Supporting Information

Immobilization of Alkali Metal ions in a 3D Lanthanide-Organic Framework: Selective Sorption and H_2 Storage Characteristics

Sudip Mohapatra,[a] K. P. S. S. Hembram,[b] Umesh Waghmare,[b] Tapas Kumar Maji[a,]*

[a]*Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India*

[b]*Theoretical Sciences Unit*, *Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India*

* Corresponding Author: E-mail: tmaji@jncasr.ac.in, Phone: (+91) 80 2208 2826, Fax: (+91) 80 2208 2766

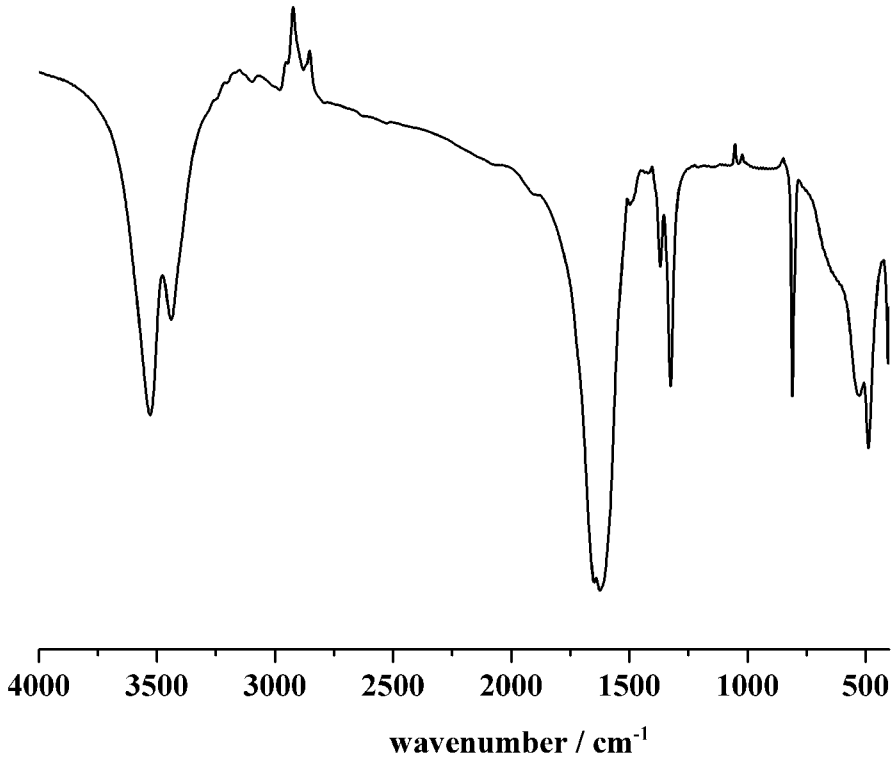

Figure S1: IR spectra for $\{KHo(C_2O_4)_2(H_2O)_4\}_n$ (**1**).

