Supporting Information

1. Powder X-Ray Diffraction Data for 2 and 3

Figure S1. Powder X-ray diffraction pattern of $(thbH)_3(H_3O)[W_{10}O_{32}](H_2O)_{7.5}$ (**2**). (Mo-Kα radiation, λ = 0.7107 Å).

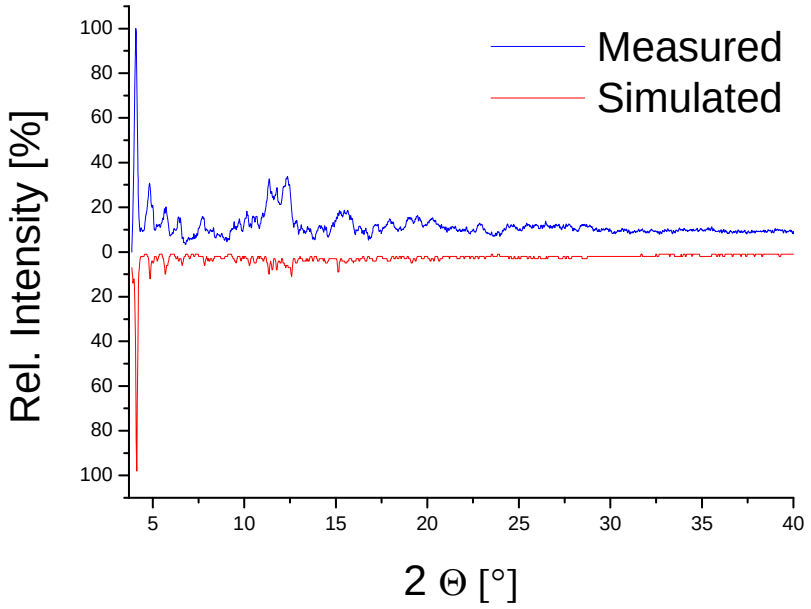
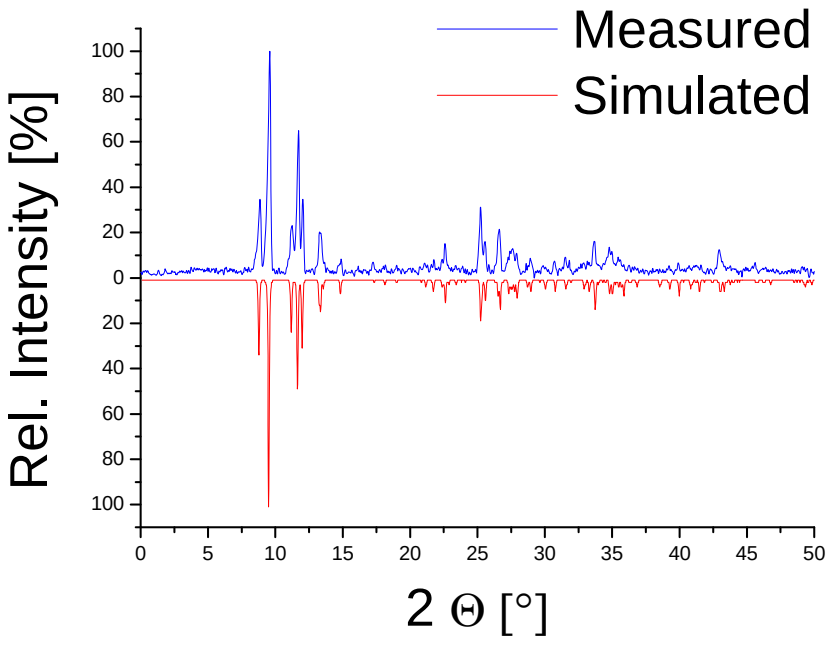


Figure S2. Powder X-ray diffraction pattern of $(thbH)_2[W_6O_{19}](H_2O)_2$. (Cu-Kα radiation, λ = 1.5406 Å).



2. DTA/TG-Measurements of 2 and 3

Figure S3. DTA/TG of $(thbH)_3(H_3O)[W_{10}O_{32}](H_2O)_{7.5}$ (**2**).

