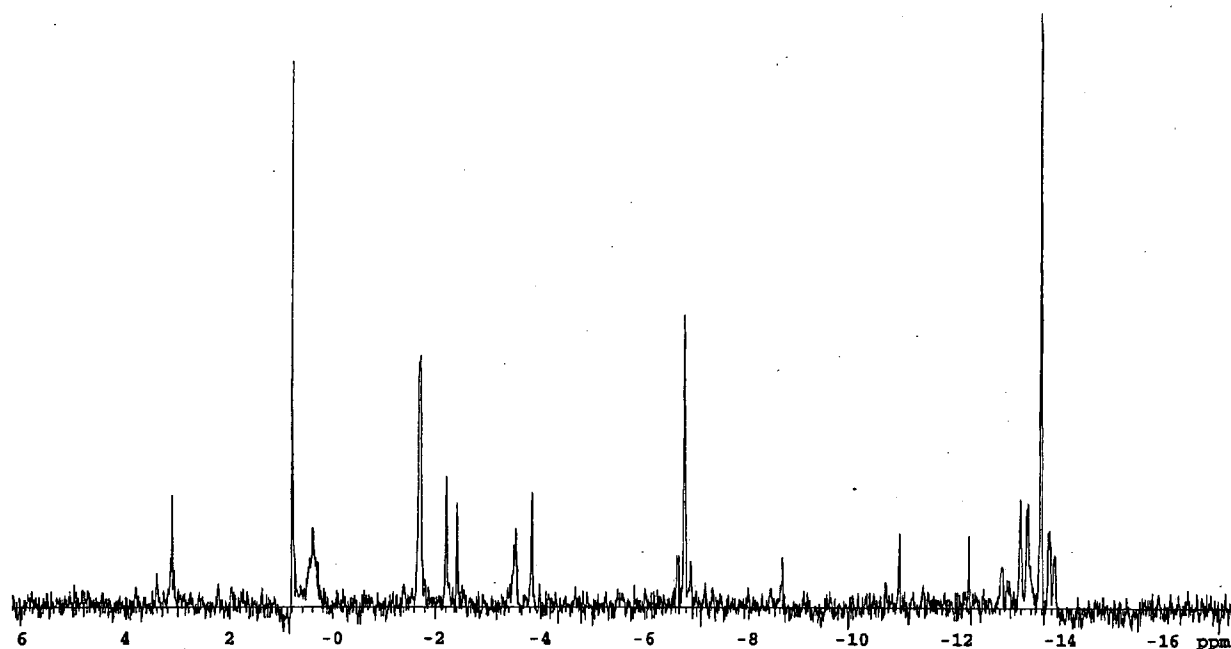


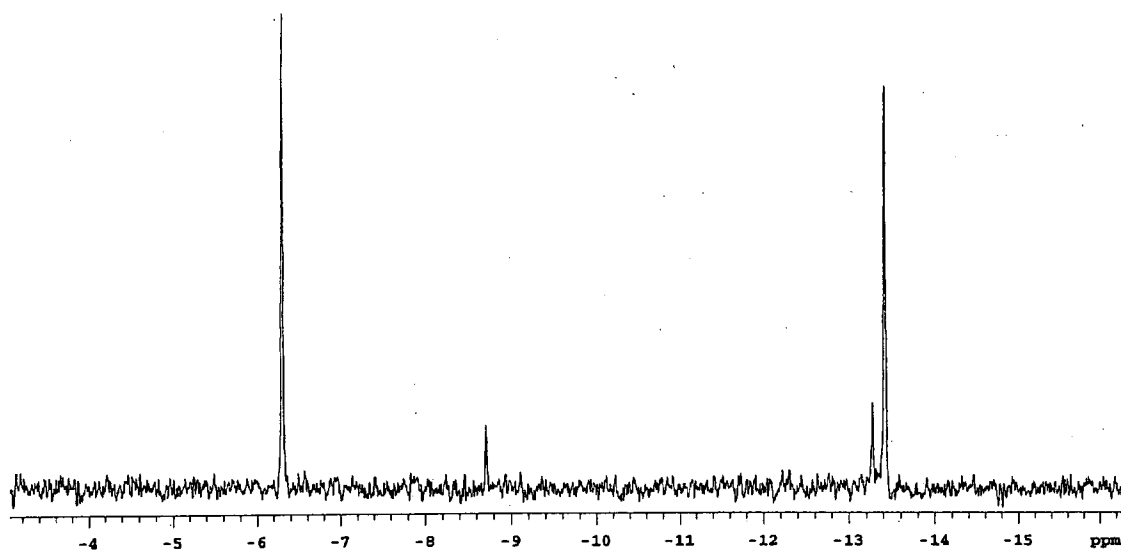
**Figure A.**  $^{31}\text{P}$  NMR of  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$  in 1.5 M HOAc / 0.5 M NaOAc / 1.0 M LiCl showing multiple peaks. Referenced to 85%  $\text{H}_3\text{PO}_4$  (0 ppm). This spectrum changes substantially over a one hour period which is consistent with reports in the literature of  $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$ 's instability in solution.<sup>1,2</sup> Note that a sample of this same material was used to prepare  $\geq 90\%$  pure  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ ; that is, the  $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$  was  $\geq 90\%$  pure before this  $^{31}\text{P}$  NMR was obtained so that  $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$  degradation in solution has occurred.



