

The Classic Wells–Dawson Polyoxometalate, $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$. Answering an 88 Year-Old Question: What Is Its Preferred, Optimum Synthesis?

Christopher R. Graham and Richard G. Finke*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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The 88-year-old problem of developing a preferred, optimized synthesis of the prototype Wells–Dawson polyoxometalate, $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$, is addressed herein. Specifically, six published syntheses of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ are listed and discussed, with emphasis given to the two most recent syntheses, Nadjo and co-workers' 2004 synthesis and a 1997 *Inorganic Syntheses* procedure by Droege, Randall, Finke et al. (hereafter D-R-F). For the starting experiment, the synthesis by Nadjo and co-workers was repeated. Next, the D-R-F synthesis and then the earlier (1984) synthesis in Droege's Ph.D. thesis were repeated and reinvestigated. The results demonstrate that the Nadjo synthesis produces over 200 g of high α -isomer purity ($\geq 97\%$ by ^{31}P NMR) $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ in four steps over 8 days in 93% yield in our hands. A recrystallization step added as part of this work (for a total of five steps over 12 days) produces an increase in purity ($>99\%$) with a concomitant loss of 8% yield (i.e., 85% overall yield) for the Nadjo-plus-recrystallization synthesis. Next, the D-R-F *Inorganic Syntheses* procedure was reinvestigated to determine the cause of "failed syntheses" occasionally encountered in our laboratories, the most recent and worst example to date being when one of us (C.R.G.) found 150 g of $K_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ as an undesired side product when, as it turns out, the D-R-F *Inorganic Syntheses* procedure is followed rather than the earlier Droege synthesis. Specifically, it is shown that the problem in the *Inorganic Syntheses* procedure is that it ambiguously says to add 210 mL of HCl until a pH of 3–4 is reached when, in fact, it takes only 130–150 mL of HCl to reach a pH 3–4. Adding the full 210 mL of HCl ensures that a pH <2 is reached, as is required to produce isomerically pure $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ from the $K_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ intermediate. The result is $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ in five steps over 10 days in 82% yield and $\geq 97\%$ purity. A table is provided comparing the details of the two best syntheses as reported herein: the Nadjo-plus-recrystallization synthesis and the D-R-F synthesis (with sufficient added HCl/proper pH control). That table makes apparent that the Nadjo-plus-recrystallization synthesis is improved on the basis of its better atom economy, its slightly higher product yields (85% vs 82%), slightly better purity ($>99\%$ vs $>97\%$), and its comparable time (2 days shorter without recrystallization but 2 days longer with recrystallization) in comparison to the D-R-F synthesis with proper pH <2 control. Perhaps most importantly, some take-home messages concerning polyoxometalate synthesis illustrated by the iterative, 88 year-old quest to the best $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ synthesis are summarized and briefly discussed.

Introduction

The Wells–Dawson polyoxometalate (POM), $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$, first characterized by Dawson,¹ is probably second only to the Keggin structure, $[\text{PW}_{12}\text{O}_{40}]^{3-}$,²

among the best-known phosphotungstate polyoxometalates (POMs).³ Hence, producing the Wells–Dawson POM in large quantities of high α isomer purity—the α form being the most stable isomer^{4–6}—is important. Large quantities

* To whom correspondence should be addressed. E-mail: rfinke@lamar.colostate.edu.

(1) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113–126.

(2) Keggin, J. F. *Proc. R. Soc. London, Ser. A* **1934**, *144*, 75–100.

(3) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983; p 70.

(4) Wu, H. *J. Biol. Chem.* **1920**, *43*, 189–220.

(5) Contant, R. *Inorg. Synth.* **1990**, *27*, 104–111.

Table 1. Primary Literature Syntheses for $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$

entry	date	author	general synthesis plus apparent, balanced stoichiometry of each synthesis ^a	scale, g (yield, %) ^{b,c}
1	1920	Wu ⁴	$18[\text{WO}_4]^{2-} + 32\text{H}_3\text{PO}_4 + 6(\text{NH}_4)^+ \rightarrow (\text{NH}_4)_6[\alpha,\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] + 30\text{H}_2\text{PO}_4^- + 18\text{H}_2\text{O}$	30 (20) ^d
2	1945, 1969	Souchay ^{13,14}	same stoichiometry as Wu's synthesis, entry 1	? ^e
3	1984	Droege ^{10,15,16}	(1) $18[\text{WO}_4]^{2-} + 32\text{H}_3\text{PO}_4 + 6\text{K}^+ \rightarrow \text{K}_6[\alpha,\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] + 30\text{H}_2\text{PO}_4^- + 18\text{H}_2\text{O}$ (2) $\text{K}_6[\alpha,\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] + 6\text{KHCO}_3 \rightarrow \text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}] + [\text{WO}_4]^{2-} + 2\text{K}^+ + 6\text{CO}_2 + 3\text{H}_2\text{O}$ (3) $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}] + [\text{WO}_4]^{2-} + 6\text{H}^+ \rightarrow \text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] + 4\text{K}^+ + 3\text{H}_2\text{O}$	60 (85)
4	1990	Contant ⁵	$18[\text{WO}_4]^{2-} + 32\text{H}_3\text{PO}_4 + 6\text{K}^+ \rightarrow \text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] + 30[\text{H}_2\text{PO}_4]^- + 18\text{H}_2\text{O}$	165 (80)
5	1997	Droege/Randall/Finke et al. ^{9,12}	same stoichiometry as Droege's synthesis, entry 2	186 (76)
6	2004	Nadjo et al. ¹¹	(1) $7[\text{WO}_4]^{2-} + 8\text{H}^+ \rightarrow [\text{W}_7\text{O}_{24}]^{6-} + 4\text{H}_2\text{O}$ (2) $80\text{H}_3\text{PO}_4 + 18[\text{W}_7\text{O}_{24}]^{6-} + 42\text{K}^+ \rightarrow 7\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] + 66[\text{H}_2\text{PO}_4]^- + 54\text{H}_2\text{O}$	232.5 (95)

^a A problem in these syntheses is that they require an excess of H_3PO_4 , as detailed in the main text (vide infra) and as compared to the minimum stoichiometry given in Table 2. ^b Yield is based on mass of $\text{Na}_2[\text{WO}_4] \cdot 2\text{H}_2\text{O}$. ^c α isomer purity not quantitated. ^d β isomer. ^e Souchay did not quantitate his products.