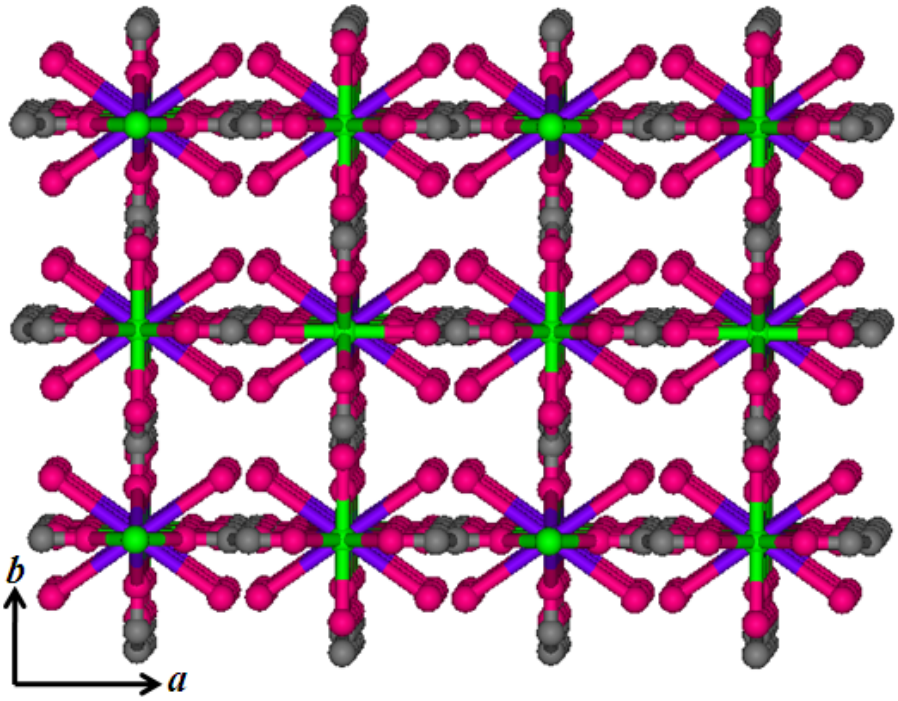

Figure S2: View of the 3D coordination framework of **1** along the crystallographic *c*-axis showing the square shaped channels are occupied by the water molecules coordinated to K^{I}.

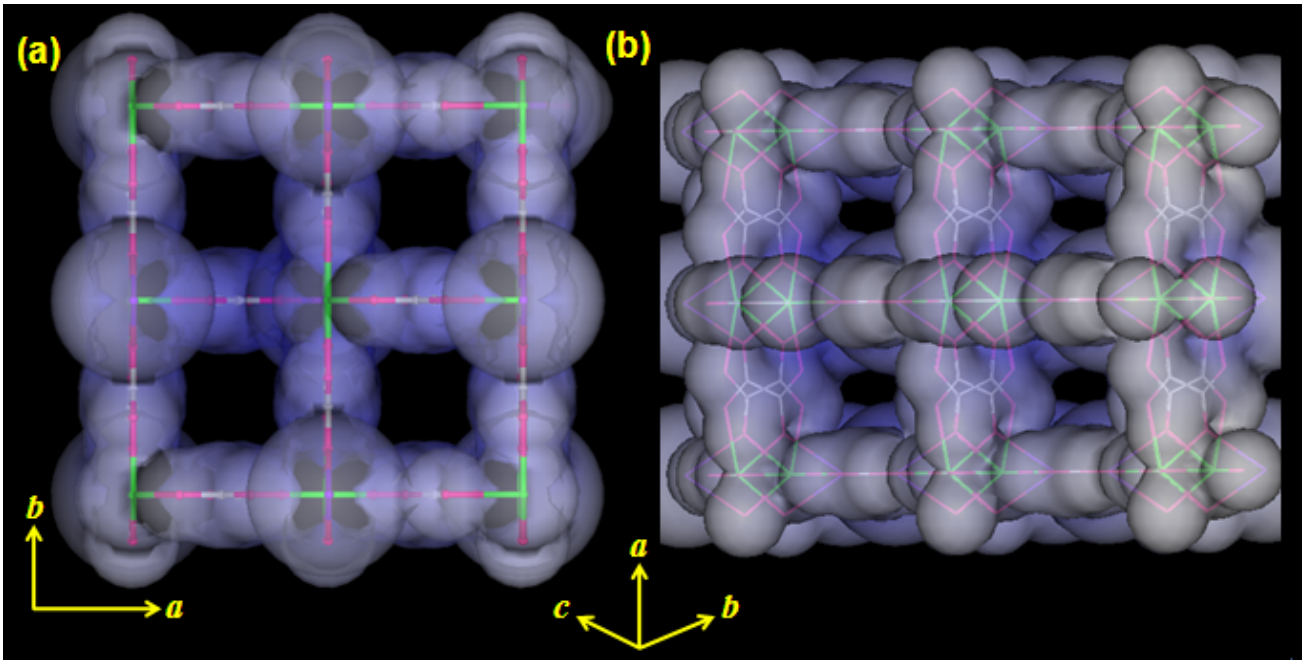

Figure S3. View of the channels: (a) square shaped channels along the crystallographic *c*-axis; (b) oval shaped small channels along parallel to the crystallographic *a*-axis.

