


Communication

# Fast Microwave-Assisted Synthesis of Wells-Dawson-Type 18-Tungsto-2-Phosphate $[P_2W_{18}O_{62}]^{6-}$

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**Abstract:** We report on a fast microwave-assisted synthetic procedure of the Wells-Dawson-type 18-tungsto-2-phosphate  $[P_2W_{18}O_{62}]^{6-}$  with a 35% yield in 24 h, rather than a week using conventional heating.

**Keywords:** microwave; NMR; polyoxometalates; synthesis; Wells-Dawson ion

## 1. Introduction

Polyoxometalates (POMs) are discrete, anionic metal-oxides of early d-block metal ions in high oxidation states (e.g.,  $W^{VI}$ ,  $Mo^{VI}$ ,  $V^V$ ). The Keggin (e.g.,  $[PW_{12}O_{40}]^{3-}$ ) and Wells-Dawson ions (e.g.,  $[P_2Mo_{18}O_{62}]^{6-}$ ) are amongst the best known and most stable POM structures [1–6]. The 18-tungsto-2-phosphate  $[P_2W_{18}O_{62}]^{6-}$  ( $P_2W_{18}$ ) has been particularly well studied; its structure was predicted by Wells in 1945 and experimentally determined by Dawson in 1953 [3,5].  $P_2W_{18}$  is one of the most studied POMs, and several different synthetic routes have been reported during the last 64 years [7–9], the most recent being the one by Nadjó's group, reported in 2004 [9]. In 2008, Finke's group compared, in detail, all known synthetic procedures for  $P_2W_{18}$ , with respect to yield, purity, and reaction time [10].

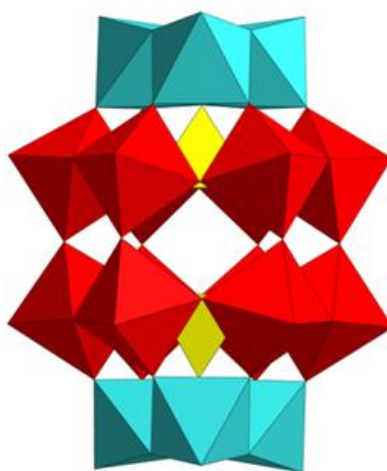
The use of household microwaves in scientific laboratories started in the 1980s, mainly for the rapid synthesis of organic compounds [11]. Later, scientific microwave instruments became available and were found to be highly suitable for heating reaction mixtures fast and energy-efficiently (green chemistry); these instruments are also used in inorganic and materials chemistry. This technique has allowed enhancing reaction rates and improving yields [11–15].

Microwave-assisted synthesis has also been used in POM chemistry, and one of the first studies was Bonchio's synthesis of  $[PW_{11}O_{39}Ru^{II}(DMSO)]^{5-}$  [16]. More recently, Ritchie has used this heating technique for the synthesis of various polyoxomolybdates in organic solvents [17–19]. Our group has also studied microwave-based heating in POM chemistry, and very recently we reported on the Preyssler-Pope-Jeannin polyanions  $[AgP_5W_{30}O_{110}]^{14-}$  and  $[NaP_5W_{30}O_{110}]^{14-}$  [20].

Here, we report on a fast, microwave-assisted synthetic procedure of the 18-tungsto-2-phosphate Wells-Dawson ion,  $P_2W_{18}$ .