Table 2. Moles of Reagents Used and Product Formed in the Synthesis of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ as well as the Minimum Moles Required for the Stoichiometry Given in Footnote *a*

synthesis	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	H_3PO_4	HCl	NH_4Cl	KCl	KHCO_3	$[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ ^c
<i>ideal, minimum moles required^a</i>	0.91	0.10	1.52	0.30	0.30	0.00	0.05
(1) Wu ^b	0.91	3.64	0.00	14.96	0.00	0.00	0.01 ^d
(2) Souchay ^b	0.91	6.64	0.00	11.22	0.00	0.00	? ^e
(3) Droege thesis ^b	0.91	6.64	1.98	0.0	8.05	1.95	0.04
(4) Contant ^b	0.91	3.70	0.00	2.80	1.04	0.00	0.04
(5) D-R-F	0.91	6.64	1.26	0.00	7.71	1.10	0.04
(6) Nadjo	0.91	1.00	1.00	0.00	2.00	0.00	0.05

^a Atom economy (minimum mole amounts) are given according to the following stoichiometry: $18[\text{WO}_4]^{2-} + 2\text{H}_3\text{PO}_4 + 30\text{H}^+ + 6(\text{K}^+ \text{ or } \text{NH}_4^+) \rightarrow (\text{K} \text{ or } \text{NH}_4)_6[\text{P}_2\text{W}_{18}\text{O}_{62}] + 18\text{H}_2\text{O}$. ^b The actual mole amounts of $\text{Na}_2[\text{WO}_4] \cdot 2\text{H}_2\text{O}$ in Wu's, Souchay's, Contant's and Droege's syntheses are 0.61, 0.61, 0.76, and 0.30, respectively. The scale, and thus moles of all reagents and products, of Wu's, Contant's and Droege's syntheses have each been increased proportionately to equal that of the other two larger scale syntheses for comparison. ^c Yield is based on 300 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. ^d Wu quantitated only $[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$. ^e Souchay did not quantitate his products.

of pure $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ are needed, in turn, for the synthesis of the monolacunary POM $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$,^{5,7,8} as well as for the synthesis of the trivacant lacunary POM $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$, "the prototype multitungsten vacant lacunary polyoxoanion of the Wells–Dawson structural type".^{5,9}

Due, therefore, to its fundamental significance in POM chemistry, the synthesis, structure, and properties of the Wells–Dawson POM have been investigated for 88 years.^{5,9–14} Table 1 gives the six most common synthetic procedures found in the literature to date,^{4,5,9,11–14} beginning with Wu's 1920 synthesis,⁴ which has remained the basis for every well-known synthesis for $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ over the intervening years, up to Nadjo and co-workers' 2004 synthesis (vide infra).¹¹

In 1945 (and then also in 1969), Souchay published a synthesis for $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ that modified Wu's by removing five recrystallizations and slightly changed the masses and volumes of reagents and solutions (see Table 2). In 1984, some 64 years after Wu's original report, Droege reported in his Ph.D. thesis a modified Wu synthesis (Table 1, entry 3) for $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$. Droege's synthesis used KCl in place of $(\text{NH}_4)\text{Cl}$ as the counteranion for $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and produced 94% purity $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (without physically separating the α and β isomers) by following Wu's insight⁴ that base decomposition of $[\alpha,\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ to $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ and WO_4^{2-} and subsequent reacidification produces isomerically pure $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (Table 1, entry 3). In 1990, Contant reported a synthesis (Table 1, entry 4) that, like Souchay's, produced $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ with fewer recrystallizations than Wu's procedure and, like Droege's procedure, used KCl in place of $(\text{NH}_4)\text{Cl}$ to produce the final $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ product. In the same 1990 *Inorganic Syntheses* publication, Contant also offered an alternative procedure which produced $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (88% purity by ³¹P NMR) without physically separating the α and β isomers first. In 1997 Droege's procedure was updated via an experimentally checked *Inorganic Syntheses* procedure performed primarily by Randall¹² during his sabbatical at the University of Oregon, a synthesis referred to herein as the Droege–Randall–Finke or, for short, D-R-F synthesis. The D-R-F synthesis reported a ca. 3-fold scale increase over

- (6) Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2008–2010.
 (7) Randall, W. J.; Lyon, D. K.; Domaille, P. J.; Finke, R. G. *Inorg. Synth.* **1998**, *32*, 242–268.
 (8) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209–7221.
 (9) Hornstein, B. J.; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 2720–2730.
 (10) Droege, M. W. *Ph.D. Dissertation*, University of Oregon, 1984.
 (11) Mbomekalle, I. M.; Lu, Y. W.; Keita, B.; Nadjo, L. *Inorg. Chem. Commun.* **2004**, *7*, 86–90.
 (12) Randall, W. J.; Droege, M. W.; Mizuno, N.; Nomiya, K.; Weakley, T. J. R.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 167–185.
 (13) Souchay, P. Contribution A L'Étude Des Hétéropolyacides Tungstiques. *Ph.D. Thesis*, Université De Paris, Paris, France, 1945.
 (14) Souchay, P. *Ions Minéraux Condensés*; Masson: Paris, 1969; p 106.

