

Supplementary Information for

Mild Hydrothermal Synthesis of the Complex Hafnium Containing Fluorides $\text{Cs}_2[\text{M}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ (M= Ni, Co, and Zn), $\text{CuHfF}_6(\text{H}_2\text{O})_4$ and $\text{Cs}_2\text{Hf}_3\text{Mn}_3\text{F}_{20}$ Based on HfF_7 and HfF_6 Coordination Polyhedra

Gyanendra B. Ayer, Vladislav V. Klepov, Mark D. Smith, and Hans-Conrad zur Loye*

Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC, United States

*e-mail: zurloye@mailbox.sc.edu

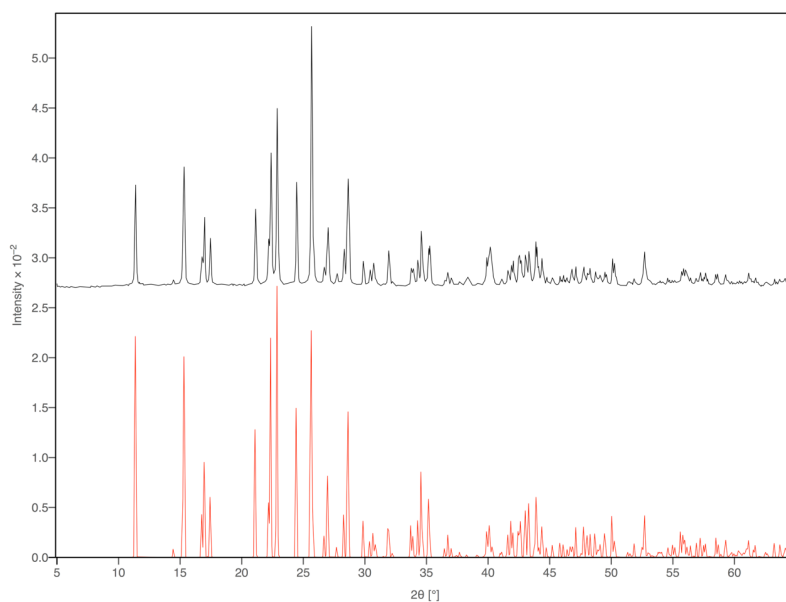


Figure S1. Experimental and calculated powder patterns of $\text{Cs}_2[\text{Ni}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ shown in black and red, respectively.

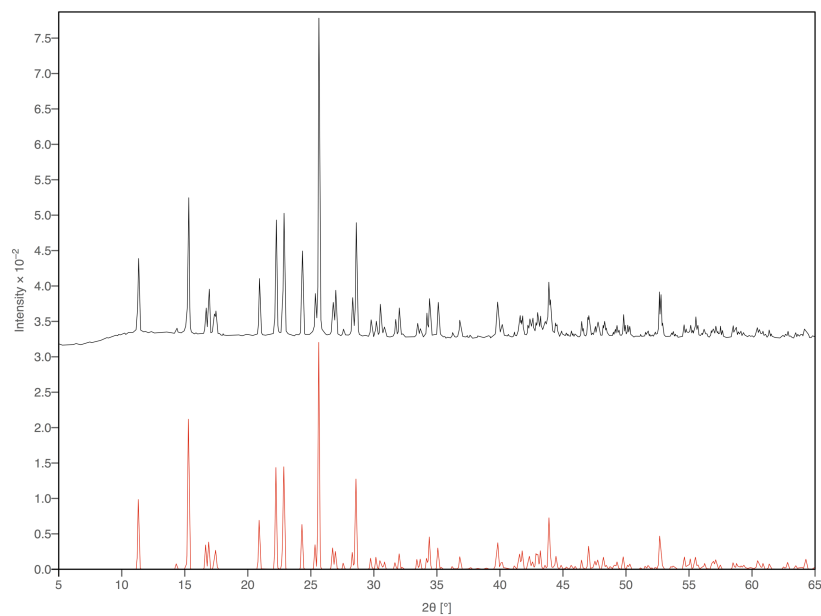


Figure S2. Experimental and calculated powder patterns of $\text{Cs}_2[\text{Co}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ shown in black and red, respectively.