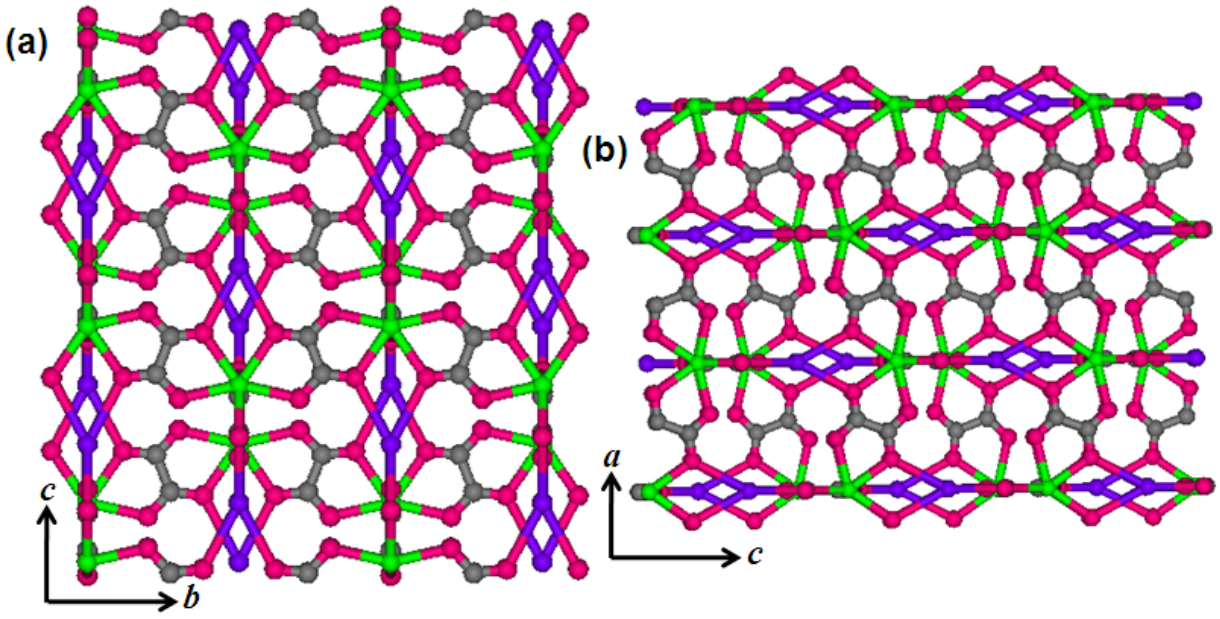

Figure S4. View of the dehydrated framework **1′**. (a) along the crystallographic *a*-axis; and (b) along the crystallographic *b*-axis.

