β, $x = 19$). This compound was made directly from the literature procedure.[4] See the Supporting Information for details.

Synthesis of $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$. This preparation was also carried out according to literature methods.[4] See the Supporting Information for details.

The Most Recent Literature Preparation of What Has Proved To Be Impure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. These attempts were carried out according to our 1997 procedure.[4] Analysis by conversion to $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ and then ^{31}P-NMR indicate that this material is 82−83% pure (experiments 10 and 13 in Table 2). See the Supporting Information for further experimental details. For three of the experiments, the pH was monitored as a function of Na_2CO_3 concentration in order to gain further insight into the decomposition of $\alpha\text{-}P_2W_{18}O_{62}{}^{6-}$ into $\alpha\text{-}P_2W_{15}O_{56}{}^{12-}$. A typical plot of pH versus Na_2CO_3 (added as a 1.0 M solution) is shown in Figure 2. These pH measurements were recorded manually with a standardized pH electrode suspended in the well-stirred solution.

Preparation of What Has Proved To Be the Best $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ Based on Contant's 1990 Method. This synthesis was carried out at the same scale that Contant used while following his synthesis closely (experiment 1 in Table 2).[3] To a 600 mL beaker containing 125 mL of water was added 38.5 g of $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$ (8.0 mmol), and the solution was stirred with gentle heating until the solid was completely dissolved. Once the solution was homogeneous, 30.6 g (250 mmol) of crystalline sodium perchlorate was added to the reaction solution, resulting in the immediate precipitation of $KClO_4$. After 20 min of vigorous

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(33) The anhydride dimer is noncrystalline as perhaps expected due to the high charge and unsymmetrical nature of the Nb−O−Nb bridged $\{H_4[P_4W_{30}Nb_6O_{123}]\}^{12-}$. However, given that the all Na^+ salt $Na_9P_2W_{15}Nb_3O_{62}$ is crystalline, it is still conceivable that by working *at higher pH values* (to avoid the Nb−O−Nb bridged anhydride formation) a crystalline form of $P_2W_{15}Nb_3O_{62}{}^{9-}$ (e.g., as its Na^+, K^+, or Me_4N^+ salts) could be developed which would improve the purity of the resultant $P_2W_{15}Nb_3O_{62}{}^{9-}$ over the present 90% maximum demonstrated herein. Note, however, that the reported Na^+ salt was prepared *from the Bu_4N^+ salt and on only a 20 mg scale.*[33b] In short, a large scale route to crystalline $P_2W_{15}Nb_3O_{62}{}^{9-}$ remains to be developed. Finke, R. G.; Lyon, D. K.; Nomiya, K.; Weakley, J. R. T. *Acta Crystallogr., Sect. C* **1990**, *46*, 1592.

stirring of the mixture at room temperature, the beaker was placed in an ice bath for 3 h. The cold solution was then filtered through a 350 mL medium porosity glass frit into a clean 250 mL filter flask. The clear, pale-yellow filtrate was transferred to a 400 mL beaker and stirred slowly until it reached room temperature (approximately 40 min).

To the room-temperature solution was added 100 mL of a freshly prepared 1.0 M Na_2CO_3 solution as rapidly as possible without exceeding pH 9.0 (approximately 4 min), as it was monitored by a pH electrode suspended in the reaction solution. Addition of about 75 mL produced a white precipitate that remained suspended in solution. After the last of the base was added, the solution was stirred for an additional 10 min, over which time the pH fell to 8.3 (note the correspondence of this pH with the plateau at essentially the same pH in Figure 2). The white solid was then collected on a 350 mL medium porosity glass frit and dried under aspiration for 75 min, at which time it was washed for 1−2 min with a NaCl solution prepared by dissolving 4.0 g of NaCl in 25 mL of water (2.68 M NaCl). After thoroughly drying on the glass filter (2 h), the solid was washed for 2−3 min with 25 mL of ethanol and dried for another 2 h. The ethanol wash and the 2 h drying steps were repeated, and the product was transferred to a tared weighing boat and then dried in a desiccator over concentrated H_2SO_4. After 2 days, the dry solid was weighed and transferred to a glass jar. Yield: 16.4−19.9 g, 48−58% based on $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$. This material resulted in 90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ by ^{31}P-NMR (Figure 1). Alternatively, the product can be dried in a 50 °C oven overnight with similar results. Yield: 16.8 g and 49% (experiment 2 in Table 2).