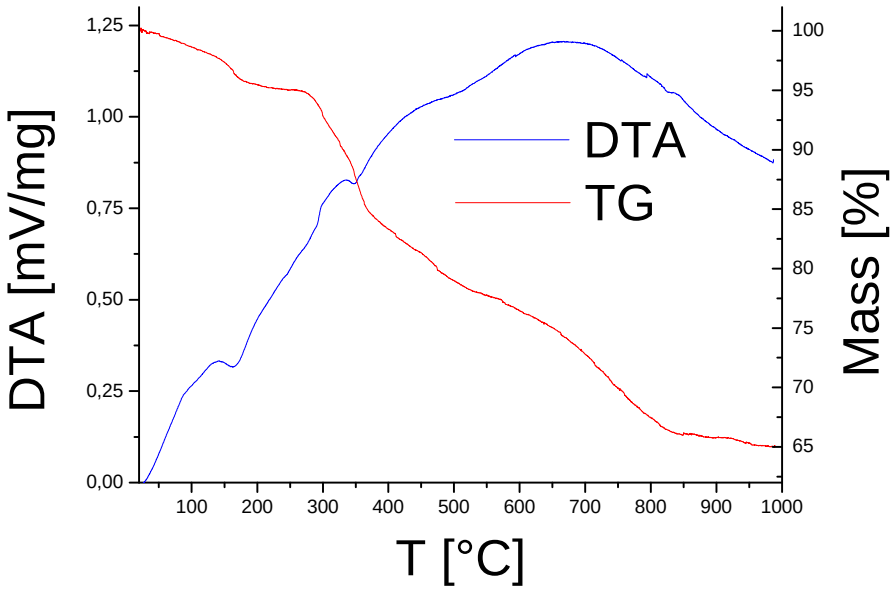
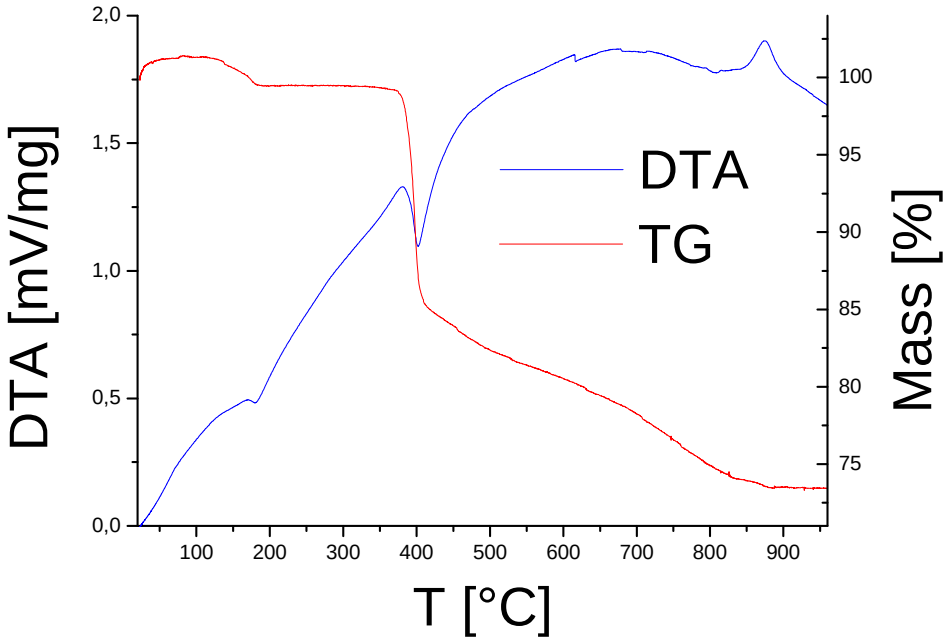


Figure S4. DTA/TG of $(thbH)_2[W_6O_{19}](H_2O)_2$ (**3**).



3. Powder X-Ray Diffraction Data for Thermolysis Residues of 2 and 3

Figure S5. X-ray powder pattern of the DTA residue of $(thbH)_3(H_3O)[W_{10}O_{32}](H_2O)_2$ (**2**) labeled **R2**. (Cu-K_α radiation, λ = 1.5406 Å) [1,2].