Table 3. ^{31}P NMR Chemical Shifts for $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ Produced Herein from a D-R-F Synthesis with Insufficient HCl Added (pH \sim 3–4) and Chemical Shifts from the Literature for Comparison

polyoxometalate	exptl conditions	chem shifts (ppm)	ref
bulk, white precipitate; D-R-F synthesis	K^+ salt and LiClO_4 in D_2O	–7.0, –13.8	this work
$\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]\cdot 15\text{H}_2\text{O}$	K^+ salt and LiClO_4 in D_2O	–6.9, –13.7	this work
$\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]\cdot 15\text{H}_2\text{O}$	K^+ and LiClO_4 in 1:1 D_2O – H_2O	–7.3, –14.1	7
$\alpha_2\text{-}[\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$	K^+ salt in 0.5 M LiCl	–6.8, –13.7	25

the Droege synthesis, reduced the molar amounts of HCl, KCl, and KHCO_3 required (see Table 2), and also increased product purity over Contant's and Droege's original syntheses, 97% vs 88% and 94%, respectively. For this reason, the D-R-F synthesis became an important and popular $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ synthesis from 1997 until recently. However, over the intervening years we have found that the D-R-F synthesis still has one main problem, at least in the hands of five of our group members and at least when one follows the *Inorganic Syntheses* version^{9,12} of the original Droege synthesis:^{10,15} occasionally as much as 100–150 g of a white precipitate is formed as a side product along with as little as 40 g (vs the expected 150–186 g^{9,12}) of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$, notably in a recent synthesis in one of our hands (C.R.G.). The white side product, if formed, always appears after the addition of, first, 6 M HCl and then KCl to the solution of $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ and $[\text{WO}_4]^{2-}$ (Table 1, entry 3, step 3). A second problem with the D-R-F synthesis is that the potassium salt of the Preyssler anion, $\text{K}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, is a byproduct formed in smaller quantities (<10 g), this anion being a known impurity formed in the synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$.^{5,9,12,17–19} As pointed out by Nadjo,¹¹ the presence of the Preyssler anion as an impurity is likely a problem of the historical use of an unjustified excess of H_3PO_4 (i.e., unjustified by stoichiometry or by synthetic optimization²⁰) in the Wu, Souchay, Contant, Droege, and D-R-F syntheses (Table 2).

While searching the literature to see if anyone else had addressed these remaining issues in the synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$, we discovered the synthesis published by Nadjo and co-workers (Table 1, entry 6).¹¹ As the stoichiometry for the Nadjo synthesis in Table 1, entry 6, reveals, the Nadjo synthesis is a significant departure from Wu's basic procedure and its subsequent modifications (Table 1, entries 1–5). The essence of the Nadjo synthesis is that it (i) premakes paratungstate A, $[\text{W}_7\text{O}_{24}]^{6-}$ ^{11,21,22,25} in situ, (ii) acidifies that to pH < 2, and (iii) uses what is described as “an appropriate but optimal excess” required amount of H_3PO_4 ,¹¹ in the presence of KCl, to yield in their hands 232.5 g (95%) of “high purity” $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$.

We were, therefore, quite intrigued and curious about Nadjo and co-workers' new synthesis; more specifically, we

had the following questions about it: does it work as well, and in the yields and purity, claimed? (The published synthesis does not quantitate the α -isomer purity.) Is some β -isomer, $\text{K}_6[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]$, impurity formed as one would expect, and what about any Preyssler anion, $\text{K}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, impurity? Has the use of less H_3PO_4 reduced or even eliminated this impurity as one would like? Can a final recrystallization step improve the purity of the final product even further?

Also, we wondered if we could readily reproduce the concise Nadjo synthesis, as a survey of it indicates that it lacks some quantitative experimental details (e.g., the speed and time required for adding reagents, the time to wait in between steps, the methods and equipment used for heating, cooling, and filtering, and a final product purity) that we,⁹ and others,^{23,24} have noted are crucial for others being able to reproduce literature POM syntheses. Overall, is the Nadjo and co-workers' synthesis an advance in the synthesis of the prototype Wells–Dawson POM and, therefore, also of the lacunary POMs derived from this key, prototype POM? Finally and perhaps most importantly, can we, by a re-examination of the $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ syntheses, clean up the remaining issues in the 88-year-old problem of the preferred synthesis of the Wells–Dawson anion *so that, once and for all, a single, preferred, 100% reliable $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ synthesis can be recommended with high confidence to the community?*

Herein, we address the questions posed above while striving to provide the definitive paper that clears up all the remaining problems with respect to obtaining a reproducible, preferred synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ to recommend to the community. Specifically, we demonstrate (i) that Nadjo and co-workers' synthesis¹¹ is improved compared to prior syntheses by the specific criteria of atom economy, synthesis time, number of steps, and percent yield of product, (ii) that the white precipitate side product formed in failed syntheses following the D-R-F *Inorganic Syntheses* procedure is simply unreacted $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ that has failed to react with the WO_4^{2-} present to re-form $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, a failure that results due to the incorrect pH 3–4 directive written in the *Inorganic Syntheses* procedure being followed rather than the directive to add 210 mL of HCl, (iii) that the Preyssler anion,

$[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, does form as the potassium salt $\text{K}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ in the D-R-F synthesis (<10 g), as verified by its ^{31}P NMR chemical shift and IR spectrum which match those in the literature,^{17,18} and (iv) that this Preyssler impurity is traceable to the excess H_3PO_4 used in the Wu, Souchay, Contant, Droege,

(15) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886–3896.

(16) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692–1704.

(17) Alizadeh, M. H.; Harmalkar, S. P.; Jeannin, Y.; Martin-Frère, J.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2662–2669.

(18) Jeannin, Y.; Martin-Frere, J. *Inorg. Synth.* **1990**, *27*, 115–118.

(19) Pope, M. T. *Polyoxo Anions: Synthesis and Structure In Comprehensive Coordination Chemistry*; McCleverty, J., Meyer, T. J., Eds.; Pergamon Press: Oxford, U.K., 2004; Vol. 4, pp 635–678.

(20) Mbomekalle, I. M.; Keita, B.; Nadjo, L.; Contant, R.; Belai, N.; Pope, M. T. *Inorg. Chim. Acta* **2003**, *342*, 219–228.

(21) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983; p 50.