This synthesis has been scaled up to 176 g of $K_6[\alpha\text{-}P_2W_{18}O_{62}]$ (experiment 6 in Table 2) with no observed effect on the purity of the resulting $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ (90−92% by ^{31}P-NMR). The yield of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ on this larger scale was 106 g and 68%.

Control Experiment Examining Contant's 1990 Preparation of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ with Slow Addition of 1.0 M Na_2CO_3. The procedure used was identical to the one above, except the 100 mL of 1.0 M Na_2CO_3 was added continuously over 1 h (experiment 3 in Table 2). Yield: 19.9 g and 58% based on $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$. This material led to 90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ by ^{31}P-NMR.

Control Experiment Examining Contant's 1990 Synthesis of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ at 10 and 45 °C. Since Contant's 1990 synthesis does not specify the temperature of the reaction solution when the 1.0 M Na_2CO_3 is added, two control experiments were carried out to test the effects of the temperature on the synthesis. These experiments were carried out according to Contant's 1990 procedure described above, except the aqueous solution of $K_6[\alpha\text{-}P_2W_{18}O_{62}]$ was either cooled in an ice bath to 10 °C or, in a separate experiment, warmed to 45 °C on a heating plate prior to the addition of the room-temperature 1.0 M Na_2CO_3. At no time during the addition of base did the temperature rise above 10 °C (or fall below 45 °C in the higher-temperature experiment). For the 10 °C experiment, the yield was 19.0 g (57% based on $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$), and the purity of the resulting $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ was 89% by ^{31}P-NMR (experiment 4 in Table 2). Similar results were obtained for the 45 °C experiment: the yield was slightly higher at 22.6 g (66% based on $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$), and the purity of the resulting $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ was 90% by ^{31}P-NMR (experiment 5 in Table 2).

Attempts to Obtain the ^{31}P-NMR Spectra of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. Attempts to record the ^{31}P-NMR spectra of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ directly were made in 1.5 M HOAc/1.00 M NaOAc/1.00 M LiCl buffer as described in ref 18 and in 1 M HOAc/1 M LiOAc as described in ref 3.[3] To minimize the documented decomposition of α-$P_2W_{15}O_{56}^{12-}$ in solution,[3,18] the elapsed time between the sample preparation and introduction into the NMR instrument was as small as possible, <20 min. Both attempts produced multiline spectra shown in Figures A and B of the Supporting Information. Note that this same batch of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ was used in the preparation of ≥90% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$.

Synthesis of $[(n\text{-}C_4H_9)_4N]_5H_4[P_2W_{15}Nb_3O_{62}]$. This compound was synthesized with minor adjustments to the literature procedure, at 100% and 50% scales with similar results.[11] See the Supporting Information for details.

Synthesis of $[(n\text{-}C_4H_9)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$. This product was made on a 50% scale directly from the published procedure,[10] except the niobium source was $NbCl_5$, as mentioned in our earlier paper.[11] Details of this synthesis are provided in the Supporting Information.

Synthesis of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$. This compound was prepared according to the literature procedure from the mixed salt $[(n\text{-}C_4H_9)_4N]_5H_4[P_2W_{15}Nb_3O_{62}]$.[11]

Synthesis of $K_7H[Nb_6O_{19}]\cdot 13H_2O$. The hexaniobate synthesis was carried out following the literature procedure.[10,34] See the Supporting Information for details.

Synthesis of $K_8H[P_2W_{15}V_3O_{62}]\cdot 9H_2O$. This compound was synthesized as a control experiment to check if pure $K_8H[P_2W_{15}V_3O_{62}]$ could be made from impure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. The target compound was prepared on a $^1/_8$ scale of the published synthesis,[26] using $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ obtained from our 1997 synthesis which exhibited only 83% purity $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ in a separate experiment. Sodium metavanadate (0.5 g, 4.1 mmol) was dissolved in 85 mL of hot water and cooled to room temperature, followed by the addition of 2 mL of 6 M HCl (12 mmol). To this rapidly stirred pale-yellow solution was slowly added 5.75 g (1.34 mmol) of solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. The solution became homogeneous, and within a few minutes became red-orange. Stirring was continued for an additional 10 min after the solution became homogeneous, followed by addition of 12.5 g (169 mmol) of solid KCl. The resulting precipitate was isolated by filtration and dried in air at 60 °C to yield 5.0 g (85% yield based on pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$) of crude material. ^{31}P-NMR (pD 1.9, D_2O, δ): −6.3, −8.7, −13.3, and −13.4 ppm for ca. 80% pure $K_8H[P_2W_{15}V_3O_{62}]$ (Figure C, Supporting Information).