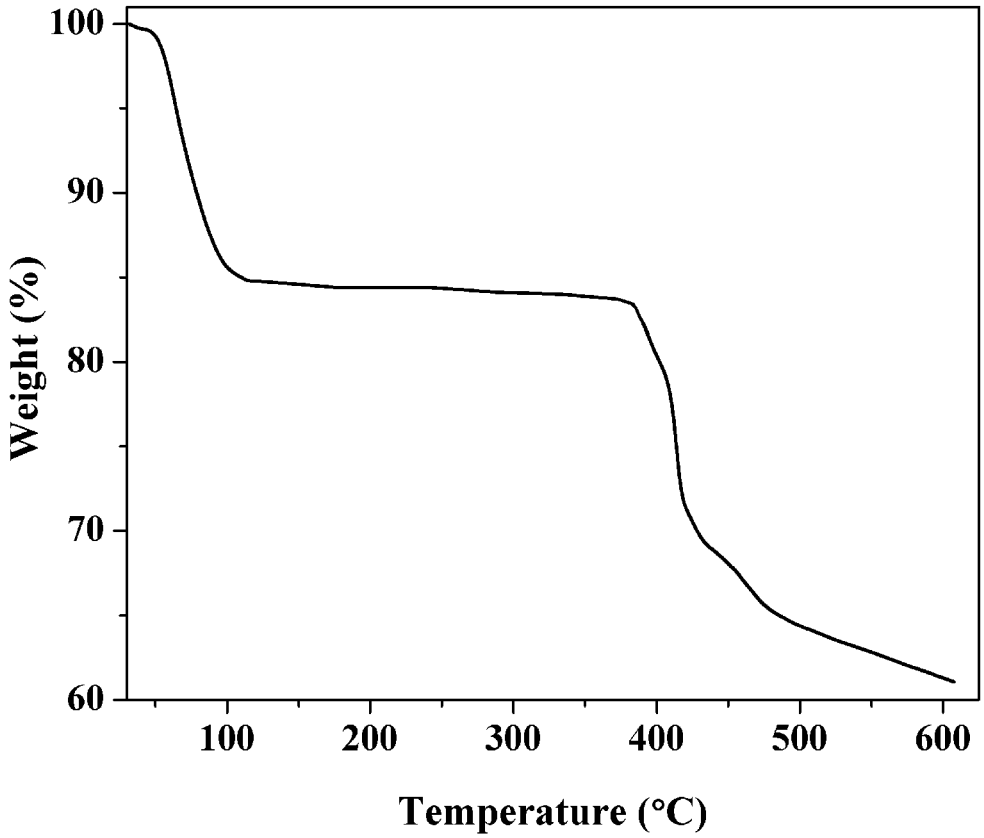

Figure S5. TGA for $\{KHo(C_2O_4)_2(H_2O)_4\}_n$ (**1**) over the temperature range from 25 – 600 °C at a heating rate of 3 °C/ min under the N2 atmosphere.

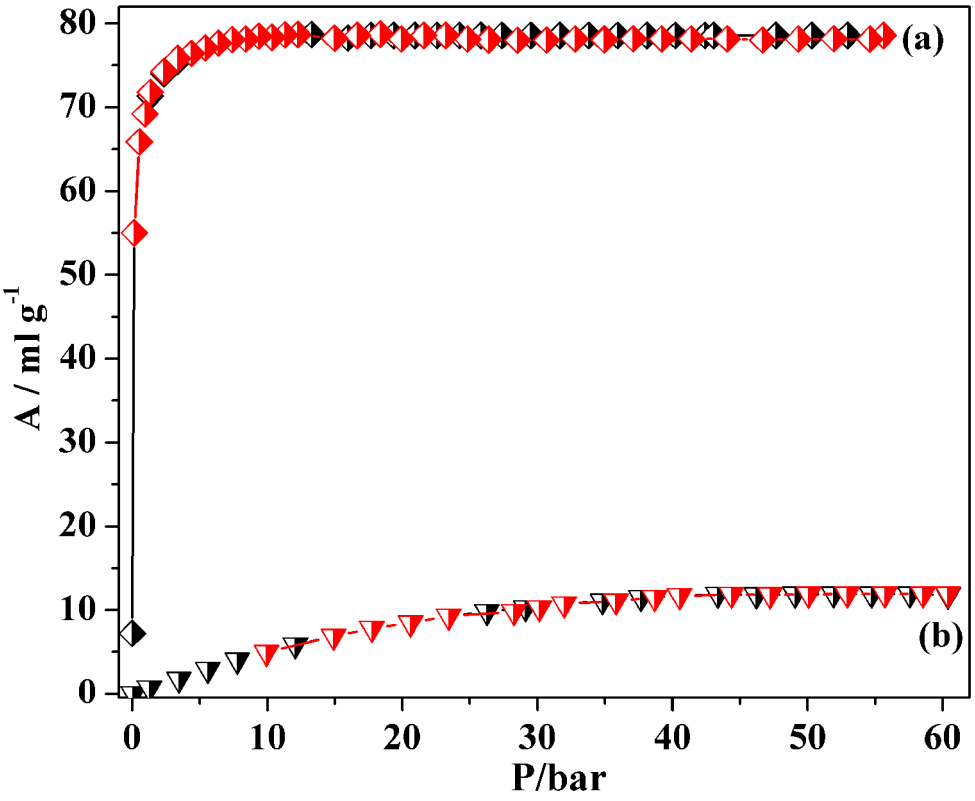

Figure S6. High pressure H_2 adsorption (black) and desorption (red) isotherm for **1′**. (a) at 77 K; (b) at 195 K.