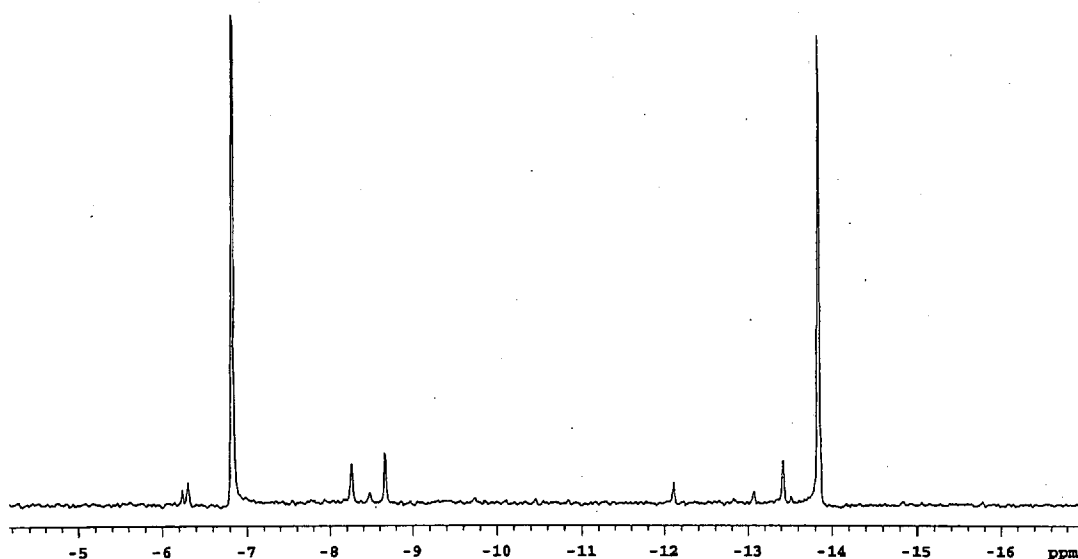
**Figure B.**  $^{31}\text{P}$  NMR of  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$  in 1.0 M HOAc / 1.0 M LiOAc showing multiple peaks. Referenced to 85%  $\text{H}_3\text{PO}_4$  (0 ppm). This same material was used to prepare  $\geq 90\%$  pure  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ , so that as in Figure A,  $\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}^{12-}$  degradation in solution has occurred.

**Synthesis of  $\text{Na}_{16}[\text{Zn}_4(\text{H}_2\text{O})_2(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2]$** 

This preparation was carried out according to the literature procedure<sup>3</sup> starting with 75% pure  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$  to check whether or not *pure*  $\text{Na}_{16}[\text{Zn}_4(\text{H}_2\text{O})_2(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_2]$  could be made from *impure*  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$ . A clear solution of zinc chloride (0.34 g, 2.49 mmol) and sodium chloride (2.92 g, dissolved in 50 mL of water, 1 M) is prepared in a 100 mL beaker at room temperature. The sodium salt of the complexing anion,  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$  (5.00 g, 1.25 mmol), is added to this solution all at one time as a dry, powdered solid with vigorous stirring using a magnetic stirring bar on a heater/stirrer. The solution is heated with stirring to about 80 °C to yield a turbid solution. This hot solution is rapidly, gravity filtered through a Whatman No. 5 filter paper. (The filter funnel and paper are preheated by passing about 50-100 mL of boiling water through them just prior to this filtration.) The clear filtrate is collected in a clean 100 mL beaker and placed in the refrigerator at 5 °C overnight. The product is retrieved on a medium-frit, filter funnel and washed first with absolute ethanol ( $3 \times 100$  mL) and then with anhydrous diethyl ether ( $3 \times 10$  mL). The product is then dried overnight on an open watch glass, or in a weighing pan, in a drying oven at 50 °C overnight to yield a white granular product which weighs 2.82 g; 55% yield assuming pure  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$ . <sup>31</sup>P NMR (1:1 D<sub>2</sub>O:H<sub>2</sub>O):  $\delta$  -4.3, -14.3 ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>; <sup>4</sup> purity >95% by <sup>31</sup>P NMR. Literature results:<sup>3</sup> yield 3.61 g, 71%; <sup>31</sup>P NMR (1:1 D<sub>2</sub>O:H<sub>2</sub>O):  $\delta$  -4.5, -14.5 ppm relative to 85% H<sub>3</sub>PO<sub>4</sub> by the substitution method;<sup>4</sup> purity >95% by <sup>31</sup>P NMR



**Figure C.**  $^{31}\text{P}$  NMR of 80% pure  $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]$  in pD 1.9  $\text{D}_2\text{O}$ . The major impurity peaks correspond to  $\text{P}_2\text{W}_{16}\text{V}_2\text{O}_{62}^{8-5}$ .



**Figure D.**  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ) of 82% pure  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  (Experiment 13, Table 2) relative to 85%  $\text{H}_3\text{PO}_4$  (0 ppm). The peaks at  $-8.7$  and  $-13.2$  ppm are believed to be due to  $\text{P}_2\text{W}_{16}\text{Nb}_2\text{O}_{62}^{8-}$ , although isolation and purification somehow, followed by complete characterization of this impurity would be necessary to unequivocally establish this point.