(22) Maksimovskaya, R. I.; Burtseva, K. G. *Polyhedron* **1985**, *4*, 1559–1562.

and D-R-F syntheses as Nadjo had implied (and since we cannot detect it ($\leq 1\%$) in Nadjo's synthesis using less H_3PO_4). In addition, (v) we report an experimentally more detailed version of the Nadjo synthesis that is repeatable in our hands and that, therefore, may assist others who are less experienced in POM synthesis but who wish to use this synthesis. Finally and perhaps most importantly, (vi) by considering our previous experience with $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-9}$ and our current work with the syntheses of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$, we summarize some take-home messages about polyoxometalate synthesis that continue to reappear and thus merit emphasis en route to improved, trouble-free, reliable POM and related inorganic self-assembly syntheses.

Experimental Section

Materials. All materials were used as received: $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (99%) and LiClO_4 (95+%) (Aldrich), KCl , KHCO_3 , and Na_2CO_3 (Fisher), H_3PO_4 (85%) and HCl (37.6%) (Mallinckrodt), D_2O (99.9%) (Cambridge Isotope Laboratories). Aqueous solutions were prepared using in-house deionized water.

Instrumentation. pH measurements were made using EMD colorpHast nonbleeding pH indicator strips or, where indicated, a Corning 125 pH meter equipped with a Beckman Coulter Futura gel-filled combination electrode. The pH meter was calibrated using Fisher Scientific standard buffer solutions. ^{31}P NMR spectra were obtained at 22°C on a Varian Inova 300 MHz instrument. Spectral parameters for ^{31}P NMR: tip angle, 88.2° ; acquisition time, 1.600 s; sweep width, 10 000.0 Hz. ^{31}P NMR samples were dissolved in D_2O or a 1:1 solution of D_2O – H_2O and transferred to a 5 mm o.d. NMR tube. A Li^+ metathesis using LiClO_4^7 was performed on every ^{31}P NMR sample prior to analysis to produce the more aqueous soluble Li^+ POM salt and precipitate the insoluble, and therefore easily removed, KClO_4 . All ^{31}P NMR samples were referenced to 85% H_3PO_4 (0.00 ppm) in an internal capillary. ^{183}W NMR spectra were obtained at 25°C or, where indicated, higher temperatures (49 – 53°C) on a Varian Inova 500 MHz NMR instrument. Spectral parameters for ^{183}W NMR: relaxation delay, 5.000 s; tip angle, 36.0° ; acquisition time, 0.498 s; sweep width, 12 839.0 Hz. All ^{183}W NMR samples were dissolved in D_2O and transferred to a 10 mm o.d. NMR tube. All ^{183}W NMR samples were referenced to a 2.0 M aqueous (D_2O) solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.00 ppm) by the substitution method. All ^{31}P and ^{183}W NMR spectra were analyzed using MestReC Lite version 4.9.9.6. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet Magna-IR 760 ESP IR spectrometer. FT-IR spectral parameters: resolution, 4.000; sample gain, 8.0; mirror velocity, 0.6329; aperture, 69.00. All FT-IR samples were prepared as KBr pellets using a KBr die and Carver Laboratory Press.

POM Syntheses. Original Droege 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 exactly as described in Droege's Ph.D. thesis¹⁰ and as reproduced elsewhere.¹⁵

Droege/Randall/Finke et al. Synthesis of the Mixed (α,β) Isomer $\text{K}_6[\alpha,\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot x\text{H}_2\text{O}$ ($x = 14$ for α , $x = 19$ for β). The procedure for this synthesis was followed exactly as written in the literature.^{9,12}

Droege/Randall/ Finke et al. Synthesis of Isomerically Pure (α) $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$. The procedure for this synthesis was followed exactly as written in the literature.^{9,12}

Additional-Acid Experiments for Droege/Randall/Finke et al. Synthesis. These experiments were performed to confirm that the addition of more acid will promote the formation of

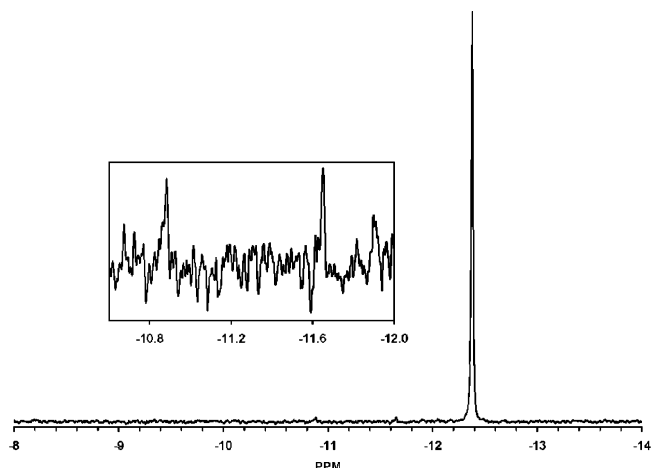


Figure 1. ^{31}P NMR of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ (purity $\geq 97\%$) from Nadjo synthesis. The α -isomer peak is shown at -12.3 ppm. Small β -isomer impurity peaks can be seen around -10.8 and -11.6 ppm. There is no detectable ($\leq 1\%$) $[\text{NaP}_3\text{W}_{30}\text{O}_{110}]^{14-}$ (-9.3 ppm) in this spectrum.

$[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ in a solution that contains the precipitate $\text{K}_{10}[\text{P}_2\text{W}_{17}\text{O}_{61}]$ and $[\text{WO}_4]^{2-}$. The details of these experiments are provided in the Supporting Information.

Contant Synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$. The procedure followed for this synthesis is listed under "Alternative Procedure" in the *Inorganic Syntheses* publication of Contant's synthesis for $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$.⁵

Synthesis of $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}] \cdot 15\text{H}_2\text{O}$. The literature synthesis of this POM was followed, and products were analyzed, exactly as written elsewhere.⁷

Nadjo Synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$. The procedure for this synthesis is found in the literature.¹¹ The additional specific experimental details we followed for this procedure are provided in the Supporting Information for the interested reader,²⁴ including the recrystallization procedure contributed as part of the present paper.