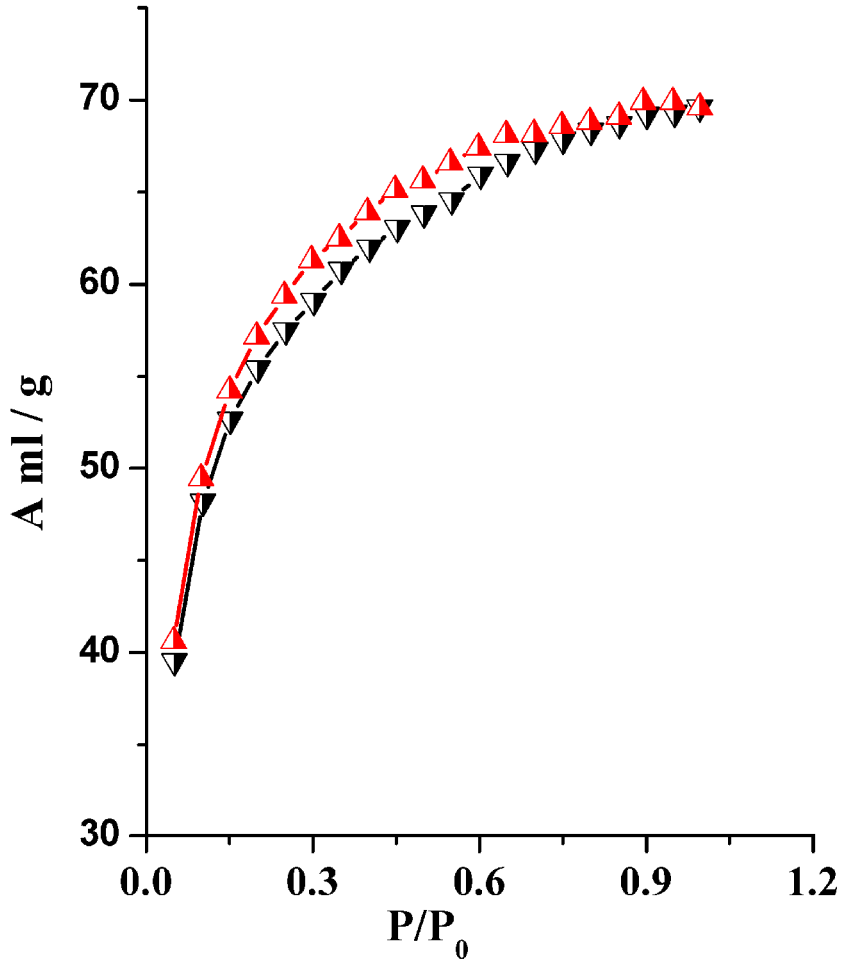

Figure S7. H_2 sorption studies for **1′** at 77 K.