**Synthesis of  $K_6[\alpha,\beta-P_2W_{18}O_{62}]\cdot xH_2O$  (for  $\alpha$ ,  $x = 14$  and for  $\beta$ ,  $x = 19$ )**

This compound was made directly from the literature procedure, and the wording below is taken directly from that report,<sup>3</sup> but repeated here for the convenience of those needing this synthesis. A 2 or 3 L, three-necked round bottomed flask set in a heating mantle, which is regulated by a potentiostat and placed on top of a magnetic stirrer, fitted with a reflux condenser, and a 500 mL Teflon-stoppered, pressure equalizing, dropping funnel. Solid  $Na_2WO_4\cdot 2H_2O$  (300 g, 909 mmol.), distilled water (1050 mL) and a large magnetic stirring bar are placed in the 2 or 3 L flask. The sodium tungstate is dissolved with stirring and heating and the solution is brought to a boil. While the mixture is coming to a boil, 450 mL of concentrated  $H_3PO_4$  solution (85 %) is placed in the dropping funnel, and the funnel is placed in one neck of the flask. After the solution in the flask boils, the heating is reduced and the phosphoric acid drip is started at the rate of 2-3 drops/sec. **Caution:** *This is a concentrated acid being introduced into a hot, strongly basic solution. Do not rush the addition or a violent steam explosion is possible.* The slow addition of the acid is obviously necessary for safety reasons but also appears to avoid the formation of an unwanted side product, which, if present, will be seen upon the addition of the KCl in the next precipitation step. The acid is allowed to drip into the reaction flask at this rate until all of it is added, usually about 1-2 hours. After almost 50 mL of the acid is added, the solution turns from colorless to a light yellow-green, and remains this color throughout the reaction. When the addition of the acid is complete, the dropping funnel is removed, that neck is stoppered, and the reaction mixture is allowed to reflux for 15-24 hours. Higher yields of this intermediate qualitatively correlate to longer reflux times. The hot solution is transferred to a 4 L beaker and allowed to cool to room temperature in an ice bath with stirring. Solid, granular KCl (300 g) is added slowly and continuously over 10-20 seconds to this solution. If no unwanted side product is present, no precipitation will occur until almost 20% of the KCl has been added. If the unwanted side product is present, a white, granular product will precipitate immediately upon the first addition of the KCl. (This white side product was identified as  $K_{14}Na[P_5W_{30}O_{110}]\cdot xH_2O$ ,<sup>1</sup> but we find that the IR spectrum is different from that published.<sup>6</sup> This unwanted product will be removed in the synthesis of the next intermediate.) After the addition of the KCl, the solution is stirred for approximately 1 hour, cooled with additional stirring to approximately 5 °C in an ice for 2-3 hours, and the solid is collected on a 600 mL, medium porosity glass frit with aspiration. The last of the solid product is washed from the 4 L

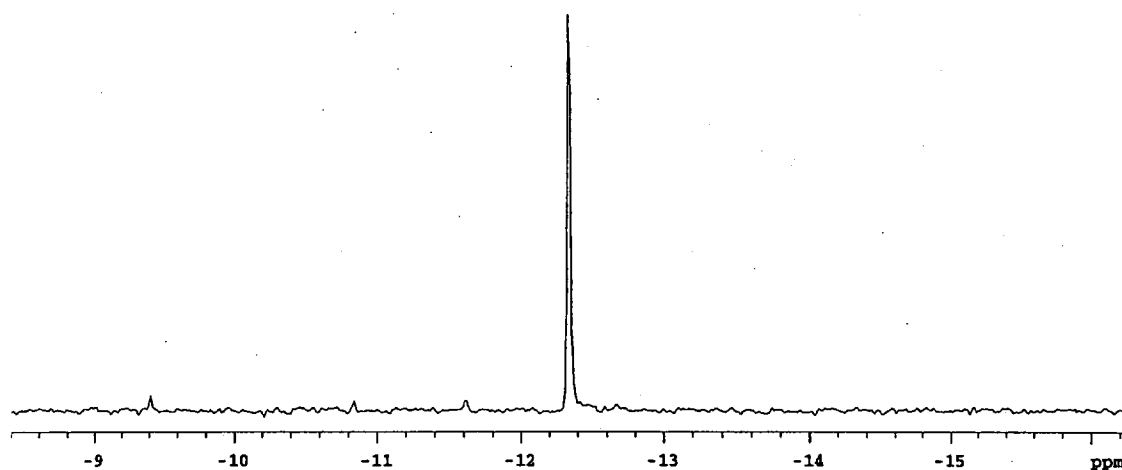
beaker with small portions of the mother liquor using a wash bottle. This wet precipitate is dried on the funnel with aspiration until no more liquid is seen to come through the funnel (this takes from 2-3 hours), then transferred to a 400 mL beaker and dissolved in boiling water. **Caution:** *Use only plastic or ceramic spatulas when handling these wet products, inasmuch as metal (even stainless-steel) spatulas will cause reduction of the tungstates to a blue, reduced form.* Boiling water (75-80 mL) is poured over the fresh precipitate and the mixture is brought to a boil. More boiling water is added in small portions with stirring until a clear, boiling solution is obtained using a *minimum* amount of boiling water (usually 100-150 mL). The beaker is covered with a watch glass, cooled to room temperature, and placed in a refrigerator at 5 °C for at least overnight. The product is filtered, transferred to a tared, 10 cm plastic weighing pan and dried in an oven at 50 °C overnight. Yield 190-220 g, 77-90 %. This product is approximately 80 % alpha isomer by  $^{31}\text{P}$  NMR: ( $\alpha$ )  $\delta$  -12.7; ( $\beta$ )  $\delta$  -11.0 and -11.6 ppm relative to 85%  $\text{H}_3\text{PO}_4$  (0 ppm).<sup>7</sup>