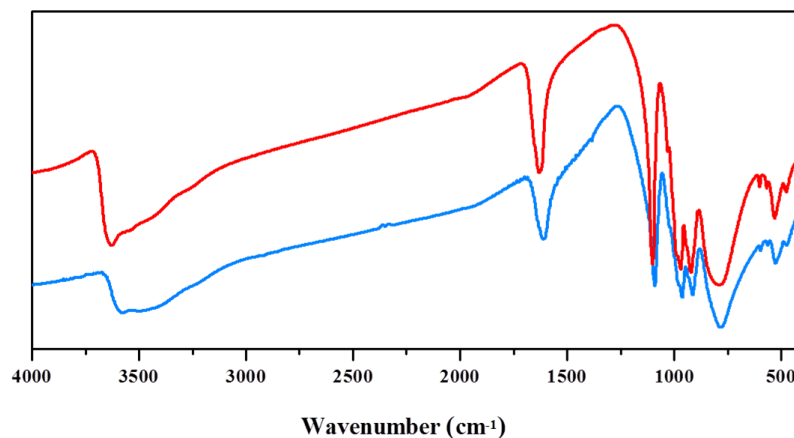
## 2. Results

The 18-tungsto-2-phosphate  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  ( $\text{P}_2\text{W}_{18}$ ) is a plenary POM comprising 18  $\text{WO}_6$  octahedra and two internal  $\text{PO}_4$  tetrahedra, resulting in a structure with two caps and two belts (see Figure 1). This polyanion is the precursor for the synthesis of several interesting and useful lacunary polyanions, such as  $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ ,  $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ ,  $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ ,  $[\text{H}_6\text{P}_4\text{W}_{24}\text{O}_{94}]^{18-}$ , and  $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$ . Considering that the conventional synthesis of  $\text{P}_2\text{W}_{18}$  takes around a week [9], we decided to try and develop a significantly faster procedure by using microwave-assisted synthesis. We modified the 24 h reflux step in the conventional procedure by instead heating for 5 min in a scientific microwave oven. Then, the solution was cooled to 5 °C, and impurities were removed by filtration. KCl was added to the filtrate solid, resulting in a green-yellow precipitate, which was dissolved in hot water and then recrystallized to obtain pure  $\text{P}_2\text{W}_{18}$  with a 35% yield. The detailed synthetic procedure is shown in the Experimental Section. The yield is lower for the microwave-based procedure than for the conventional procedure, but the former is significantly faster by several days.



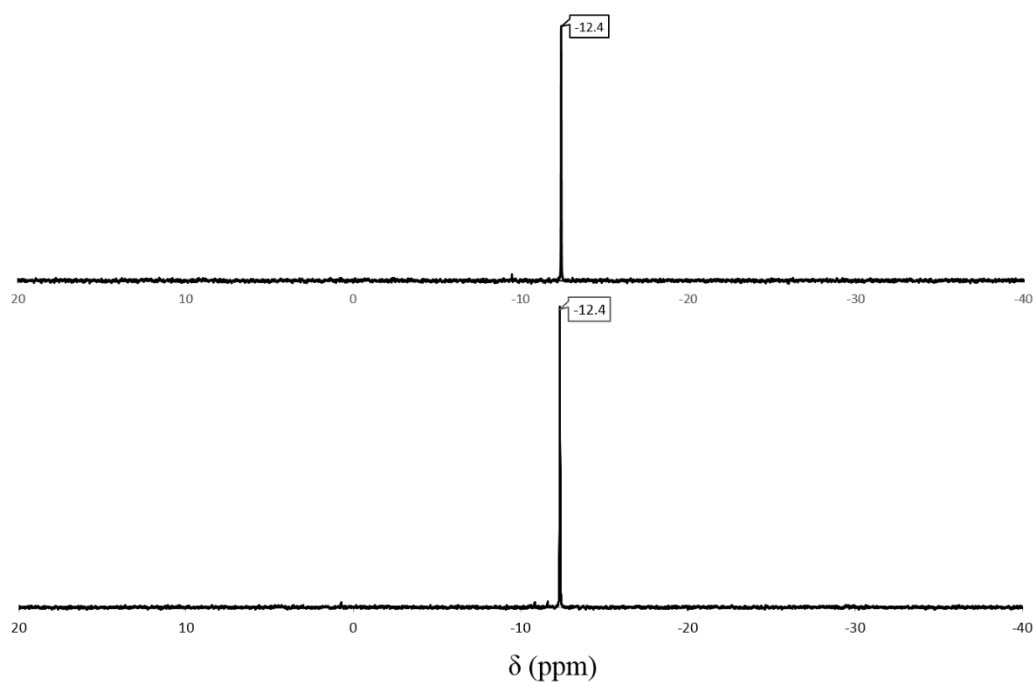
**Figure 1.** Polyhedral representation of  $\text{P}_2\text{W}_{18}$ , with the two belts of six  $\text{WO}_6$  octahedra each in red, the two caps of three  $\text{WO}_6$  octahedra each in turquoise, and the two  $\text{PO}_4$  tetrahedra in yellow.