Results and Discussion

Nadjo Synthesis. To start, we repeated the synthesis procedure as published by Nadjo and co-workers¹¹ as exactly as we could. Even on our first attempt we were able to reproduce their synthesis, with the small exception of slightly lower product yield (our first product yields were 10–11% less than those reported,¹¹ yields which are, however, still 4–20% higher than the other syntheses listed in Table 1; our subsequent yields are 93%). The purity of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$ produced from the Nadjo synthesis is high, $\geq 97\%$, as the ^{31}P NMR in Figure 1 demonstrates. The potassium salt of the Preysslery anion, $\text{K}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, a common impurity produced in the various syntheses of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 14\text{H}_2\text{O}$,^{5,9,12,17–19} is absent ($\leq 1\%$) in the Nadjo synthesis, as judged by the lack of

(23) A POM synthesis procedure that lacks all the necessary procedural details is often a problem, particularly for beginning researchers unfamiliar with POM synthesis. In 1990, for the 27th volume of *Inorganic Syntheses*, volume editor Ginsburg correctly wrote that the syntheses of POMs represent "the synthesis of a class of compounds that are notably difficult to prepare in pure form. The successful preparation of many of these compounds requires close attention to the details of the procedure, and in several cases critical details taken for granted by the submitters were brought out by the checkers."²⁴

(24) Ginsberg, A. P. *Inorg. Synth.* **1990**, *27*, viii.

(25) Contant, R.; Herve, G. *Rev. Inorg. Chem.* **2002**, *22*, 63–111.

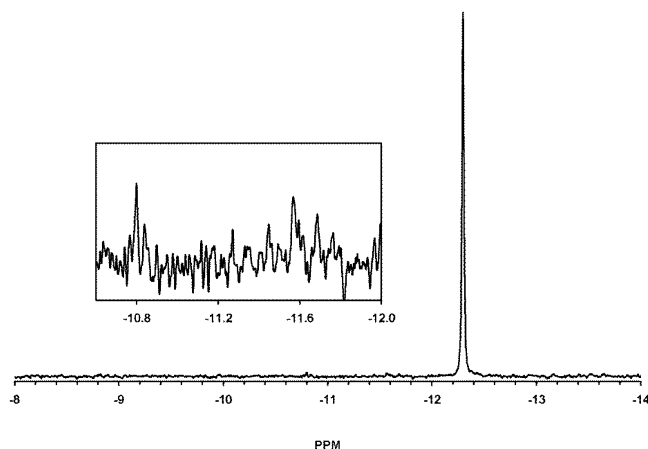


Figure 2. ^{31}P NMR of recrystallized $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ from Nadjo synthesis (purity 99+%).

a detectable ^{31}P NMR peak at -9.4 ppm.²⁵ The only ^{31}P NMR detectable side product in the Nadjo synthesis is $\leq 3\%$ $[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (Figure 1).

Another strength of the Nadjo synthesis is its minimal use of reagents, that is, its “atom economy”,^{26,28} as shown in Table 2. Table 2 makes apparent that the Wu, Souchay, Contant, and D-R-F syntheses are non-optimum in their use of large excesses of H_3PO_4 , as Nadjo and co-workers have noted.¹¹ Table 2 also makes apparent the slow, iterative nature of improving self-assembly syntheses—over decades of effort—that looks to be unavoidable in the absence of the required mechanistic insights into self-assembly and productive intermediates along the self-assembly route (e.g., Nadjo and co-workers’ use of $[\text{W}_7\text{O}_{24}]^{6-}$; vide infra).

The underlying basis of the Nadjo synthesis is that it starts from paratungstate A, $[\text{W}_7\text{O}_{24}]^{6-}$,^{11,21,22,25} a point we have verified by direct detection of $[\text{W}_7\text{O}_{24}]^{6-}$ by ^{183}W NMR (see the Supporting Information). Restated, a key to the Nadjo synthesis is its “building-block approach” rather than strict self-assembly from $\text{WO}_4^{2-}/\text{H}^+/\text{PO}_4^{3-}$.

We have also tested whether a simple recrystallization of the final product of a Nadjo synthesis would yield higher purity $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$; in fact, a single recrystallization yields $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ from the Nadjo synthesis that is 99+% pure by ^{31}P NMR (Figure 2) with only a small loss (8%) in the final yield, the highest combined yield and purity of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ ever reported. (Note that (i) both Figures 1 and 2 come from the same batch of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ before and after recrystallization, respectively, and (ii) both figures are displayed on a common scale for their easy comparison. The insets to Figures 1 and 2 are also displayed on the same scale so that the β -product peaks can be easily compared before and after recrystallization.)

Finally, we have added some quantitative experimental details (such as the speed and time required for adding reagents, the time to wait between steps, and the methods and equipment used for heating, cooling and filtering, all

reported in the Supporting Information) to aid others in the successful use of this synthesis. None of those details are more than minor; however, *the synthesis of Nadjo and co-workers works as reported in our hands*, including by a researcher (C.R.G.) with little previous POM synthesis experience.

Re-Examination of the D-R-F Synthesis. The D-R-F synthesis^{9,12} is based on Droege’s exploitation of Wu’s observation that when α or β $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (identified by Wu as forms B and A, respectively^{4,6}) is degraded with base and then reacidified, only the α product forms.^{4,8} As shown in the stoichiometry in Table 1, entry 3, the base degradation of α or β $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ forms $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]$ and $[\text{WO}_4]^{2-}$, a fact we confirmed herein using ^{31}P and ^{183}W NMR and IR, as described in the Supporting Information. The proper acidification of the $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]/[\text{WO}_4]^{2-}$ solution using 6 M HCl should then produce isomerically pure $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$.^{4,10,12}

