

Electronic Supporting Information

Controlled Synthesis of a Functionalized Polytungstate Ligand and a $\{M_aM_bM_c(PW_9)_2\}$ Sandwich Complex**

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1. General methods and procedures

Polytungstates $\text{K}_{10}[\text{P}_2\text{W}_{20}\text{O}_{70}(\text{H}_2\text{O})_2]\cdot 22\text{H}_2\text{O}$ ^[1] and $((\text{CH}_3)_2\text{NH}_2)_6\text{K}[\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{20}\text{O}_{70}(\text{H}_2\text{O})_2]\cdot 11\text{H}_2\text{O}$ (**1**)^[2] were synthesized according to published procedures and their purities were checked by ³¹P NMR and FT-IR. The compounds $(\text{C}_6\text{H}_5)_3\text{SnCl}_3$, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, and $(\text{CH}_3)_2\text{NH}\cdot \text{HCl}$ were purchased from Alfa Aesar and used as received. Elemental analyses of C, H and N were performed by Atlantic Microlab (Norcross, Georgia), and heavy atoms (K, Rb, Cu, Sn, P, and W) were performed by Columbia Laboratory (Tucson, Arizona). Infrared spectra (2% sample in KBr) were recorded on a Thermo Nicolet 6700 instrument. ³¹P NMR measurements were made in 100% D₂O on a Varian INOVA 400 MHz spectrometer, and peaks were referenced to 85% H₃PO₄. Thermogravimetric data were collected on a TGA 1000 instrument.

2. X-ray crystallographic studies

(a) Instrumentation and methods. The complete datasets for complexes **2a**, **2b**, **3** and **4** were collected at Emory University. Single crystals suitable for X-ray analysis, were each coated with Paratone-N oil, suspended in a small fiber loop, and placed in a cooled gas stream on a Brüker D8 SMART APEX CCD sealed tube diffractometer. Diffraction intensities were measured using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K and a combination of ϕ and ω scans with 10 s frames traversing about ω at 0.5° increments. Data collection, indexing, and initial cell refinements were carried out using SMART,^[3] frame integration and final cell refinements were done using SAINT.^[4] The molecular structure of each complex was determined using Direct

Methods and Fourier techniques and refined by full-matrix least squares. A multiple absorption correction, including face index, for each dataset at 173(2) K was applied using the program SADABS.^[5] The largest residual electron density for each structure was located close to (less than 1.0 Å from) W atoms and was most likely due to imperfect absorption corrections frequently encountered in heavy-metal atom structures.

(b) Refinement details. The structures of **2a**, **2b**, **3** and **4** were solved using Direct Methods and difference Fourier techniques. All the heavy atoms were refined anisotropically. Some of the potassium ions and solvent water molecules were refined with partial occupancies; not all the counteranions and solvent water molecules could be located in difference Fourier maps because of disorder. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*. Structure solution, refinement, graphic and generation of publication materials were performed by using SHELXTL, V6.14 software.^[6]

3. Synthesis and characterization of $\text{Rb}_6\text{K}_5[\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]$ (**2**)

$\text{K}_{10}[\text{P}_2\text{W}_{20}\text{O}_{70}(\text{H}_2\text{O})_2]\cdot 22\text{H}_2\text{O}$ (3.00 g, 0.528 mmol) is dissolved in 18 mL of water and $(\text{C}_6\text{H}_5)\text{SnCl}_3$ (0.095 mL, 0.578 mmol) is added dropwise. The resulting solution is stirred for 2 h at room temperature and then white particles that form are filtered. The pH of the resulting clear filtration is increased from 2.4 to 4.8 by the dropwise addition of 0.33 M KOH (approximately 8-9 mL base is used until the pH is stabilized for 5 minutes). After the successful adjustment of pH, a solution of 5.0 M RbCl (0.633 mL) is added and the solution is filtered. Evaporation of the clear filtrate gives colorless, diamond-shaped prisms of **2** in 3 d at room temperature (1.35 g, yield

45%). FT-IR (2% KBr pellet): 1083(s), 1023(m), 949(s), 930(sh), 890(w), 849(m), 786(m), 746(w), 708(m), 593(m), 517(m), 443(m), 418(m) cm^{-1} . ^{31}P NMR (D_2O): -10.30 ppm. ^1H NMR (D_2O): 8.05 (d, 2H), 7.57 (m, 3 H) ppm. Anal. Calcd. for $\text{Rb}_6\text{K}_5[\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$: C, 1.20%; W, 58.26%; Sn, 1.98%; P, 1.03%; Rb, 8.55%; K 3.26%. Found: C, 1.22%; W, 57.93%; Sn, 1.87%; P, 0.94%; Rb, 8.86%; K 3.24%. [MW = 5995 g/mol] Crystals **2a** and **2b** suitable for single crystal X-ray diffraction were obtained by the above procedure but without the addition of RbCl. Evaporation at room temperature for a week gives colorless blocks of **2a**, while diffusion of acetone to the aqueous reaction solution gives colorless prisms of **2b** in 3 d.