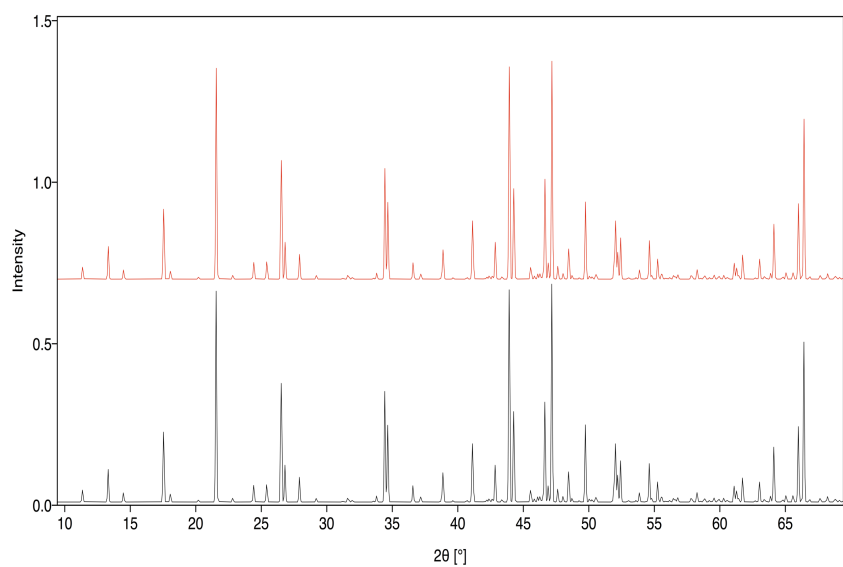


Figure S3. Experimental and calculated powder patterns of $\text{Cs}_2\text{Hf}_3\text{Mn}_3\text{F}_{20}$ shown in black and red, respectively.

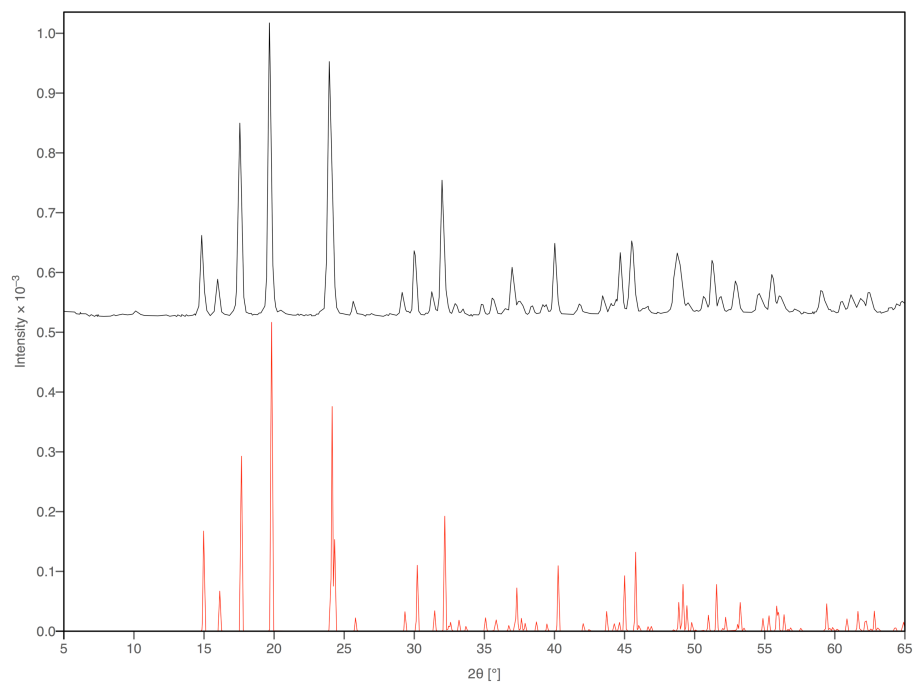
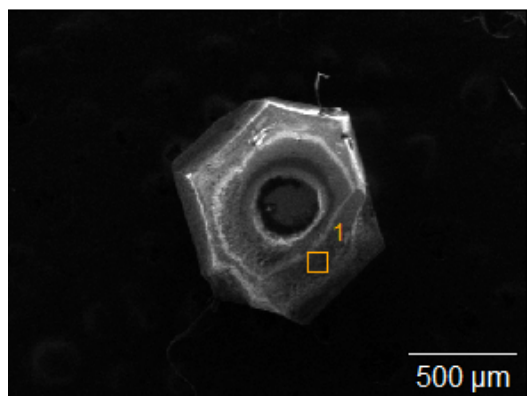
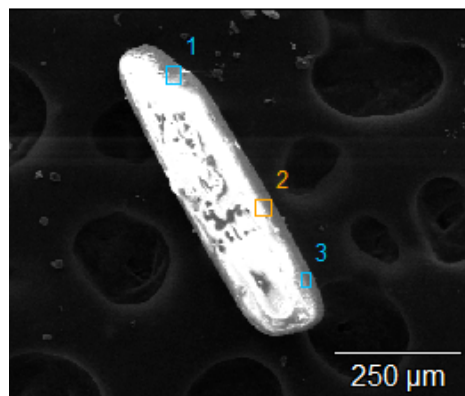


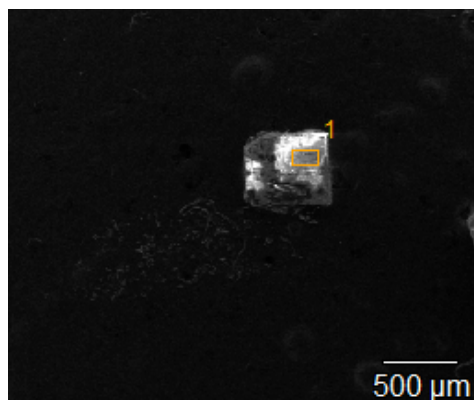
Figure S4. Experimental and calculated powder patterns of $\text{CuHfF}_6(\text{H}_2\text{O})_4$ shown in black and red, respectively.