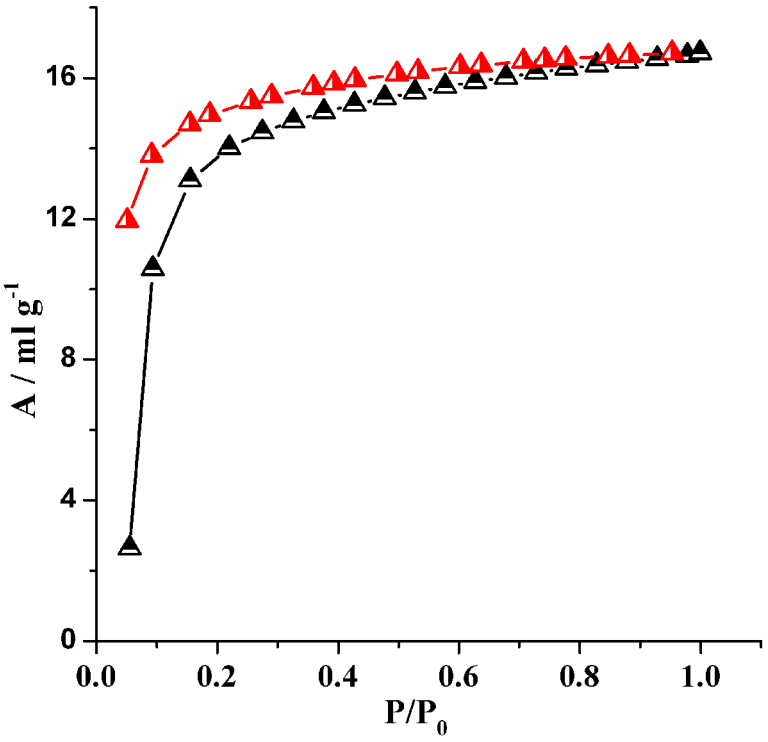

Figure S8. CO_2 sorption studies for **1′** at 298 K.

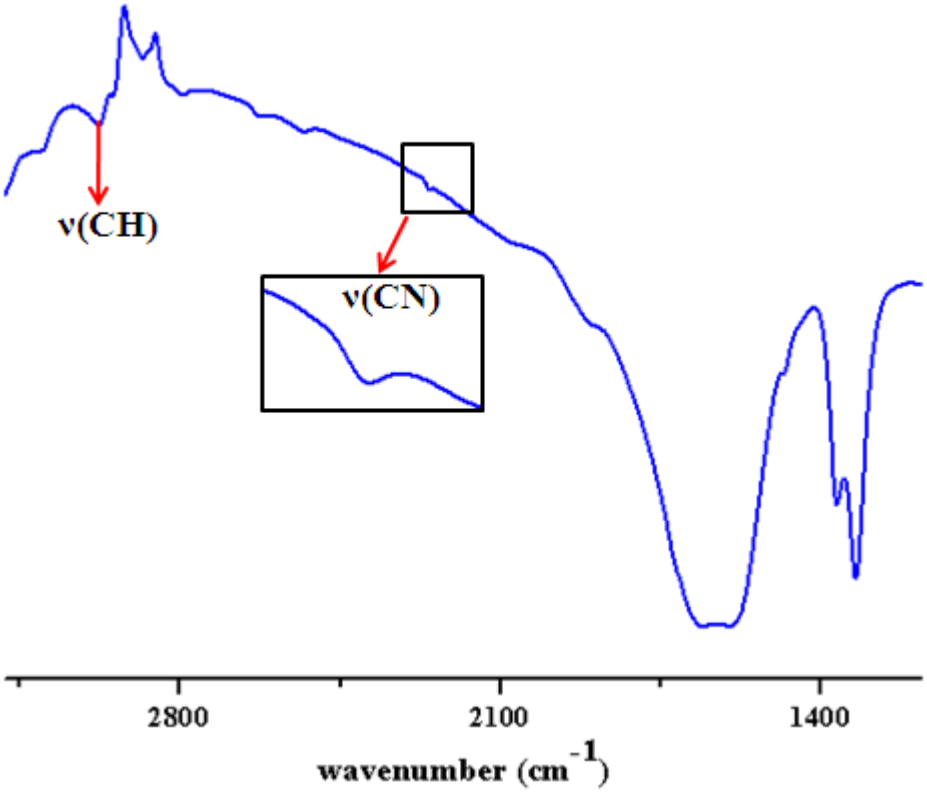

Figure S9: IR spectra for CH_3CN vapor exposed compound of **1´.**

Table S1: Selected bond lengths and angles for $\{KHo(C_2O_4)_2(H_2O)_4\}_n$ (**1**)