Table S1. Crystal data and structural refinement for **2a** and **2b**

complex	2a	2b
molecular formula	C ₆ H ₅₃ K ₁₁ O ₉₃ P ₂ SnW ₁₉	C ₆ H ₃₉ K ₁₁ O ₈₆ P ₂ SnW ₁₉
formula wt. (g mol ⁻¹)	5717.13	5591.02
temperature (K)	173(2)	173(2)
radiation (λ, Å)	0.71073	0.71073
crystal system	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	11.809(7)	11.914(5)
<i>b</i> (Å)	24.155(13)	18.028(7)
<i>c</i> (Å)	35.310(19)	24.593(13)
α (°)	109.785(8)	109.060(8)
β (°)	95.200(8)	92.994(8)
γ (°)	94.589(9)	108.872(5)
Volume (Å ³)	9373(9)	4650(3)
<i>Z</i>	4	2
ρ _{calcd} (g cm ⁻³)	3.920	3.913
μ (mm ⁻¹)	24.048	24.200
F(000)	9649	4772
crystal size (mm ³)	0.35 × 0.16 × 0.09	0.19 × 0.11 × 0.06
θ range	1.24 to 30.37°	0.89 to 30.32°
reflections collected	170688	83570
independent reflections	52507 [R(int) = 0.0668]	25921 [R(int) = 0.0560]
max./min. transmission	0.2208 and 0.0434	0.3246 and 0.0911
refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²
data/restraints/param.	52507/0/1345	25921/0/1049
goodness-of-fit on F ²	1.039	1.034
final R indices	R1 ^a = 0.0486	R1 ^a = 0.0428
[R > 2σ (I)]	wR2 ^b = 0.1193	wR2 ^b = 0.1103
R indices (all data)	R1 ^a = 0.0636 wR2 ^b = 0.1265	R1 ^a = 0.0581 wR2 ^b = 0.1194
largest diff. peak and hole (e Å ⁻³)	6.183 and -3.333	4.893 and -3.208

$$^a R_1 = \Sigma ||F_o| - |F_c|| / |F_o|$$

$$^b wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}$$

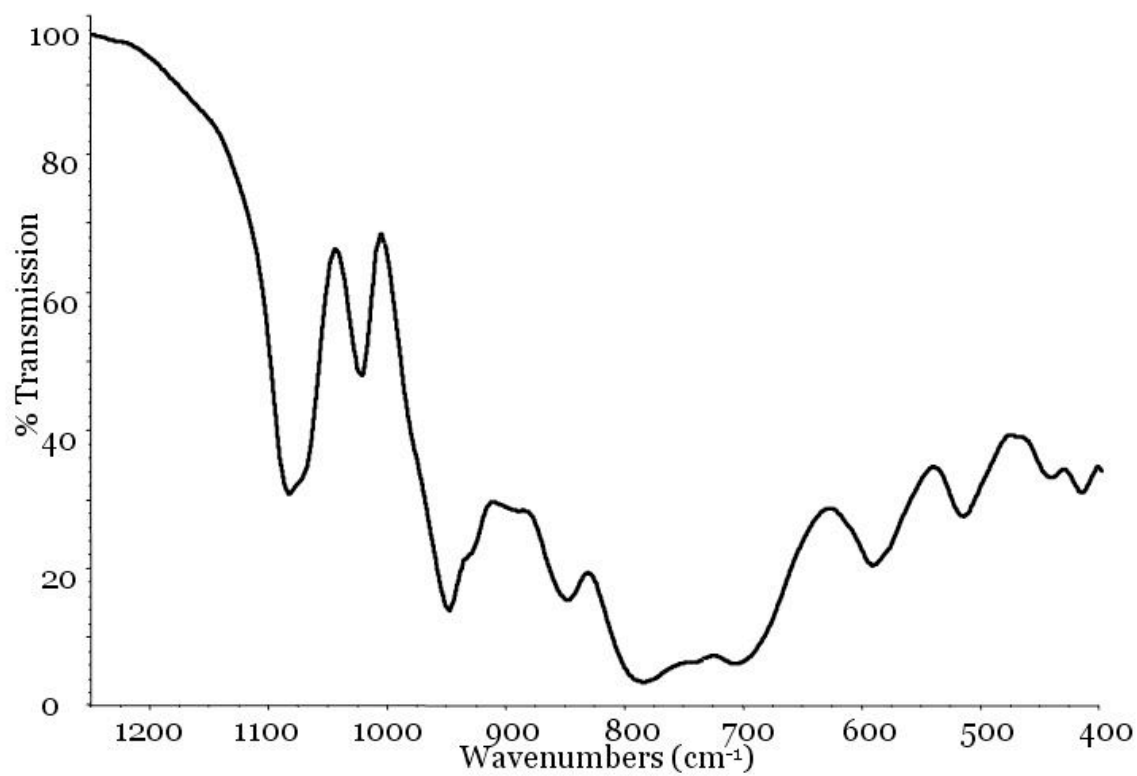
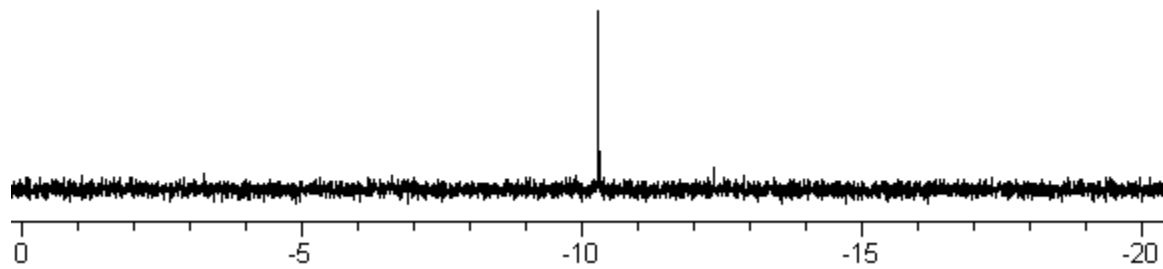