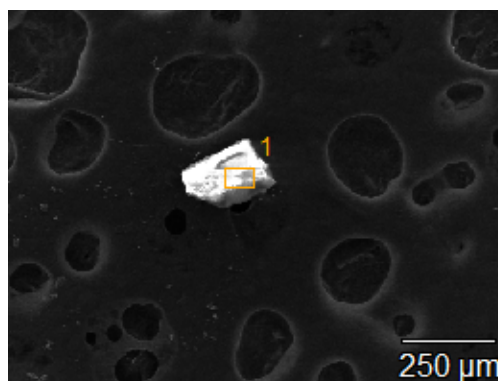
(a)



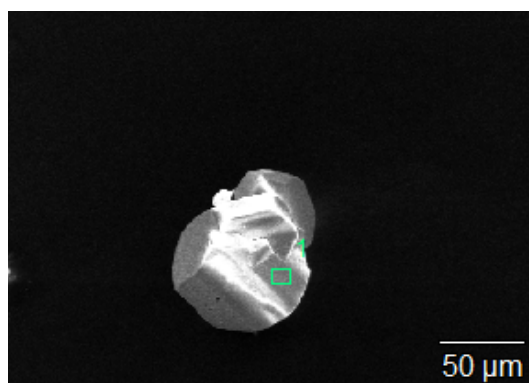
(b)



(c)



(d)



(e)

Figure S5. SEM images of crystals of $\text{Cs}_2[\text{Ni}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ (a), $\text{Cs}_2[\text{Co}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ (b), $\text{Cs}_2[\text{Zn}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ (c), $\text{CuHfF}_6(\text{H}_2\text{O})_4$ (d), and $\text{Cs}_2\text{Hf}_3\text{Mn}_3\text{F}_{20}$ (e).

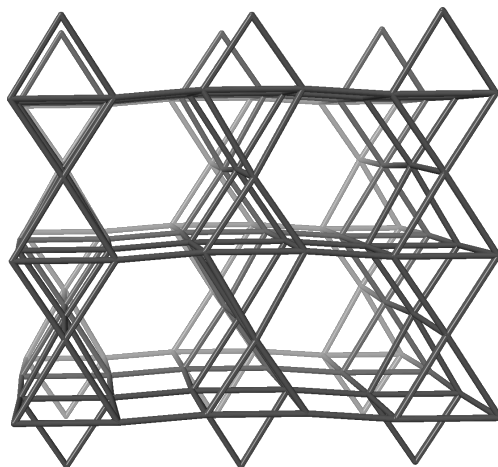


Figure S6. The simplified net of the $\text{Cs}_2\text{Hf}_3\text{Mn}_3\text{F}_{20}$ framework exhibiting **btu** topology.