Ho1-O1	2.339(6)	Ho1-O2_c	2.377(5)
Ho1-O1_e	2.339(6)	Ho1-O2_f	2.377(5)
Ho1-O2_k	2.377(5)	Ho1-O1_n	2.339(6)
Ho1-O2_s	2.377(5)	Ho1-O1	2.339(6)
K1-O2	2.844(5)	K1-O3	2.888(14)
K1-O2_g	2.844(5)	K1-O3_g	2.888(14)
O1-Ho1-O2_c	79.56(13)	O1-Ho1-O1_e	92.78(5)
O1-Ho1-O2_f	68.1(2)	O1-Ho1-O2_k	137.4(2)
O1-Ho1-O1_n	154.6(2)	O1-Ho1-O2_s	79.56(13)
O1-Ho1-O1	92.78(5)	O1_e-Ho1-O2_c	68.1(2)
O2_c-Ho1-O2_f	132.58(12)	O2_c-Ho1-O2_k	132.58(12)
O1_n-Ho1-O2_c	79.56(13)	O2_c-Ho1-O2_s	69.32(19)
O1-Ho1-O2_c	137.4(2)	O1_e-Ho1-O2_f	79.56(13)
O1_e-Ho1-O2_k	79.56(13)	O1_e-Ho1-O1_n	92.78(5)
O1_e-Ho1-O2_s	137.4(2)	O1_e-Ho1-O1	154.6(2)
O2_f -Ho1-O2_k	69.32(19)	O1_n-Ho1-O2_f	137.4(2)
O2_f-Ho1-O2_s	132.58(12)	O1-Ho1-O2_f	79.56(13)
O1_n-Ho1-O2_k	68.1(2)	O2_k-Ho1-O2_s	132.58(12)
O1-Ho1-O2_k	79.56(13)	O1_n-Ho1-O2_s	79.56(13)
O1_n-Ho1-O1	92.78(5)	O1-Ho1-O2_s	68.1(2)

Symmetry Code: c = 1/4+y,1/4-x,-1/4+z; e = 1/4+y,-1/4+x,5/4-z; f = 1/2-x,y,3/2-z; g = 1/4-y,1/4-x,3/4-z; k = 1/2+x,y,3/2-z; n = 1-x,y,z; s = 3/4-y,1/4+x,-1/4+z

Indexing results of powder sample of 1´

a = 14.690(5) Å; b = 11.428(4) Å; c = 7.879(2) Å; α = 90.0 °; β = 91.50(5)°; γ = 90.0°

V = 1322.39 Å^3

H	K	L	2θobs	2θcalc
2	0	0	12.052	12.044
1	0	1	12.875	12.882
-1	1	1	14.807	14.800
0	2	0	15.484	15.495
2	2	1	22.835	22.863
-1	0	2	23.231	23.210
4	1	4	25.448	25.463
3	3	0		29.692
-3	1	2	29.763	29.760
-2	2	2		29.855
0	4	0	31.261	31.282
4	2	1		31.315
1	4	0	31.890	31.884
0	1	3	35.047	35.038
-3	0	3	38.435	38.448
-6	1	1	39.030	39.021

NUMBER OF OBS. LINES = 13; NUMBER OF CALC. LINES = 16

M(13)= 9 AV.EPS.= 0.0000450; F 13 = 9.(0.011962, 133)

0 LINES ARE UNINDEXED ; M-TEST= 9 UNINDEXED IN THE TEST= 0

Program used to index TREOR90

Table S2: Comparison of the bond lengths (Å) and angles (°) dehydrated (**1′**) and optimized structure.

Bond specification in **1′**	Bond length (Å) Theory	Bond length (Å) Experiment
Ho - O1	2.340	2.339
Ho - O2	2.393	2.377
K - O2	2.815	2.844
Angle specification in **1′**	Bond angles (°) (Theory)	Bond angles (°) (Experiment)
O1 - Ho - O1	92.75	92.78
O1 - Ho - O1	153.05	154.6
O2 - Ho - O2	69.35	69.32
O1 - Ho - O2	78.85	79.56
O1 - Ho - O2	137.56	137.4
O2 - K - O2	56.93	56.75
O2 - K - O2	140.42	140.73