Figure S1. FT-IR spectrum of $\text{Rb}_6\text{K}_5[\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$ (**2**).

Full spectrum



Zoomed spectrum

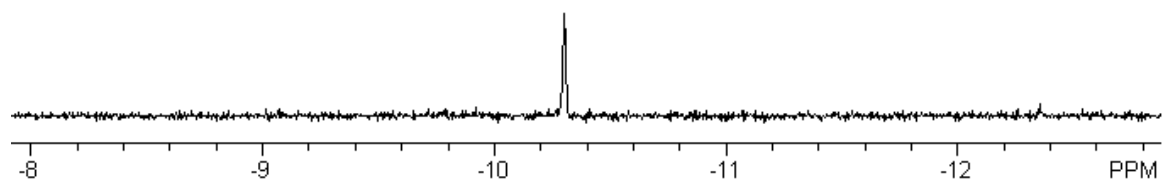


Figure S2. ^{31}P NMR of $\text{Rb}_6\text{K}_5[\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]$ (**2**) in D_2O , referenced to 85% H_3PO_4 (0.0 ppm) as an external reference.

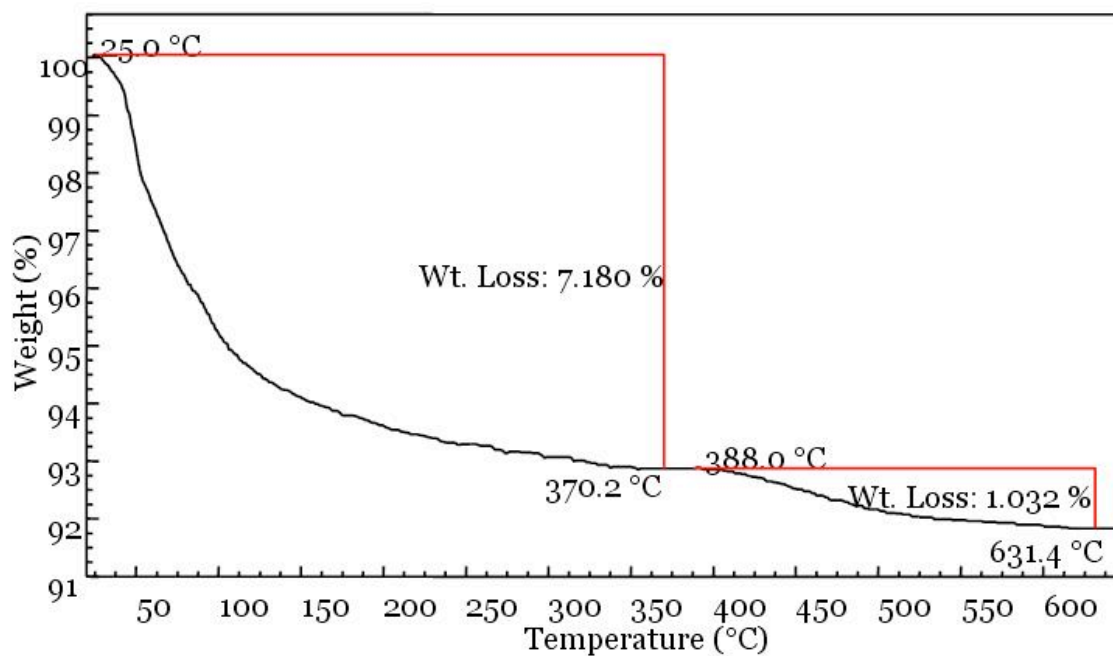


Figure S3. TGA weight loss curve of $\text{Rb}_6\text{K}_5[\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$ (2). A 15.5772 mg sample is analyzed under inert atmosphere. The first wave corresponds to the loss of 22 waters of hydration and the 2 metal-coordinated water molecules. The second wave corresponds to the loss of 1.0 equivalent of phenyl.