However, this is where the details of a POM synthesis matter and often “rear their ugly head” if insufficient detail is presented. In Droege’s 1984 synthesis he states “About 110 mL 6 M HCl was carefully added to the P_2W_{17} mixture regenerating a clear yellow solution and $\alpha\text{-P}_2\text{W}_{18}$.”^{10,15} Small missing, but useful, details here include (a) the precise pH of the final solution, (b) a specific addition rate and total time (i.e., vs the imprecise “carefully”), and (c) a total reaction time (e.g., in case there are any hidden kinetic issues involved in the reaction). The *Inorganic Syntheses* modification of the original Droege synthesis performed primarily by Randall strives to provide the needed additional details, stating “210 mL of 6 M HCl is slowly, but continuously added over 5–10 minutes to produce a clear, yellow solution. The solution must be clear, but do not add more than just enough HCl to accomplish this *neutralization* (italics added). The pH at this point should be around 3–4”.¹² In fact, during our investigation into the problems surrounding the D-R-F synthesis discussed herein, we find that dropping the pH of a D-R-F $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]/[\text{WO}_4]^{2-}$ solution to 3–4 never requires 210 mL of 6 M HCl, as stated in the procedure quoted above. Usually only 130–150 mL of 6 M HCl is required to obtain a solution pH of 3–4. Moreover, we find that pH < 2 is needed for the synthesis of pure $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ in high yield, as Nadjo’s synthesis implies (vide infra).^{11,29}

On more than one occasion, and in several different researchers’ hands, we have found that a white precipitate can be formed in solution after adding, first, 6 M HCl to pH 3–4 and then KCl. When large amounts of the white precipitate formed (in the worst case to date up to 150 g in one of our hands; C.R.G.), the yield of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ was low (e.g., < 40 g vs the expected 150–186 g).¹² Hence, as part of the present work, we analyzed this bulk white precipitate and confirmed, as expected, that it is the lacunary intermediate, $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]\cdot 15\text{H}_2\text{O}$. The IR spectrum and ^{31}P NMR chemical shifts confirm its identity, in comparison to authentic

(26) Trost, B. M. *Science* **1991**, *254*, 1471–1477.

(27) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695–705.

(28) National Research Council., *Beyond the Molecular Frontier*; The National Academies Press: Washington, DC, 2003; p. 25.

(29) Smith, B. J.; Patrick, V. A. *Aust. J. Chem.* **2004**, *57*, 261–268.

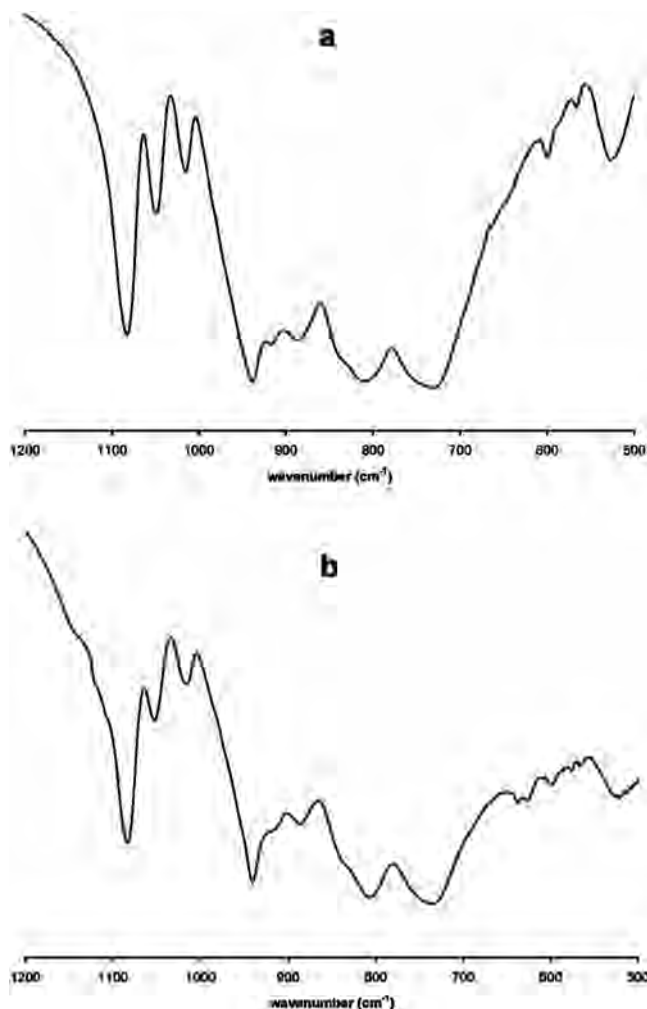


Figure 3. (a) IR spectra of (a) bulk white precipitate formed from a D-R-F synthesis with insufficient HCl added (pH ~3–4) and (b) authentic $K_{10}[\alpha_2-P_2W_{17}O_{61}] \cdot 15H_2O$ produced from a literature procedure (97% pure by ^{31}P NMR).⁷

$K_{10}[\alpha_2-P_2W_{17}O_{61}] \cdot 15H_2O$ produced from a literature procedure⁷ (Figure 3 and Table 3).

The presence of $K_{10}[\alpha_2-P_2W_{17}O_{61}]$, plus the reaction stoichiometry of the D-R-F synthesis shown in Table 1 (entry 3, step 3), revealed the problem: incomplete acidification of the intermediate $K_{10}[\alpha_2-P_2W_{17}O_{61}]/[WO_4]^{2-}$ solution and a resulting incomplete re-formation of the desired $[\alpha-P_2W_{18}O_{62}]^{6-}$. Hence, adding the full amount of 6 M HCl needed—that is, simply doing what Droege originally said in 1984 that one should do!^{10,15}—should correct the problem. Indeed, in one D-R-F synthesis the procedure was followed exactly (except for convenience at one-third scale) until formation of the white, $K_{10}[\alpha_2-P_2W_{17}O_{61}]$ precipitate occurred. More 6 M HCl was added until the solution became clear again (10 mL; the pH of the final solution was 1.7). The final product of that synthesis was $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ in 65% yield and 94% purity as detailed in the Supporting Information. In short, after nearly a quarter of a century since Droege's original synthesis, and post more than a year of the researcher involved being side-tracked from his original research goals by this synthesis, we had rediscovered the correct version of the D-R-F synthesis (i.e., Droege's original synthesis), including identification of the key, conflicting details which were inhibiting the successful comple-