### Synthesis of $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$

This preparation was carried out according to literature methods.<sup>3</sup> The wording that follows is identical to that in the literature procedure except where underlined text is added. If 220 g of  $\text{K}_6[\alpha,\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot x\text{H}_2\text{O}$  from the previous synthesis is used for this conversion, it is placed in a 3 or 4 L beaker and dissolved in 825 mL of distilled water at room temperature; about 0.2-0.4 mL of liquid bromine is added with a Pasteur pipet (to assure complete oxidation of the tungstate to the VI oxidation state), upon which the solution turns yellow. **Caution:** *Bromine is a corrosive and a health hazard. This procedure should be completed in a good fume hood!* A solution of 10 % (w/v)  $\text{KHCO}_3$  (1.10 L) is added slowly over 3-5 min. After approximately 750 mL of the  $\text{KHCO}_3$  solution has been added, a white granular precipitate forms. After the solution has stirred at room temperature for about 1 hour, 210 mL of 6 M  $\text{HCl}$  solution is slowly, but continuously added over 5-10 min. to produce a sometimes clear, yellow solution. Even if the solution is not completely clear, do not add more than just enough  $\text{HCl}$  to accomplish this neutralization. The pH at this point should be around 3-4 (as tested by Hydrion paper). This solution is reduced in volume to approximately 1.8-2.0 L with gentle boiling and slow stirring on a magnetic stirrer/heater (ca. 3-4 hours). Solid  $\text{KCl}$  (275 g) is added and the solution is stirred to dissolve all of the  $\text{KCl}$ . The solution should be clear and yellow. If the hot mixture contains a

white, insoluble, granular precipitate at this stage, an undesired side product is present and the solution should be gravity-filtered through a 600 mL, medium porosity glass frit, or through a large fine-paper filter. The clear, yellow solution is allowed to cool to room temperature and then placed in a refrigerator at 5 °C for at least overnight. This cold suspension is filtered and the solid is collected in a 600 mL, medium porosity glass frit, and thoroughly air dried with aspiration (2-3 hours). The resultant pale yellow precipitate is transferred to a 400 mL beaker and boiling, distilled water (50-60 mL) is poured over the solid. The beaker with the suspension is placed on a hot plate and returned to boiling, then small portions of boiling water are added until a clear solution forms (usually a total of 75-125 mL of water is needed). This solution is covered with a watch glass, allowed to cool on the bench until it has reached room temperature, then placed in a refrigerator at 5 °C for at least overnight. (A higher yield of the pure alpha isomer is obtained if the solution is left in the refrigerator for longer.) This cold suspension is broken up by a heavy ceramic spatula, and the precipitate is collected in a 150 mL (or larger) medium porosity glass frit, thoroughly dried with aspiration (2-3 hours), transferred to a tared 10 cm, plastic, weighing pan, and dried in a 50 °C drying oven overnight. The resulting light yellow, powdered  $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$  weighs 150-186 g, 61-76% based on 300 g  $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ .  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  -12.3 ppm relative to 85 %  $\text{H}_3\text{PO}_4$ , Figure E below.





**Figure E.**  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ) of  $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]$  showing >95% purity.  $\delta$  -12.3 ppm relative to 85%  $\text{H}_3\text{PO}_4$  (0 ppm). Resonances from remaining traces of the  $\beta$  isomer are observed at -10.8 and -11.6 ppm.<sup>8</sup>

### The Most Recent Literature Preparation of What Proved to be Impure $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$

These attempts were carried out according to our 1997 procedure.<sup>3</sup> The wording that follows is identical to that in the literature except where underlined. The entire amount of product (186 g)  $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$ , is dissolved in 620 mL of distilled water at room temperature in a 1 L beaker. Solid, crystalline  $\text{NaClO}_4$  (265 g) is added to this clear solution and the suspension is stirred for 20-30 minutes. The beaker is then placed in an ice bath and stirring is continued for about 2 hours at which time the temperature of the suspension is 2-4 °C. The  $\text{KClO}_4$  metathesis product is removed from the solution by filtration through a medium-frit, sintered-glass, filter funnel and the filtrate is placed in a 4-L beaker. A solution of 1.0 M  $\text{Na}_2\text{CO}_3$  is added (approximately 1700 mL) until the pH of the suspension is  $9.0 \pm 0.05$  as monitored by a calibrated pH meter with a combination glass and calomel electrode. The pH is maintained at this value with vigorous stirring for 1 hour. The total amount of sodium carbonate solution needed is approximately 1700 mL. The solid precipitate is collected in a 600-mL, medium-frit, sintered-glass, filter funnel and thoroughly dried with aspiration. The solid is first washed with a saturated  $\text{NaCl}$  solution at room temperature ( $3 \times 50$  mL), then with absolute ethanol ( $3 \times 50$  mL), and finally with anhydrous diethyl ether ( $3 \times 50$  mL). During these washing steps the solid is thoroughly mixed with the rinsing solution before aspiration is reapplied. The resulting powder is placed on a tared, 10-cm, plastic, weighing pan and dried overnight in a drying oven at 50 °C to give 129 g of the desired  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot 18\text{H}_2\text{O}$  (78% conversion). A representative  $^{31}\text{P}$  NMR of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  made from this material is shown in Figure D above. This synthesis was carried out twice at full scale and five times on smaller scales (see Table 2 in the main text). Each of these experiments resulted in similar yields and purities.

### Synthesis of $\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 13\text{H}_2\text{O}$

The hexaniobate synthesis was carried out following the literature procedure.<sup>9,10</sup> The solids  $\text{Nb}_2\text{O}_5$  (10 g, 37.6 mmol) and 85% KOH (35 g, 530 mmol) are placed in a nickel crucible. The crucible is heated cautiously in a hood, using a low flame (to prevent boil-over and minimize splattering), until the contents occasionally boil. During heating, the reaction mixture changes color from white to gray throughout the formation of a transparent melt. The crucible is heated using a high flame for ten minutes and then allowed to cool to room temperature (about 30 minutes). The crucible containing the solidified melt (now gray) is placed in a 250 mL beaker with 200 mL deionized water. After the solidified melt has dissolved (this may be hastened by stirring with a glass rod), the crucible is removed and the warm solution is filtered through Celite to remove any insoluble material. The solution is transferred to a beaker and, while stirring rapidly with a glass rod, 200 mL of 95% ethanol is added to the solution. The product separates first as an oil, which is readily transformed into a white powder with continued stirring (for about 15 minutes). After standing for 30 minutes, the product is collected on a medium glass frit and washed twice with 25 mL portions of 95% ethanol. The reprecipitation from 200 mL of water by the addition of 200 mL of ethanol is repeated twice more. The white powder is spread in a 14 cm weighing dish and then dried at 60 °C overnight. Yield: 9.3-13.4 g, 54-78%.