Both potassium salts of  $\text{P}_2\text{W}_{18}$  ( $\text{K-P}_2\text{W}_{18}$ ) synthesized by the microwave-based (see Exp. Section) and conventional procedures, respectively, were characterized by FT-IR,  $^{31}\text{P}$  NMR, and thermogravimetric analysis (TGA). The IR spectra of both  $\text{K-P}_2\text{W}_{18}$  products were identical (Figure 2), with the fingerprint region exhibiting signals at 1091(s), 1020(m), 960(s), 917(s), 780(s), 600(w), 568(w), 531(w), and 476(w)  $\text{cm}^{-1}$  (s = strong, m = medium, w = weak).



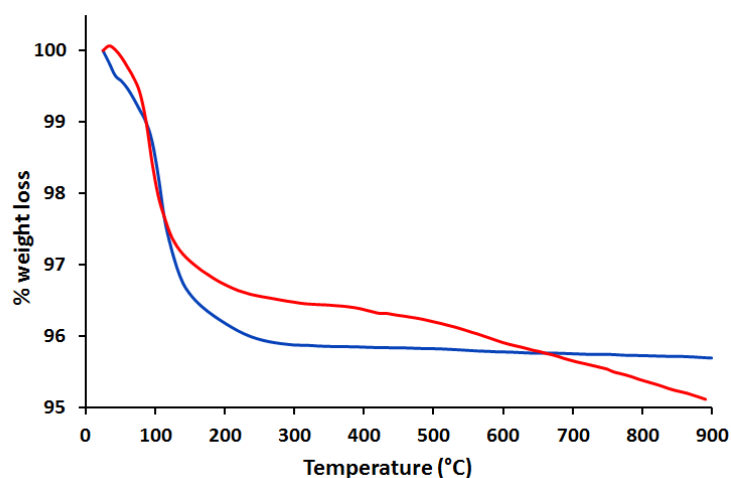
**Figure 2.** FT-IR spectra of  $\text{K-P}_2\text{W}_{18}$  synthesized by microwave-based (blue) and conventional (red) methods.

The  $^{31}\text{P}$  NMR spectrum of  $\text{K-P}_2\text{W}_{18}$  synthesized by the microwave-assisted procedure shows a singlet at  $-12.4$  ppm, just like the material prepared conventionally (see Figure 3). This result is consistent with the observations of earlier reports [7–10]. It should be noted that very small amounts of the beta-isomer  $[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  ( $-10.9$  and  $-11.6$  ppm) and free phosphate ( $0.7$  ppm) are also present. Finke's group has demonstrated how to further purify such a mixture, in order to obtain isomerically clean material [10].



**Figure 3.**  $^{31}\text{P}$  NMR spectra of solid  $\text{K-P}_2\text{W}_{18}$  dissolved in  $\text{H}_2\text{O}/\text{D}_2\text{O}$ , (lower) synthesized by microwave-assisted heating and (upper) by conventional heating. See text for details.

Figure 4 shows the thermograms of  $\text{K-P}_2\text{W}_{18}$  synthesized by microwave-assisted and conventional heating. Both samples were dried overnight in an oven at  $50$  °C before the TGA analysis. Between room temperature and  $250$  °C the microwave-synthesized  $\text{K-P}_2\text{W}_{18}$  exhibited a weight loss of ca. 4%, as compared to ca. 3.5% for the conventionally synthesized  $\text{K-P}_2\text{W}_{18}$ . This results in the formulas  $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 11\text{H}_2\text{O}$  (microwave heating) and  $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}] \cdot 9\text{H}_2\text{O}$  (conventional heating).



**Figure 4.** Thermograms of  $\text{K-P}_2\text{W}_{18}$  synthesized by microwave-assisted (blue) and conventional (red) heating.