The remaining solid was recrystallized from hot water at pH 1.5 to give orange needles which were collected on a 30 mL medium glass frit and dried in air overnight at 60 °C. Yield: 3.96 g and 66% based on pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$. ^{31}P-NMR (pD 1.9, D_2O, δ): −6.5 and −13.3 ppm, relative to 85% H_3PO_4 with >95% purity.

A Reevaluation of the Water Soluble $(CH_3)_4N^+$ Salt Intermediate, $[(CH_3)_4N]_{12}H_4[(P_4W_{30}Nb_6O_{61})_2O]$. The $[(CH_3)_4N]_{12}H_4[(P_4W_{30}Nb_6O_{61})_2O]$ salt was made in two separate experiments from 72% and 90% pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ and reprecipitated from hot (>80 °C) water at pH 4.6, according to the literature procedure.[4] Conversion of $[(CH_3)_4N]_{12}H_4[(P_4W_{30}Nb_6O_{61})_2O]$ to $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ and then analysis by ^{31}P-NMR showed purities of 75 ± 3% and 88 ± 3%, respectively. See the Supporting Information for further details.

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(34) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125. Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93. Flynn, C. M.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 178.

In an attempt to isolate a crystallizable salt of the $P_2W_{15}Nb_3O_{62}^{9-}$ anion while avoiding Nb−O−Nb bridged formation, $[(CH_3)_4N]_{12}H_4[(P_4W_{30}Nb_6O_{61})_2O]$ was made from 82% pure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ and reprecipitated from hot (>80 °C) water at pH 6.8. The resulting purity of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ was 82 ± 3% by ^{31}P-NMR. See the Supporting Information for further details.

An attempt to crystallize the $[(CH_3)_4N]_5H_4[P_2W_{15}Nb_3O_{62}]$ from water at pH 6.8 was made and resulted in a fine pale-yellow powder. A 1.4 g sample of $[(CH_3)_4N]_5H_4[P_2W_{15}Nb_3O_{62}]$ was added to a 250 mL beaker equipped with a magnetic stir bar. The solid was dissolved in a minimal amount of hot (>80 °C) water at pH 6.8, resulting in a clear solution, which was cooled to room temperature. A fine white powder in the bottom of the beaker was visible after 2 h. After sitting on the bench for an additional 2 h, the solution was moved to a 5 °C refrigerator for 4 days. Only a fine pale-yellow powder was recovered.

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Supporting Information Available: Figures: Figure A showing ^{31}P-NMR spectra of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ in 1.5 M HOAc/0.5 M NaOAc/1.0 M LiCl, Figure B showing ^{31}P-NMR spectra of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ in 1.0 M HOAc/1.0 M LiOAc showing multiple peaks, synthesis of $Na_{16}[Zn_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]$ (text), Figure C showing ^{31}P-NMR spectra of 80% pure $K_8H[P_2W_{15}V_3O_{62}]$ in pD 1.6 D_2O, Figure D showing ^{31}P-NMR spectra (CD_3CN) of 82% pure $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$. **Text:** synthesis of $K_6[\alpha,\beta\text{-}P_2W_{18}O_{62}]\cdot xH_2O$ (for α, $x = 14$ and for β, $x = 19$), synthesis of $K_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$, Figure E showing ^{31}P-NMR spectra (D_2O) of $K_6[\alpha\text{-}P_2W_{18}O_{62}]$ showing >95% purity, the most recent literature preparation of what proved to be impure $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$, synthesis of $K_7H[Nb_6O_{19}]\cdot 13H_2O$, synthesis of $[(n\text{-}C_4H_9)_4N]_5H_4[P_2W_{15}Nb_3O_{62}]$, synthesis of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$, a re-evaluation of the water soluble $(CH_3)_4N^+$ salt intermediate, synthesis of the water soluble $[(CH_3)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$, synthesis of $[(n\text{-}C_4H_9)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$, synthesis of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ from $[(n\text{-}C_4H_9)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$, attempt to make crystalline $[(CH_3)_4N]_5H_4[P_2W_{15}Nb_3O_{62}]$ from $[(CH_3)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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