### Synthesis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$

This compound was synthesized, with minor adjustments to the literature procedure, on 100% and 50% scales with similar results.<sup>11</sup> The wording in what follows is exactly that in the literature except where underlined.  $\text{K}_7\text{HNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ <sup>12</sup> (5.90 g, 4.30 mmol) was placed in a 1500 mL beaker equipped with a magnetic stir bar. Addition of  $\text{H}_2\text{O}_2$  (650 mL of 0.5 M) resulted in a pale yellow solution of pH 4.12. Next, 1 M HCl (58 mL, 58 mmol) was added whereupon the solution color changed to bright yellow (solution pH 1.46). *Immediately* after the addition of HCl, and while the mixture was rapidly stirred, finely powdered  $\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]$  (36.5 g, 8.42 mmol) was added in a single step,<sup>13</sup> resulting in a clear to slightly cloudy, yellow solution of pH 3.93. **Caution:** *The following step yields a vigorous reaction in which  $\text{SO}_2$  is evolved. Proceed with caution in a well-ventilated fume hood.* After the solution became homogeneous,  $\text{NaHSO}_3$  (50 g, 480.4 mmol,) was added gradually over 10-15 minutes, destroying excess hydrogen peroxide, to yield a clear and colorless solution. Stirring was continued for 0.5

hour. Next,  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$  (25.0 g, 77.5 mmol) was added in a single step, immediately producing a white precipitate. Stirring of the suspension was continued until it had air-cooled to room temperature (approximately 1 hour). The white precipitate was allowed to settle and was then collected on a 350 mL medium glass frit, transferred to a 1 L beaker, and thoroughly washed with 500 mL of 40-50 °C in-house distilled water. This material was, once again, collected on a 350 mL glass frit and without further drying, dissolved in 250-300 mL of acetonitrile. (If the solution was cloudy at this stage, it was gravity filtered through a Whatman No. 2 filter paper.) Addition of 30-40 mL deionized water gave a cloudy solution which was reduced in volume by rotary evaporation to about 200 mL. A green-yellow oily, lower  $\text{CH}_3\text{CN}$  layer<sup>14</sup> containing the tetrabutylammonium salt of the polyoxometalate formed. The upper, cloudy aqueous layer was removed with a pipet, and the remaining yellow-green oily layer was transferred to a 250 mL separatory funnel and washed four times with 80 mL (320 mL total) acetonitrile:water (1:1). After 3 hours (allowing the layers to fully separate) a clear, oily layer separated which was transferred to a 250 mL beaker. Next, this oil was triturated 5 times with 40 mL (200 mL total) diethyl ether to yield a yellow powder. The powder was collected on a 100 mL medium glass frit by suction filtration and dried overnight under < 10 mm Hg vacuum at 40 °C. Yield: 28-30 g; 62-67 % yield.

### Synthesis of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$

This compound was also prepared according to the literature procedure.<sup>11</sup> The wording that follows is exactly that in our literature except where underlined. In a 50 mL round-bottomed flask,  $[(\text{C}_4\text{H}_9)_4\text{N}]_5\text{H}_4[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  (1.0 g, 0.19 mmol) was dissolved in acetonitrile (20 mL). Argon was bubbled through the solution for at least 15 min (to remove any dissolved  $\text{CO}_2$ ) after which time the solution was kept under a constant argon stream with the gas outlet above the solution surface to prevent recontamination with atmospheric carbon dioxide. Two drops of phenolphthalein indicator were added and the solution was titrated with aqueous tetrabutylammonium hydroxide (0.692 M) to the endpoint of the indicator as detailed below; in all cases, the number of equivalents of  $\text{OH}^-$  required was  $4.0 \pm 0.2$  (determined from at least eight independently prepared samples of  $[(\text{C}_4\text{H}_9)_4\text{N}]_5\text{H}_4[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  prepared by four different researchers, see the Supporting Information, Table D elsewhere.<sup>11</sup>) [The titration was judged