4. Synthesis and characterization of $\text{Rb}_2\text{K}_6[(\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O}))_2\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]$ (**3**)

Complex $(\text{C}_6\text{H}_5)\text{SnCl}_3$ (0.030 mL, 0.183 mmol) is added dropwise to a stirring solution of 9.0 mL water. Ground solid sample of **2** (1.00 g, 0.169 mmol) is added all at once producing a cloudy solution that becomes clear over a period of 1 min. After 2 h, 0.400 mL of a saturated KCl solution and 0.113 mL of a 3.0 M RbCl solution are added and the solution is filtered. Evaporation of the clear filtrate gives colorless prisms in 3 d (0.505 g) which are recrystallized in a solution of 5 mL of water with 10 drops of 0.1 M HCl, 0.230 mL saturated KCl solution and 0.058 mL 3.0 M RbCl solution (pH = 2.60). Evaporation of the clear solution gives colorless prisms of **3** in 4 d (0.328 g, yield 33%). FT-IR (2% KBr pellet): 1090(s), 1073(m), 1032(m), 959(s), 942(sh), 903(m), 762(s), 700(m), 583(m), 519(m). ^{31}P NMR (D_2O): -11.01 ppm. ^1H NMR (D_2O): 7.99 (d, 2H), 7.60 (m, 3 H) ppm. Anal. Calcd. for $\text{Rb}_2\text{K}_6[(\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O}))_2\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$: C, 2.44 %; W, 59.1%; Sn, 4.02 %; P, 1.05 %; Rb, 2.89 %; K, 3.97 %. Found: C, 2.47 %; W, 58.5 %; Sn, 3.80 %; P, 0.97 %; Rb, 2.71 %; K, 3.91 %. [MW = 5906 g/mol]

Table S2. Crystal data and structural refinement for **3**

complex	3
molecular formula	C ₁₂ H ₆₀ K ₆ O ₉₄ P ₂ Rb ₂ Sn ₂ W ₁₉
formula wt. (g mol ⁻¹)	5906.40
temperature (K)	173(2)
radiation (λ, Å)	0.71073
crystal system	monoclinic
space group	C2/c
a (Å)	32.678(4)
b (Å)	14.1708(19)
c (Å)	39.662(5)
α (°)	90
β (°)	94.992(2)
γ (°)	90
Volume (Å ³)	18297(4)
Z	8
ρ _{calcd} (g cm ⁻³)	4.124
μ (mm ⁻¹)	25.787
F(000)	19759
crystal size (mm ³)	0.45 × 0.15 × 0.11
θ range	1.63 to 32.59°
reflections collected	194610
independent reflections	31826 [R(int) = 0.0758]
max./min. transmission	0.1672 and 0.0304
refinement method	full-matrix least-squares on F ²
data/restraints/param.	31826/0/1067
goodness-of-fit on F ²	1.047
final R indices	R1 ^a = 0.0458
[R > 2σ (I)]	wR2 ^b = 0.1331
R indices (all data)	R1 ^a = 0.0747
	wR2 ^b = 0.1508
largest diff. peak and hole (e Å ⁻³)	2.995 and -6.613