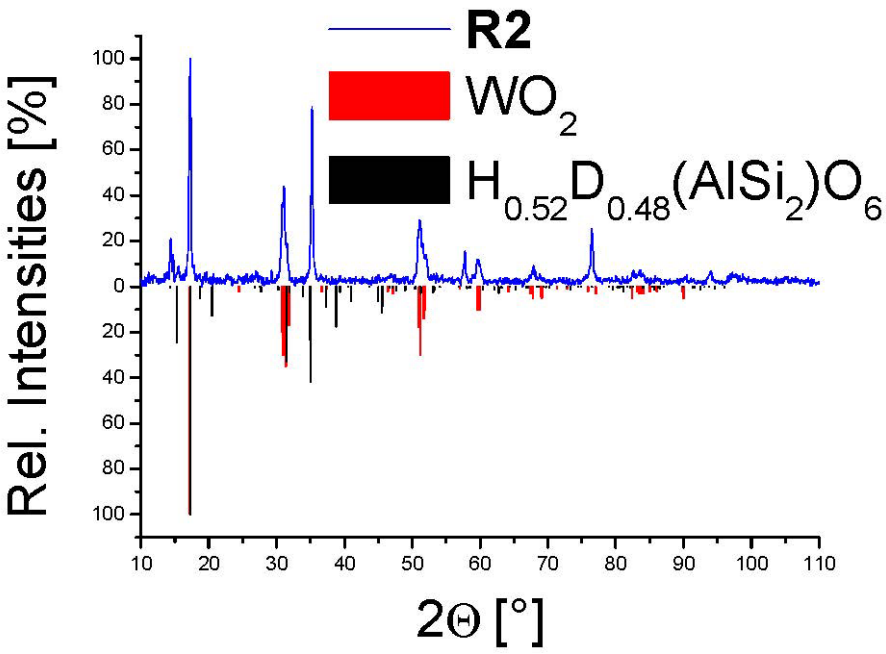
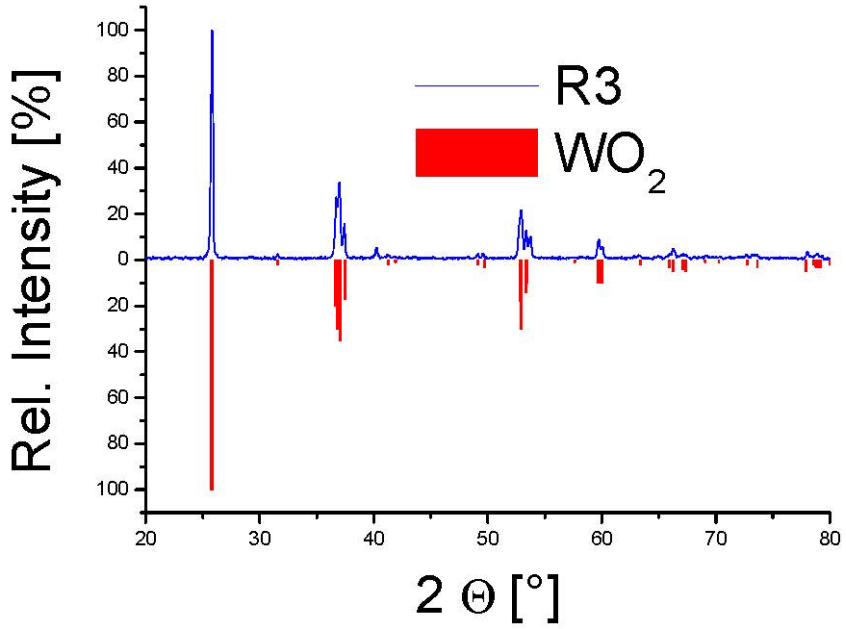


Figure S6. X-ray powder pattern of the DTA residue of $(thbH)_2[W_6O_{19}](H_2O)_2$ **(3)** labeled **R3**. (Cu-K_α radiation, λ = 1.5406 Å) [1].



4. Hydrogen Bond Geometry Tables

Table S1. Hydrogen-bond geometry of the compound $(GuaH)_4[W_{10}O_{32}](H_2O)_4$ (**1**) (Å, °).