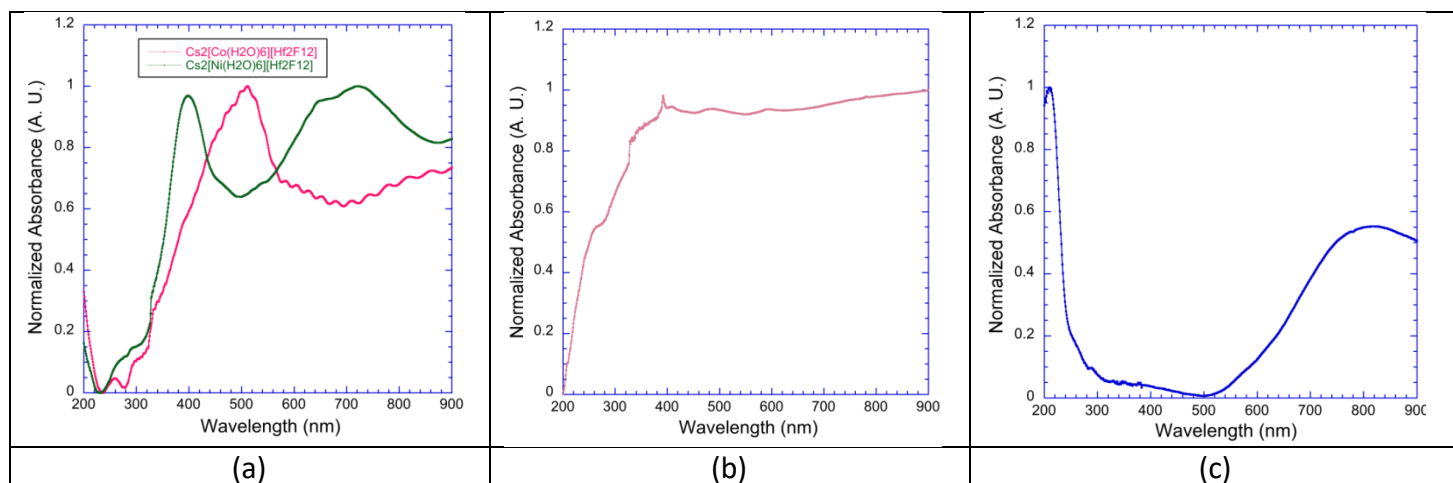


Figure S7. UV-Vis spectra of (a) $\text{Cs}_2[\text{M}(\text{H}_2\text{O})_6][\text{Hf}_2\text{F}_{12}]$ ($\text{M} = \text{Ni}$ and Co) and (b) $\text{Cs}_2\text{Hf}_3\text{Mn}_3\text{F}_{20}$ and (c) $\text{CuHfF}_6(\text{H}_2\text{O})_4$.

Table S1. Elemental composition determined by EDS

Cs₂[Ni(H₂O)₆][Hf₂F₁₂]		Cs₂[Co(H₂O)₆][Hf₂F₁₂]		Cs₂[Zn(H₂O)₆][Hf₂F₁₂]	
Element	Atom %	Element	Atom %	Element	Atom %
Cs	5.75	Cs	2.45	Cs	4.74
Hf	1.84	Hf	2.66	Hf	3.42
Ni	2.78	Co	1.13	Zn	1.21
O	14.58	O	15.57	O	24.45
F	75.06	F	78.19	F	66.18

CuHfF₆(H₂O)₄		Cs₂Hf₃Mn₃F₂₀	
Element	Atom %	Element	Atom %
Cu	3.18	Cs	8.22
Hf	2.31	Hf	13.24
O	27.81	Mn	14.37
F	66.69	F	64.17

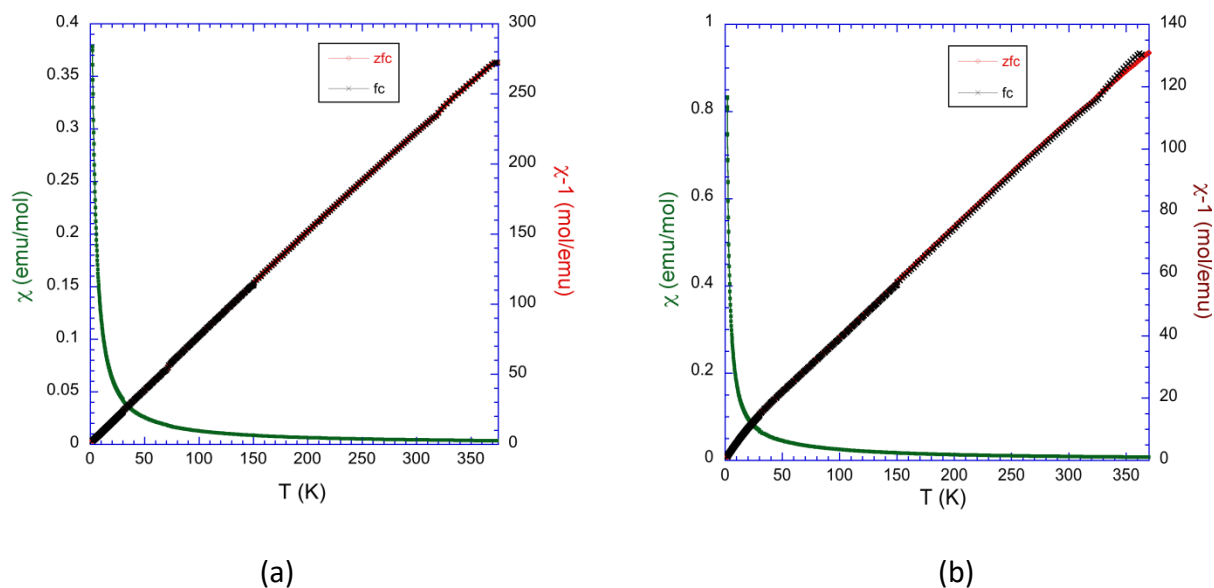


Figure S8. Overlapping zero-field and field cooled magnetic susceptibility curves of (a) Cs₂[Ni(H₂O)₆][Hf₂F₁₂] and (b) Cs₂[Co(H₂O)₆][Hf₂F₁₂]