$${}^a R_1 = \Sigma ||F_o| - |F_c|| / |F_o|$$

$${}^b wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}$$

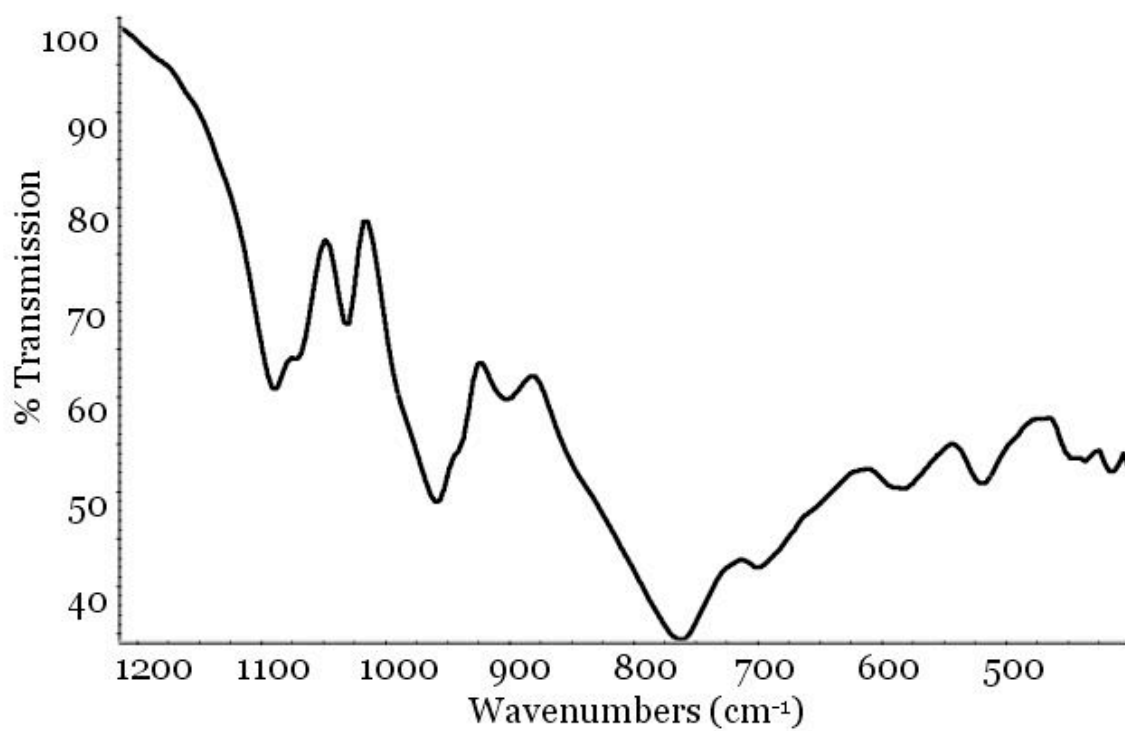
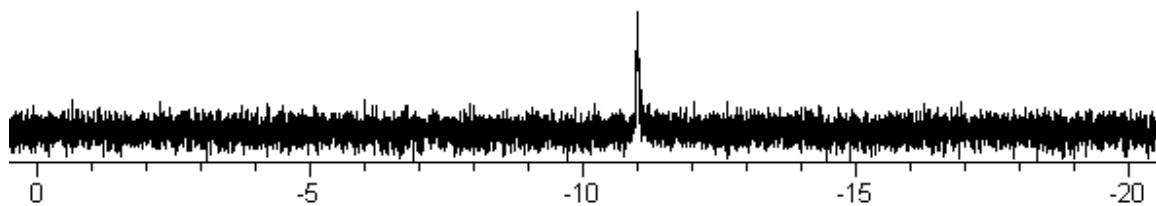


Figure S4. FT-IR spectrum of $\text{Rb}_2\text{K}_6[(\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O}))_2\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$ (**3**).

Full spectrum



Zoomed spectrum

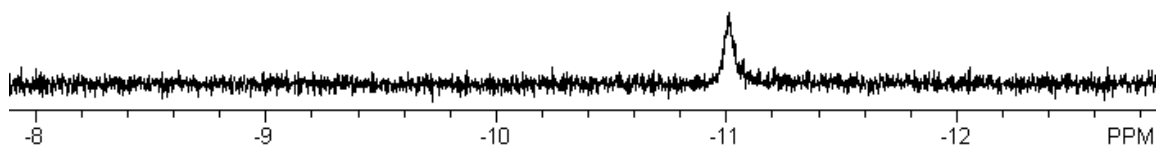


Figure S5. ^{31}P NMR of $\text{Rb}_2\text{K}_6[(\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O}))_2\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$ (**3**) in D_2O , referenced to 85% H_3PO_4 (0.0 ppm) as an external reference.