complete when the color change of the indicator to red *persisted for at least 15 minutes* under a continuous argon flow; this is crucial for a successful, reproducible titration. Undertitration of this solution results in a pair of impurity peaks that can be observed in the  $^{31}\text{P}$  NMR (-8.3 and -13.4 ppm relative to 85 %  $\text{H}_3\text{PO}_4$ ). One should note, however, that on this scale (i.e., 1 g of  $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$ ) and when a buret (KIMAX) calibrated in 0.02 mL increments is used, each drop of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{OH}$  solution (0.02 mL) added beyond the *true* endpoint results in approximately 8% excess of  $\text{OH}^-$ . As shown in reference 11, this is a sufficient excess to affect significantly the support of organometallic cations; hence, we urge that care be taken when approaching the endpoint in the titration.] Next, the solution was evaporated to dryness under vacuum and 200 mg of the recovered light-purple-colored (i.e., phenolphthalein-stained) solid was dissolved in  $\text{CD}_3\text{CN}$  for  $^{31}\text{P}$  NMR spectroscopy. If the  $^{31}\text{P}$  NMR of the product showed the expected two line spectrum, then a bulk  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{OH}$  addition in the *absence* of phenolphthalein indicator was performed on a larger scale (typically 10 g of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  in 50 mL acetonitrile). (If the titrated material *did not* show the expected two line  $^{31}\text{P}$  NMR spectrum, then the titration was repeated on a second gram of material. If the second titration produced material that also did not show the expected two line  $^{31}\text{P}$  NMR spectrum, then the material was discarded.) The bulk  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{OH}$  addition was carried out in the *absence* of phenolphthalein indicator with the amount of aqueous tetrabutylammonium hydroxide to be added *calculated* from the above small-scale experiment. (Again, the aqueous tetrabutylammonium hydroxide was added dropwise to the stirred solution.) The colorless solid formed after evaporation of the solvent was dried overnight at  $40^\circ\text{C}$  in *vacuo* and then immediately transferred into the drybox for storage at room temperature.  $^{31}\text{P}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  -6.5, -13.6 ppm relative to 85%  $\text{H}_3\text{PO}_4$ , see Figure 1 of the main text.<sup>11</sup>

**A Reevaluation of the Water Soluble  $(\text{CH}_3)_4\text{N}^+$  Salt Intermediate.** As noted in the Introduction of the main text, our original strategy as published in our 1988 paper was to make a water recrystallizable, and thus purifiable, salt of  $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$  before its conversion to the (non-crystallizable or purifiable)  $(\text{C}_4\text{H}_9)_4\text{N}^+$  salt.<sup>3,15</sup> Although this general synthetic strategy still appears to be the correct one, it remained to be demonstrated whether or not (a) the prior use of a  $(\text{CH}_3)_4\text{N}^+$  salt reprecipitation step actually provides any purification, and if not, then (b) can the use of a higher pH solution lead to a crystallizable salt of the  $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$  while avoiding Nb-

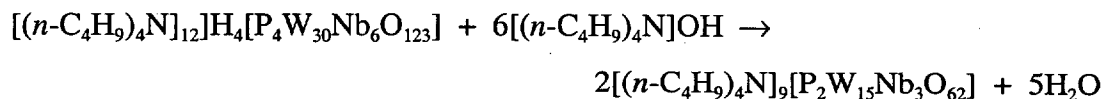
O-Nb bridged formation to yield the to date uncrystallizable  $[(P_2W_{15}Nb_3O_{61})_2O]^{16-}$  (i.e.,  $P_4W_{30}Nb_6O_{123}^{16-}$ ). The availability of a  $\alpha$ - $P_2W_{15}O_{56}^{12-}$  precursors of known purity (72 and 90 ( $\pm 3$ )%) allowed us to do the experiments reported below.

**Synthesis of the Water Soluble  $[(CH_3)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$ .** This product was made on a 50% scale following the published procedure,<sup>3</sup> except using  $NbCl_5$  as the niobium source as mentioned in our earlier paper.<sup>11</sup> A yellow solution is prepared by dissolving  $NbCl_5$  (3.48 g, 12.9 mmol) in 315 mL of 0.5 M  $H_2O_2$ , which has been prepared by diluting 18.4 mL of 30% aqueous  $H_2O_2$  to a volume of 325 mL with water. Next, 54 mL of 1.0 M NaOH is added. Immediately thereafter, *finely powdered*  $Na_{12}[P_2W_{15}O_{56}] \cdot 18H_2O$  (18.2 g, 4.23 mmol) is added *in a single step*. After complete dissolution of the  $Na_{12}[P_2W_{15}O_{56}]$ ,  $NaHSO_3$  (25 g) is added gradually over 10-15 min. to destroy the peroxides, resulting in a clear, colorless solution. **Caution:** *This reaction is quite exothermic and evolves  $SO_2$ ; hence, it should be carried out with caution in a hood.* The solution is stirred to 1-2 hours until it has cooled to room temperature. A large excess (10 g) of solid tetramethylammonium chloride is added to the solution in a single step, causing a white precipitate to form. The white precipitate is collected on a Whatman No. 2 filter paper laid inside a Büchner funnel and dried in an oven at 60 °C overnight. At this stage, the yield is typically about 20 g of crude material. The product is purified as follows by reprecipitation from a homogeneous solution of *hot* ( $>80$  °C), unbuffered, pH 4.6 water. The compound is dissolved in pH 4.6 water, kept hot ( $>80$  °C) in a steam bath, and then filtered once through a folded filter paper (Whatman No. 2). The volume of the clear filtrate is reduced to 75 mL, and the solution is cooled in an ice bath. The first crop of the product,  $[(CH_3)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}] \cdot 16H_2O$ , is collected on a Whatman No. 2 filter paper laid inside a Büchner funnel, washed several times with small portions of unbuffered (pH 4.6) water, and dried at room temperature under vacuum overnight. The combined filtrate and washings are reduced in volume to approximately 75 mL by rotary evaporation, and the solution is cooled in a ice bath. A second crop of product is collected, washed, and dried as above. Combined yield of the first and second crops: 13.9-15.1 g, 70-76%.