D*–H···*A	***D*–H**	**H···*A***	***D*···*A***	***D*–H···*A***
N1–H1···O1W	0.88	1.91	2.786 (17)	170.8
N2–H2A···O3W [i]	0.88	2.57	3.27 (3)	137.1
N2–H2A···N1A [i]	0.88	2.39	3.27 (4)	173.2
N2–H2B···O2WA	0.88	2.21	2.89 (3)	133.5
N7–H7···O3W	0.88	1.75	2.49 (3)	139.8
N7–H7···O2WB [ii]	0.88	2.35	3.21 (4)	164.2
N9–H9···O16G [iii]	0.88	1.91	2.77 (3)	165.6
C8–H8···O1 [iv]	0.95	2.31	3.05 (2)	133.6
N11–H11···O2 [v]	0.88	2.10	2.927 (18)	157.2
N12–H12A···O12 [vi]	0.88	2.65	3.31 (2)	133.2
N12–H12A···N1A [vii]	0.88	2.54	3.01 (4)	114.6
N12–H12B···O2 [v]	0.88	2.41	3.16 (2)	143.2
N12–H12B···O1 [v]	0.88	2.63	3.355 (19)	141.0
N17–H17···O6G [v]	0.88	1.91	2.774 (16)	166.2
N19–H19···O14 [viii]	0.88	2.53	2.980 (15)	112.8
N19–H19···N13 [ix]	0.88	2.06	2.909 (16)	162.2
C18–H18···O2WA [x]	0.95	2.55	3.22 (3)	128.1
C18–H18···O2WB [x]	0.95	2.65	3.40 (4)	135.9
C2A–H2A2···O16G [xi]	0.98	2.50	3.13 (4)	122.1

Notes: Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y + 1, z$; (iii) $x, y, z - 1$; (iv) $x - 1, -y + 3/2, z - 1/2$; (v) $-x + 1, -y + 1, -z + 1$; (vi) $x - 1, -y + 1/2, z + 1/2$; (vii) $-x, y - 1/2, -z + 1/2$; (viii) $-x + 1, y - 1/2, -z + 1/2$; (ix) $-x, -y + 1, -z + 1$; (x) $x, -y + 1/2, z + 1/2$; (xi) $x, y + 1, z - 1$.

Table S2. Hydrogen-bond geometry of the compound $(ThbH)_3(H_3O)[W_{10}O_{32}](H_2O)_{7.5}$ (**2**) (Å, °).

D*–H···*A	***D*–H**	**H···*A***	***D*···*A***	***D*–H···*A***
N21–H21···O6*W*	0.86	2.10	2.92 (2)	158
N9–H9···O16*T*	0.86	1.86	2.705 (13)	168
C27–H27*A*···O26*T*	0.96	2.51	3.21 (2)	129
C27–H27*C*···O23 [i]	0.96	2.31	3.24 (2)	163
N19–H19···O1*W*	0.86	1.82	2.668 (16)	170
C23–H07*A*···O2*W*	0.96	2.58	3.52 (3)	166
C23–H07*B*···O6 [iv]	0.96	2.28	3.18 (2)	156
C17–H17*A*···O16*T*	0.96	2.44	3.159 (15)	131
C17–H17*B*···O25 [v]	0.96	2.40	3.222 (14)	144
C17–H17*C*···O14 [vi]	0.96	2.44	3.271 (14)	145
N1–H1···O2*T* [vii]	0.86	2.03	2.877 (13)	169
N29–H29···O2*W*	0.86	1.87	2.719 (18)	169
N11–H11···O31	0.86	2.03	2.858 (12)	161
C8–H8···O29 [vi]	0.93	2.21	3.135 (13)	177
C7–H7*A*···O6*T*	0.96	2.51	3.223 (15)	131
C7–H7*B*···O12*T* [vi]	0.96	2.64	3.171 (14)	115
C7–H7*C*···O22*T* [vi]	0.96	2.24	3.188 (19)	170

Table S2. *Cont*.

D*–H···*A	***D*–H**	**H···*A***	***D*···*A***	***D*–H···*A***
C13–H13*A*···O1*W*	0.96	2.55	3.50 (2)	171
C28–H28···O6*T* [i]	0.93	2.42	3.234 (18)	146

Notes: Symmetry codes: (i) –*x* + 2, −*y* + 1, −*z* + 1; (iv) *x*, *y*, *z* + 1; (v) *x* − 1, *y*, *z*; (vi) –*x* + 1, −*y* + 1, −*z* + 1; (vii) –*x* + 2, −*y*, −*z* + 1.