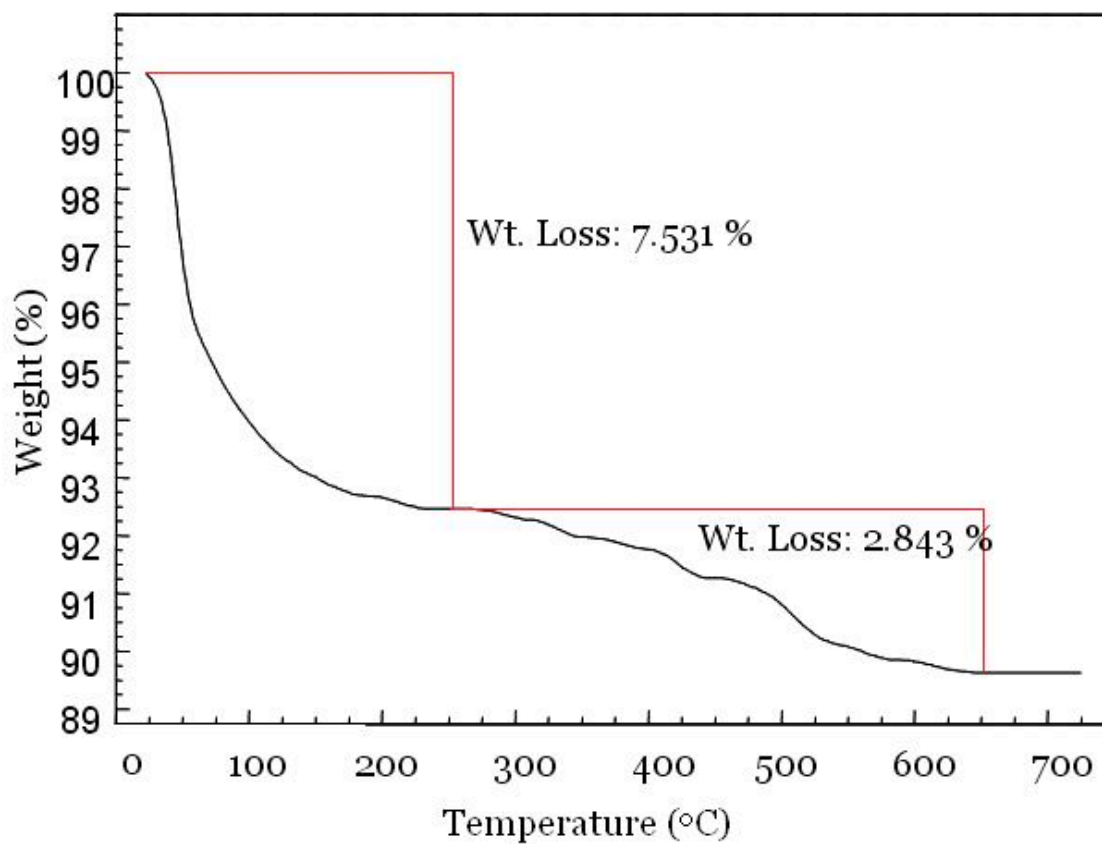


Figure S6. TGA weight loss curve of $\text{Rb}_2\text{K}_6[(\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O}))_2\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 22\text{H}_2\text{O}$ (3). A 14.032 mg sample is analyzed under inert atmosphere. The first curve accounts for the loss of 22 waters of hydration and 3 metal-coordinated water molecules. The second curve accounts for 2.0 equivalents of phenyl.

5. Synthesis and characterization of $((\text{CH}_3)_2\text{NH}_2)\text{Rb}_4\text{K}_4[\text{Cu}(\text{H}_2\text{O})\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{-P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]$ (4**)**

To a stirred solution of **2** (0.50 g, 0.095 mmol) in 17 mL of water, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.0270 g, 0.112 mmol) is added. The solution is stirred for 1 h and then a solution of 5.0 M $(\text{CH}_3)_2\text{NH} \cdot \text{HCl}$ (0.33 mL) is added under stirring and the solution is filtered. Evaporation of the clear blue filtrate gives light blue crystals of **4** in 9 d (0.160 g, yield 32%). FT-IR (2% KBr pellet): 1094 (s), 1085 (sh), 1026 (s), 954 (s), 931 (s), 896 (w), 779 (s), 737 (w), 697 (w), 583 (m), 522 (m) cm^{-1} . ^{31}P NMR (D_2O): broad peak -22 ppm. ^1H NMR (aromatic, D_2O): 8.42 (broad), 7.70 (broad), and 7.64 (broad) ppm. Anal. Calcd. for $((\text{CH}_3)_2\text{NH}_2)\text{Rb}_4\text{K}_4[\text{Cu}(\text{H}_2\text{O})\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})] \cdot 16\text{H}_2\text{O}$: C, 1.66%; N, 0.24%; W, 60.17%; Sn, 2.05%; P, 1.07%; Cu, 1.09%; Rb, 5.89%; K, 2.69%. Found: C, 1.70%; N, 0.25%; W, 59.54%; Sn, 1.91%; P, 0.96%; Cu, 1.13%; Rb, 5.67%; K, 2.51%. [MW = 5805 g/mol]

Table S3. Crystal data and structural refinement for **4**

complex	4
molecular formula	C ₈ H ₅₁ CuK ₄ NO ₈₈ P ₂ Rb ₄ SnW ₁₉
formula wt. (g mol ⁻¹)	5804.87
temperature (K)	173(2)
radiation (λ, Å)	0.71073
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> (Å)	12.071(7)
<i>b</i> (Å)	17.845(10)
<i>c</i> (Å)	24.577(13)
α (°)	69.222(7)
β (°)	80.827(8)
γ (°)	70.812(8)
Volume (Å ³)	4669(4)
<i>Z</i>	2
ρ _{calcd} (g cm ⁻³)	4.051
μ (mm ⁻¹)	26.170
F(000)	4942
crystal size (mm ³)	0.25 × 0.12 × 0.08
θ range	0.89 to 30.39°
reflections collected	87288
independent reflections	26442 [R(int) = 0.0594]
max./min. transmission	0.2286 and 0.0588
refinement method	full-matrix least-squares on F ²
data/restraints/param.	26442/0/1028
goodness-of-fit on F ²	1.034
final R indices	R1 ^a = 0.0432
[R > 2σ (I)]	wR2 ^b = 0.1081
R indices (all data)	R1 ^a = 0.0596
	wR2 ^b = 0.1155
largest diff. peak and hole (e Å ⁻³)	4.364 and -4.082