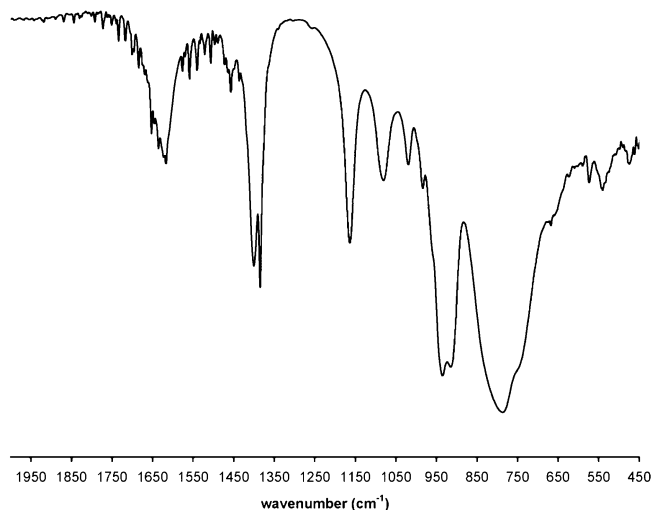


Figure 4. IR spectrum of $K_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ formed as byproduct of the D-R-F synthesis. This spectrum matches that found in the literature for authentic $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$.¹⁸

tion of that synthesis—the incorrect directive to acidify the solution to pH 3–4 vs the correct directive of adding 210 mL of 6 M HCl to the solution! As final verification of Droege's original synthesis procedure, we followed his Ph.D. dissertation procedure¹⁰ as exactly as we could and found that it produced pure $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$ precisely as Droege described (86% yield, 94% α -isomer purity by ^{31}P NMR). In short, we discovered that it was one small but vital piece of misinformation that was the problem: the conflicting pH 3–4 vs 210 mL HCl directives in the D-R-F *Inorganic Syntheses* procedure.

We also confirmed that the potassium salt of the Preyssl anion, $K_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, forms as a byproduct of the D-R-F synthesis, albeit in <1% yield by ^{31}P NMR (see the Supporting Information) and IR. The IR spectrum of $K_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ obtained matches that for authentic $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ found in the literature^{17,18} (Figure 4). These studies would appear to complete the investigation of the issues remaining around the synthesis of $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$.

The general lessons here for polyoxometalate synthesis seem clear: (i) first, one needs to write complete, balanced stoichiometries up front for any POM or other synthesis, a point (of, in hindsight, freshman chemistry) that we have emphasized before,⁹ (ii) one should, in general, be wary of using nonstoichiometric reagent ratios in self-assembly syntheses unless there are good reasons to do so,^{11,20} and very importantly (iii) it is impossible to write down too many experimental details for a polyoxoanion or other self-assembly—or for that matter probably any other—synthesis³⁰ and, of course, those details need to be accurate and quantitative.

Direct Comparison of the Top Two Syntheses of $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$. Table 4 compares the synthetic details and attributes of the top two syntheses of $K_6[\alpha-P_2W_{18}O_{62}] \cdot 14H_2O$. The times for all the syntheses are long, but in the case of the Nadjo-plus-recrystallization synthesis for example, 10 out of the 12 days involve solutions simply being heated or cooled or product being dried. As can be seen from Tables 2 and 4, the Nadjo-plus-recrystallization

Table 4. Comparison of the Key Points of the Top Two Syntheses of $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$

synthesis	total exptl steps	total exptl time (days)	obsd impurities (amt (%))	yield (%) ^a	α -isomer purity (%)
(1a) Nadjo et al. w/o recryst	4	8	$K_6[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] (\leq 3)$	93	≥ 97
(1b) Nadjo et al. with recryst	5	12	$K_6[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] (\leq 1)$	85	> 99
(2) D-R-F with pH < 2 ensured	5	10	$K_6[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}] (\leq 3)$ $K_{14}[\text{NaP}_3\text{W}_{30}\text{O}_{110}] (\leq 1)$	82	≥ 97

^a The percent yields given in this table are the highest yields obtained by one of us (C.R.G.). The observed ranges (and thus “estimated error bars”) on the yields are $\pm 2\%$.

synthesis is improved vs the runner-up D-R-F (plus proper pH < 2) synthesis in terms of its atom economy, slightly better demonstrated purity ($\geq 99\%$ vs $\geq 97\%$), higher percent yield (85% vs 80%), comparable total required time (12 days vs 10 days), and fewer number of steps (4 vs 5). As such, we recommend to the community that the Nadjo-plus-recrystallization synthesis be used henceforth.

Summary and Conclusions

The most important findings in this report are, then, as follows.

(1) The self-assembly synthesis of the Wells–Dawson complex, $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$, even after 88 years and more than 5 published syntheses, required further optimization; this fact exemplifies the difficulty in synthesizing pure POMs and in understanding and executing selective self-assembly syntheses in general, especially when mechanistic insights—such as possible key intermediate species that are, therefore, synthetic targets—are lacking.

(2) As was made clear by our previous experience with the synthesis of $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$,⁹ some simple “guidelines/rules” to follow in POM and related self-assembly syntheses include (i) to write down—and follow in at least one’s first

(30) While investigating this current problem, we were again reminded of how easily important quantitative details can be lost from one publication to another, as the following example illustrates. In 1987, we published a paper in *Inorganic Chemistry* that detailed Droege’s original synthesis procedure,¹⁰ quoting: “A 10% KHCO_3 solution was slowly poured into the stirring P_2W_{18} solution. After addition of ca. 250 mL of KHCO_3 , the solution became cloudy and the white salt $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ precipitated. The KHCO_3 addition was continued until the solution was colorless and no more salt formed. Approximately 400 mL more KHCO_3 was needed to reach this point. About 110 mL 6 M HCl was carefully added to the P_2W_{17} mixture, regenerating a clear yellow solution of $\alpha\text{-P}_2\text{W}_{18}$.”¹⁵ In 1988, only 1 year later but in the hands of a new postdoctoral researcher still learning the subtleties of synthetic work, a paper was published in *Organometallics* that described Droege’s synthesis but failed to cite (actually removed!) many quantitative details, “To this clear light yellow solution was added 10% KHCO_3 until all the white $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ had precipitated and the supernatant was colorless. Six molar HCl was then added slowly in 5–10 mL portions to regenerate a clear yellow solution of pure $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}$.”¹⁶ This one example illustrates the vigilance necessary—at least in our own laboratories—to ensure that crucial quantitative and descriptive details are not changed or simply omitted as syntheses pass from one generation of students to the next, even in the same laboratory. This example also teaches that, if one has a checked, reliable, and repeatable synthesis, then it is actually better experimental reporting to simply but precisely report that “the synthesis elsewhere^{xx} was repeated exactly” (i.e., rather than having yet another researcher write down his or her version of the (they often believe) “improved” synthesis). Such concise experimental reporting does, however, rely on the researcher involved to actually repeat that synthesis “exactly”, which, again and in turn in this “Catch 22” situation, requires that the synthesis be written up with sufficient detail that it can be repeated “exactly” by a (hypothetical) “average” researcher. In short, checked and typically reliable syntheses such as *Inorganic, Organic, or Materials Syntheses* are extremely important to the advance of both synthetic chemistry and science in general.