**Synthesis of  $[(n-C_4H_9)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$ .** This compound was made from  $[(CH_3)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}]$  according to the literature procedure.<sup>3</sup> The  $[(CH_3)_4N]_{12}H_4[P_4W_{30}Nb_6O_{123}] \cdot 16H_2O$  (15 g, 16 mmol) is dissolved in 500 mL of hot, unbuffered (pH 4.6) water; the clear solution is then allowed to cool to room temperature. Addition of solid

tetrabutylammonium bromide (7.0 g, 22 mmol) *in a single step* results in the formation of a white precipitate. The precipitate is collected and washed on a coarse glass frit as follows (this revised collection and washing procedure reduces the long filtration times inherent in our original procedure<sup>16</sup>): 1) the solution is placed on a coarse glass frit for 1 hour without aspiration (weak aspiration is also acceptable); three layers appear (some water passed through the glass frit). 2) The top layer and then about one half of the second layer are carefully removed by a pipette that is connected to an aspirator. 3) Approximately 100-200 mL of water is added without stirring. 4) Steps 1-3 are repeated three or four times (i.e. with the precipitate on the same glass frit). 5) About 1050 mL (3 × 350 mL portions) of water are added, using a normal rinsing procedure of the precipitate employing suction via aspiration. This washing procedure usually requires 1-2 hours. (If the amount of water used in the washing is smaller than that indicated, the yield is higher, but subsequent CH<sub>3</sub>CN solutions of [(CH<sub>3</sub>)<sub>4</sub>N]<sub>12</sub>H<sub>4</sub>[P<sub>4</sub>W<sub>30</sub>Nb<sub>6</sub>O<sub>123</sub>] are cloudy.) The sample is spread in a 14 cm weighing dish and dried at 60 °C overnight. Yield: 6.72-10 g, 38-56%.

**Synthesis of [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>9</sub>[P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>] from [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>12</sub>H<sub>4</sub>[P<sub>4</sub>W<sub>30</sub>Nb<sub>6</sub>O<sub>123</sub>].** This conversion is identical to that of the mixed salt monomer (see above for details) except that 6 equivalents of [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]OH rather than 4 are required,<sup>11</sup> as shown in the equation below.



The entire synthesis was carried out twice starting with two separate batches of Na<sub>12</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>] and resulted in products that are 75 and 88 (± 3)% by <sup>31</sup>P NMR. These results show that the reprecipitation of the water soluble intermediate does not act as a purification step since similar purities were obtained with the same two batches of Na<sub>12</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>] (72 and 90 (± 3)%) when the formation of the (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> salt was avoided (i.e., when the synthesis was carried out according to our most recent synthesis of [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>9</sub>[P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>]).<sup>11</sup>

**Attempt to Make Crystalline [(CH<sub>3</sub>)<sub>4</sub>N]<sub>5</sub>H<sub>4</sub>[P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>] From [(CH<sub>3</sub>)<sub>4</sub>N]<sub>12</sub>H<sub>4</sub>[P<sub>4</sub>W<sub>30</sub>Nb<sub>6</sub>O<sub>123</sub>].** The initial product, [(CH<sub>3</sub>)<sub>4</sub>N]<sub>12</sub>H<sub>4</sub>[P<sub>4</sub>W<sub>30</sub>Nb<sub>6</sub>O<sub>123</sub>], was made by the published procedure,<sup>3</sup> except the niobium source was NbCl<sub>5</sub> as mentioned in our earlier paper.<sup>11</sup> A yellow solution is prepared by dissolving NbCl<sub>5</sub> (6.79 g, 25 mmol) in 650 mL of 0.5 M H<sub>2</sub>O<sub>2</sub>, which has been prepared by diluting 18.4 mL of 30% aqueous H<sub>2</sub>O<sub>2</sub> to a volume of 650 mL with water. Next, 108 mL of 1.0 M NaOH is added. Immediately thereafter, *finely*

powdered  $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$  (36.5 g, 8.46 mmol) is added in a single step. After complete dissolution of the  $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$ ,  $\text{NaHSO}_3$  (50 g) is added gradually over 10-15 min. to destroy the peroxides, resulting in a clear, colorless solution. **Caution:** *This reaction is quite exothermic and evolves  $\text{SO}_2$ ; hence, it should be carried out with caution in a hood.* The solution is stirred to 1-2 hours until it has cooled to room temperature. A large excess (20 g) of solid tetramethylammonium chloride is added to the solution in a single step, causing a white precipitate to form. The white precipitate is collected on a Whatman No. 2 filter paper laid inside a Büchner funnel and dried in an oven at 60 °C overnight. At this stage, the yield is typically about 40 g of crude material.

Rather than reprecipitation from a pH 4.6 aqueous solution as used in the literature preparation of the Nb-O-Nb bridged dimer,  $[(\text{CH}_3)_4\text{N}]_{12}\text{H}_4[\text{P}_4\text{W}_{30}\text{Nb}_6\text{O}_{123}]$ , a reprecipitation is carried out at pH 6.8 with hot (>80 °C) water. To a 250 mL beaker equipped with a magnetic stir bar, 10 g of solid  $[(\text{CH}_3)_4\text{N}]_{12}\text{H}_4[\text{P}_4\text{W}_{30}\text{Nb}_6\text{O}_{123}]$  is added and dissolved in unbuffered pH 6.8 hot (>80 °C) water (110 mL). The clear solution is then filtered hot through a folded filter paper (Whatman No. 2), cooled to room temperature on the bench top and then placed in an ice bath for 1 hour. The first crop of the product, is collected on a Whatman No. 2 filter paper laid inside a Büchner funnel, washed several times with small portions of unbuffered (pH 6.8) water, and dried at room temperature under vacuum overnight. The combined filtrate and washings are reduced in volume to approximately 75 mL by rotary evaporation, and the solution is cooled in an ice bath. A second crop of product is collected, washed, and dried as above. Combined yield of the first and second crops: 5.7 g, 59% based on formation of the mixed salt of the monomer.