Table S3. Hydrogen-bond geometry of the compound $(ThbH)_2[W_6O_{19}](H_2O)_2$ (**3**) (Å, °).

D*–H···*A	***D*–H**	**H···*A***	***D*···*A***	***D*–H···*A***
N9–H9···O1*W*	0.86	1.90	2.741 (18)	166
N1–H1···O2*T* [ii]	0.86	2.04	2.894 (16)	175
C8–H8···O2*T* [iii]	0.93	2.20	3.090 (19)	160
C3–H3*C*···O7 [iv]	0.96	2.37	3.133 (19)	136
C7–H7*A*···O6*T*	0.96	2.48	3.19 (2)	131

Notes: Symmetry codes: (ii) –*x* + 3/2, −*y* + 3/2, −*z*; (iii) *x*, −*y* + 1, *z* + 1/2; (iv) *x* + 1/2, *y* − 1/2, *z*.

5. BVS Calculations [3]

Table S4. Selected bond valence sums of the compound $(GuaH)_4[W_{10}O_{32}](H_2O)_4$ (**1**).

Atom No.	**Bond valence Sum**	**% Deviation from assumed valence state**
W1	5.933	1
W2	6.003	0
W3	6.051	1
W4	6.077	1
W5	6.227	4
O1	1.698	15
O2	1.775	11
O3	1.819	9
O4	1.839	8
O5	1.910	5
O6	1.743	13
O7	1.807	10
O8	1.921	4
O9	2.033	2
O10	1.812	9
O11	1.973	1
O12	1.788	11
O13	1.966	2
O15	2.106	5
O16	2.167	8

Table S5. Selected bond valence sums of the compound $(ThbH)_3(H_3O)[W_{10}O_{32}](H_2O)_{7.5}$ (**2**).

Atom No.	Bond valence Sum	% Deviation from assumed valence state
W1	6.143	2
W2	6.264	4
W3	5.960	1
W4	6.155	3
W5	6.075	1
W6	6.190	3
W7	6.091	2
W8	6.025	0
W9	6.174	3
W10	6.107	2
O1	1.769	12
O2	1.954	2
O3	1.919	4
O4	1.906	5
O5	1.898	6
O6	1.862	7
O7	2.000	0
O8	1.741	13
O9	2.017	1
O10	1.717	14
O11	2.011	1
O12	2.122	6
O13	2.006	0
O14	1.812	9
O15	2.104	5
O16	1.759	12
O17	2.108	5
O18	1.832	8
O19	2.019	1
O20	1.736	13
O21	2.001	0
O22	2.121	6
O23	1.769	12
O24	2.025	1
O25	1.981	1
O26	1.754	12
O27	1.947	3
O28	1.905	5
O29	1.900	5
O30	1.919	4
O31	1.698	15
O32	1.872	6

Table S6. Selected bond valence sums of the compound $(ThbH)_2[W_6O_{19}](H_2O)_2$ (**3**).

Atom No.	Bond valence Sum	% Deviation from assumed valence state
W1	6.145	2
W2	6.201	3
W3	6.228	4
W4	6.109	2
O1	1.817	9
O2	1.964	2
O3	1.974	1
O4	1.992	0
O5	2.025	1
O6	1.974	1
O7	1.852	7
O8	1.326	34
O9	1.984	1
O10	1.962	2
O11	1.857	7

References

1. Palmer, D.J.; Dickens, P.G. Tungsten dioxide: Structure refinement by powder neutron diffraction. WO_2-powder diffraction data. *Acta Cryst. B* **1979**, *35*, 2199–2201.
2. Vogt, T.; Paulus, H.; Fuess, H.; Müller, G. The crystal structure of $HAlSi_2O_6$ with a keatite-type framework. $H_{0.52}D_{0.48}(AlSi_2)O_6$-powder diffraction data. *Z. Kirstallogr.* **1990**, *190*, 7–18.
3. Wills, A.S. VaList-Program. Available online: https://dl.dropboxusercontent.com/u/8933134/Website/Site/Software/Software.html (accessed on 15 February 2014).