syntheses—the balanced stoichiometries (or synthetically optimized amounts) for the proposed synthesis, (ii) to be meticulous in reporting all the details for each synthesis, with special attention to details such as the amount of acid and the resultant pH (since slower hydrolysis or M–O–M side-product-forming reactions can change pH recordings vs time), times and temperatures, order of addition of reagents, and so on, and (iii) to follow all POM (and all other!) syntheses by direct methods whenever possible.

(3) The best synthesis published to date for isomerically pure $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ is the Nadjo and co-workers’ synthesis. The Nadjo synthesis is improved in its use of the proper, apparently optimized ratios of reagents, its associated atom economy, and its $[\text{W}_7\text{O}_{24}]^{6-}$ building block/synthon-based approach. It produces over 200 g of highly pure ($\geq 97\%$) $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ and, in our hands, no side products other than $\leq 3\%$ $[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$. Moreover, with one recrystallization we have shown that the α isomeric purity can be increased to 99+%, with only a 8% loss in yield.

(4) Identification of all products in POM syntheses, including failed ones, is important and would have led to the realization much earlier that insufficient acid was being added in failed D-R-F syntheses involving the reacidification of $\text{K}_{10}[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]/[\text{WO}_4]^{2-}$. This again is reminiscent of our work on $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$, where we noted that “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”.⁹ In the present case with $K_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ the failure of earlier researchers to identify the “white precipitate” that was produced ensured that every subsequent researcher encountered the same problem as their predecessor.

(5) There is a critical need for more work into the mechanisms of self-assembly and into key intermediates or synthons of POM syntheses such as $[\text{W}_7\text{O}_{24}]^{6-}$, a point Nadjo and co-workers have also emphasized.¹¹

(6) Older POM syntheses that were published before the ready availability of modern physical methods such as ³¹P and ¹⁸³W NMR, ESI-MS, and more routine and rapid X-ray crystallography may well be nonideal and may merit reinvestigation. Any syntheses that currently require large excesses of reagents, far beyond the amounts suggested by the stoichiometry, are, the present work suggests, prime cases for re-examination.^{11,20,31}

In short, the present work, as well as our previous experience with and multiple lessons from $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$,⁹ indicate that there is still much to learn about even suppos-

(31) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983; p 15.

edly “well-known” POM syntheses as well as about self-assembly syntheses in general. Nevertheless, it is scientifically pleasing to come to an apparent definitive close to an effort began 88 years ago by Wu—a biologist frustrated enough with the lack of reliable POM syntheses that he took to improving them with his own hands—and an effort continued by Souchay, Contant and co-workers, Droegge, Randall and co-workers, Nadjo and co-workers, and now the present effort by Graham et al. Such is the nature of the present state-of-the-art POM and other self-assembly syntheses, basically requiring a group effort to iteratively refine them over, often, a long period of time, until and unless mechanistic insights advance the science more rationally. This history suggests another hypothesis: that no POM (or other self-assembly synthesis) should be published, at least ideally, until and unless it is checked by at least *two* independent research groups, one *not* necessarily “skilled in the art”.³²

Acknowledgment. We thank Dr. Chris D. Rithner of the Central Instrumentation Facility at Colorado State University for his assistance with the ¹⁸³W NMR experiments and Dr.

(32) The “two groups” here comes from the observation that even the *Inorganic Syntheses* checking procedure by a single group did not catch the seemingly small but insidious error of the incorrect pH 3–4 directive in the D-R-F *Inorganic Syntheses* procedure. Repeatability is the key hallmark of reliable science.

Murielle Watzky for her help with the translation of Souchay’s synthesis. This work was supported by DOE Grant DE-FG02-03ER15453.

Supporting Information Available: Text detailing the Nadjo synthesis procedure reproduced from the literature with additional experimental details added and two additional added acid experiments for a one-third-scale D-R-F synthesis, Figure A showing the ¹⁸³W NMR spectrum of [W₇O₂₄]⁶⁻ in D₂O produced during the Nadjo synthesis, Figure B showing the ³¹P NMR spectrum of the white precipitate filtered out from a D-R-F synthesis solution after base degradation using KHCO₃ and the spectrum of authentic K₁₀[α₂-P₂W₁₇O₆₁]·15H₂O produced from a literature procedure, Figure C showing the IR spectrum of the white precipitate filtered from a D-R-F et al. synthesis solution after base degradation and an IR spectrum of authentic K₁₀[α₂-P₂W₁₇O₆₁]·15H₂O produced from a literature procedure, Figure D showing a ¹⁸³W NMR spectrum of [WO₄]²⁻ in D₂O formed during base degradation of a D-R-F synthesis solution, Figure E showing ³¹P NMR of a D-R-F additional acid experiment product which is isomerically pure [α-P₂W₁₈O₆₂]⁶⁻, Figure F showing the titration curve for the D-R-F synthesis where the acidification after base degradation was performed via a titration and monitored by a pH meter; and Figure G showing the ³¹P NMR of [α-P₂W₁₈O₆₂]⁶⁻, a product of a D-R-F synthesis which also contains the Preyssler anion, [NaP₅W₃₀O₁₁₀]¹⁴⁻, as an impurity. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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