A 4.2 g portion of the isolated solid was converted to the  $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+ / \text{H}^+$  salt by the method reported in the literature.<sup>3</sup> The yield of the mixed salt is 0.78 g, 16% assuming the formation of the monomer. Evidence for the monomer formation is given below.

The entire amount of the isolated solid (0.78 g) is converted to the organic solvent soluble  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  species by our literature method.<sup>11</sup> This conversion requires 0.695 mL of a 0.685 M solution ( $4.76 \times 10^{-4}$  mol) of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{OH}$ , which corresponds to the expected 4 equivalents of base necessary for deprotonation of the monomeric species,  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{H}_4[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  ( $1.47 \times 10^{-4}$  mol). These titration results suggest that the isolated species is indeed the monomeric species and not the Nb-O-Nb bridged dimer. Purity of the final material is  $82 \pm 3\%$  as judged by  $^{31}\text{P}$  NMR.



An attempt to crystallize the mixed,  $(\text{CH}_3)_4\text{N}^+/\text{H}^+$ , salt from pH 6.8 water was carried out with the remaining 1.5 g of isolated material. To a 250 mL beaker equipped with a magnetic stir bar, 1.4 g of the solid was added. The solid was dissolved in a minimal amount of hot ( $>80^\circ\text{C}$ ) pH 6.8 water which resulted in a clear solution, that was then cooled to room temperature on the bench. A fine white powder in the bottom of the beaker was visible after 2 hours. After sitting on the bench for an additional 2 hours, the solution was moved to a  $5^\circ\text{C}$  refrigerator for 4 days. Only a fine pale-yellow powder was recovered.

<sup>1</sup> Contant, R. *Inorg. Synth.* **1990**, 27, 106-111.

<sup>2</sup> Pohl, M.; Lyon, D. K.; Mizuno, N.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, 34, 1413-1429.

<sup>3</sup> Randall, W. J.; Droege, M. W.; Mizuno, N.; Nomiya, K.; Weakley, T. J. R.; Finke, R. G. *Inorg. Synth.* **1997**, 31, 167-185.

<sup>4</sup> For a discussion of  $^{31}\text{P}$  NMR of heteropolyanions see Pohl, M.; Lin, Y.; Weakley, T. J. R.; Nomiya, K.; Kaneko, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1995**, 34, 767 and references 11 and 20 therein.

<sup>5</sup> Harmalkar, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, 105, 4286-4292.

<sup>6</sup> Yeannin, J.; Martin-Frère, J. *Inorg. Synth.* **1990**, 27, 115.

<sup>7</sup> 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.

<sup>8</sup> Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

<sup>9</sup> Nomiya, K.; Pohl, M.; Mizuno, N.; Lyon, D. K.; Finke, R. G. *Inorg. Synth.* **1997**, 31, 186.

<sup>10</sup> 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.

<sup>11</sup> Weiner, H.; Aiken III, J. D.; Finke, R. G. *Inorg. Chem.* **1996**, 35, 7905

<sup>12</sup> In place of  $\text{K}_7\text{HfNb}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$ ,  $\text{NbCl}_5$  may be employed as the niobium source. The following procedure was used successfully in four independent preparations:  $\text{NbCl}_5$  (6.97 g, 25.8 mmol) was dissolved in  $\text{H}_2\text{O}_2$  (0.5 M; 650 mL). Note that a typo exists in footnote 20 of the original reference.<sup>11</sup> Rather than a "5%"  $\text{H}_2\text{O}_2$  solution, a 0.5 M  $\text{H}_2\text{O}_2$  solution should be used. (The resulting yellow solution is apparently stable for at least 6 days without any visible changes.) The pH of the solution was adjusted to 1.45 by adding NaOH (108 mL of 1 M; 108 mmol). Subsequent steps in the preparation of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$  were carried out exactly as described in the main text.

<sup>13</sup> In this synthesis it is crucial that the  $\text{P}_2\text{W}_{15}$  is added in a single step rather than over a period of time to the niobium solution. This protocol also holds for the formation of the Zn adduct, however, it is interesting to note that the synthesis of V and Ti species require slow addition of the lacunary polyoxometalate to the transition metal solution.

<sup>14</sup> Organic solvent extractions of acidic aqueous solutions of (nonbasic) polyoxometalates is well-established; for example see references 11a-h elsewhere.<sup>11</sup> However, the presumable finite rate of decomposition under basic pH conditions of even stabilized polyoxoanions such as  $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$  is conceivably a limitation in this method. To test this, a control experiment was done involving 8.2 mM  $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$  in  $\text{D}_2\text{O}$  and  $^{31}\text{P}$  NMR. Even after several days at room temperature, no detectable ( $<5\%$ ) decomposition was seen in the  $^{31}\text{P}$  NMR spectrum.

<sup>15</sup> Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics*, **1988**, 7, 1692

<sup>16</sup> An alternative washing procedure that takes more time and less attention is as follows. This suspension is placed in a refrigerator at  $5^\circ\text{C}$  overnight. The clear supernatant liquid (ca. 200 mL) is then removed carefully using a pipette so that the white precipitate at the bottom of the beaker is not disturbed by the pipetting/suction process. To this precipitate is added 400 mL of water; the resulting suspension is stirred vigorously for 30 min. and then placed in a  $5^\circ\text{C}$  refrigerator overnight. The colloidal upper layer (ca. 400 mL) is again carefully removed using a pipette. After 200 mL of water is added and the suspension is vigorously stirred for 30 min., the white precipitate is collected on a Whatman No. 2 filter paper mounted on a Büchner funnel, washed with 400 mL of water (4 x 100 mL portions), and then thoroughly dried via prolonged aspiration. The product is then spread in a weighing dish and dried at  $60^\circ\text{C}$  overnight.