### 3. Materials and Methods

All chemicals were purchased from commercial sources and used as received. FT-IR spectra were recorded as KBr pellets on a Nicolet Avatar 370 spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA). UV-vis spectra were recorded on a Varian Cary 100 Bio spectrophotometer (Varian, Palo Alto, CA, USA). The  $^{31}\text{P}$  NMR spectra were recorded in 5 mm tubes on a JEOL ECX 400 spectrometer (JEOL, Tokyo, Japan) with 85%  $\text{H}_3\text{PO}_4$  as reference and a resonance frequency of 161.6 MHz. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q600 machine (TA Instruments, New Castle, DE, USA).

#### *Synthesis of $\text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot 11\text{H}_2\text{O}$ (K- $\text{P}_2\text{W}_{18}$ )*

The reaction mixture for the synthesis of  $\text{P}_2\text{W}_{18}$  was prepared following the procedure of Nadjo [9].  $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$  (3.00 g, 9.00 mmol) was dissolved in 3.5 mL of distilled water in a 15 mL glass vial with constant stirring for ca. 5 min to obtain a clear, colorless solution. Then, 2.5 mL of 4 M  $\text{HCl}_{\text{aq}}$  were added slowly and dropwise with vigorous stirring. The homogeneous solution was stirred for an additional 10 min, and the final pH of the solution was between 6 and 7. Then, 2M  $\text{H}_3\text{PO}_4$  (1.5 mL) and 4 M  $\text{HCl}$  (1 mL) were added simultaneously, resulting in a clear, pale yellow solution. This solution was premixed for 30 s and then heated with stirring using a CEM Discover XP microwave (CEM Corporation, Matthews, NC, USA) fitted with an IR sensor for temperature control and electromagnetic stirring. Borosilicate vials with a capacity of 10 mL were used in the microwave machine for 5 min at 200 °C with  $\mu\text{L} = 300\text{ W}$  at 8.0 bar. The pale yellow color of the solution became darker during the microwave experiment. Then, the solution was transferred to a 25 mL beaker and kept in a refrigerator at 5 °C for 2 h. The white precipitate was removed by filtration. To the clear, light green-yellow filtrate, solid  $\text{KCl}$  (1.50 g, 0.02 mol) was added with constant stirring, resulting in a light green-yellow precipitate, which was dissolved in a minimum amount of boiling water and then recrystallized overnight. Greenish-yellow crystals of  $\text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot 11\text{H}_2\text{O}$  (K- $\text{P}_2\text{W}_{18}$ ) were isolated by filtration and then dried at 50 °C overnight. Yield: 0.84 g, 35%.

### 4. Conclusions

The Wells-Dawson polyanion  $\text{P}_2\text{W}_{18}$  is one of the most studied POMs, and several different synthetic routes have been reported during the last 64 years. However, there have been no reports on microwave-assisted heating procedures for the synthesis of  $\text{P}_2\text{W}_{18}$ . Here, we have demonstrated that with microwave heating,  $\text{P}_2\text{W}_{18}$  can be synthesized in only 24 h, as confirmed by FT-IR and  $^{31}\text{P}$  NMR spectroscopy. The yield of such a procedure is 35%, which is lower than for the conventional procedure (95% yield), but it must be noted that the latter procedure takes around a week. Most importantly, our work suggests that microwave-based synthesis is applicable for POM chemistry in general. It remains to be seen what impact this technique will have on POM chemistry in the long run, but it is evident that at least some selected examples will appear. Currently we explore if microwave-assisted synthesis allows for the preparation of novel POMs that cannot be obtained via conventional (open beaker), reflux, or hydrothermal methods.

**Author Contributions:** U.K. and S.A.J. planned the project and the experiments. V.M.P. synthesized  $\text{P}_2\text{W}_{18}$  using the conventional procedure, whereas H.M.Q. synthesized  $\text{P}_2\text{W}_{18}$  using the microwave procedure and performed IR studies. A.H. performed NMR and TGA studies and wrote the first draft of the manuscript. A.S.M. performed NMR studies and helped edit the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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