$${}^a R_1 = \Sigma ||F_o| - |F_c|| / |F_o|$$

$${}^b wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}$$

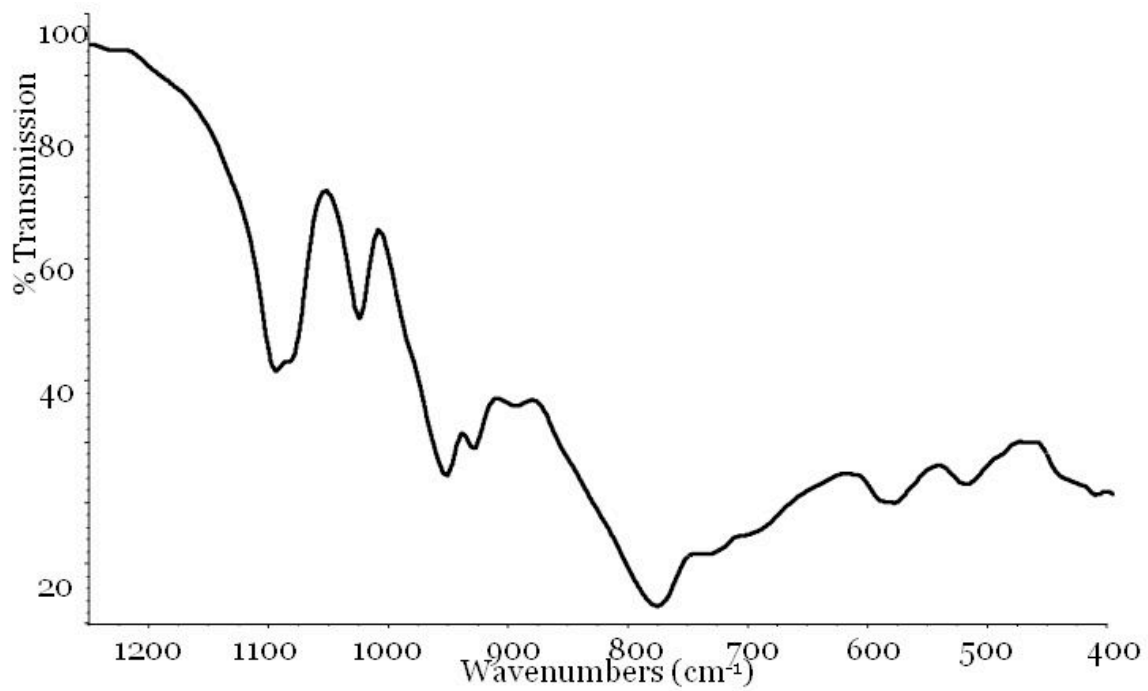


Figure S7. FT-IR spectrum of $((\text{CH}_3)_2\text{NH}_2)\text{Rb}_4\text{K}_4[\text{Cu}(\text{H}_2\text{O})\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{-P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]$ (**4**).

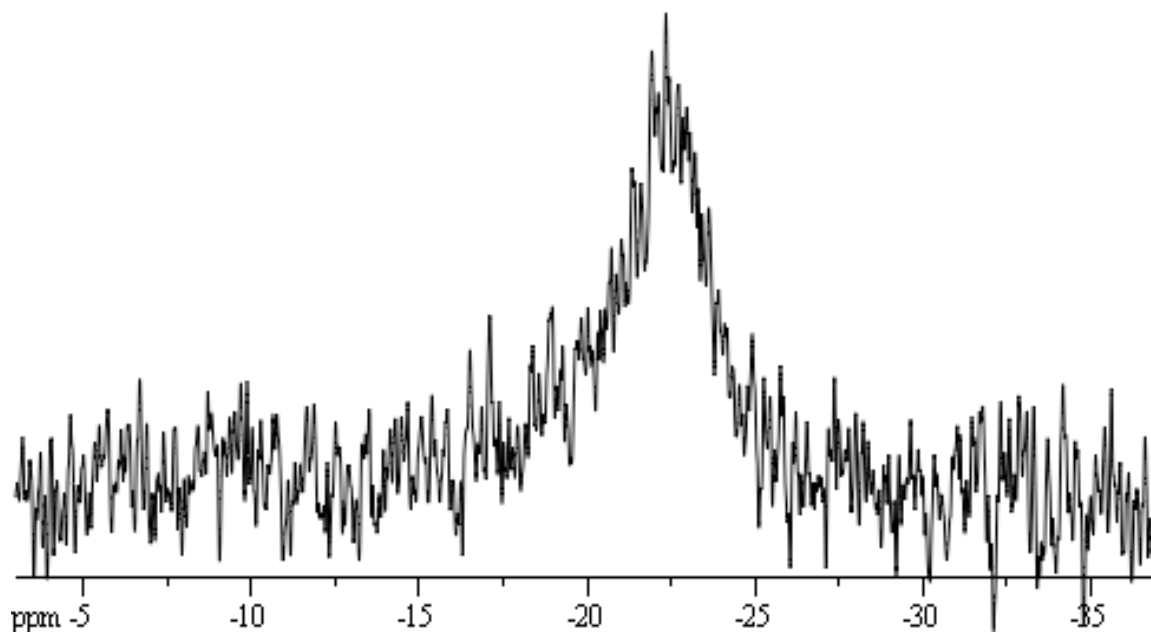


Figure S8. ^{31}P NMR of $((\text{CH}_3)_2\text{NH}_2)\text{Rb}_4\text{K}_4[\text{Cu}(\text{H}_2\text{O})\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]$ (**4**) in D_2O , referenced to 85% H_3PO_4 (0.0 ppm) as an external reference.

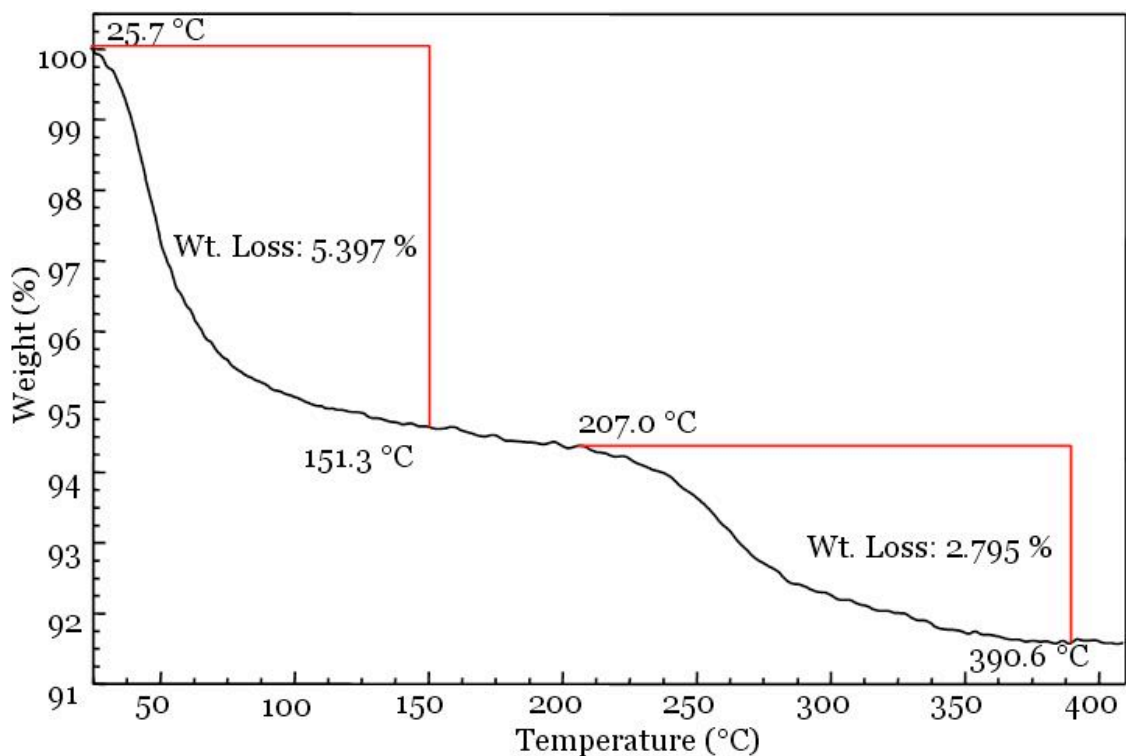


Figure S9. TGA weight loss curve of $((\text{CH}_3)_2\text{NH}_2)\text{Rb}_4\text{K}_4[\text{Cu}(\text{H}_2\text{O})\text{Sn}(\text{C}_6\text{H}_5)(\text{H}_2\text{O})\text{-P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]\cdot 16\text{H}_2\text{O}$ (**4**). A 14.2885 mg sample is analyzed under an inert atmosphere. The first curve accounts for 16 waters of hydration. The second curve corresponds to the loss of the DMA counterion, the phenyl ring, and the three metal-coordinated water molecules.

References

- [1] R. Contant, *Can. J. Chem.* **1987**, *65*, 568-573.
- [2] R. Cao, K. O'Halloran, D. A. Hillesheim, K. I. Hardcastle, C. L. Hill, *CrystEngComm* **2010**, *12*, 1518-1525.
- [3] *Bruker APEX2*, Bruker AXS Inc., Madison, Wisconsin, USA, **2007**.
- [4] *Bruker, SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, **2007**.
- [5] G. Sheldrick, *Sadabs*, 2.10 edition, **2003**.
- [6] Bruker 2007 program: G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, **2008**, *64*, 112-122.