## **SUPPORTING INFORMATION FOR:**

# Manifestations of Weak O–H…F Hydrogen Bonding in $M(H_2O)_n(B_{12}F_{12})$ Salt Hydrates: Unusually Sharp FTIR v(OH) Bands and Latent Porosity (M = Mg–Ba, Co, Ni, Zn)

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Abbreviations:  $Z^{2-} = B_{12}F_{12}^{2-}$ ; SC-XRD = single-crystal X-ray diffraction;  $\odot = B_{12}$  centroid. Notes: All FTIR spectra were recorded at room temperature unless otherwise indicated; the references cited in this document are collected at the end of this document; the reference numbers in this document are different than in the main text.

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#### Synthesis and crystallization of M(H<sub>2</sub>O)<sub>n</sub>(Z) compounds

 $Mg(H_2O)_6(Z)$ . Equivalent amounts of  $Ag_2(CH_3CN)_4(Z)$  dissolved in  $CH_3CN$  and  $MgCl_2 \cdot 6H_2O$  dissolved in  $H_2O$  were mixed and vigorously stirred for 10 min. Filtration followed by slow evaporation of the mixture of solvents afforded colorless crystals of  $Mg(H_2O)_6(Z)$  suitable for diffraction in 85% yield.

 $Ca(H_2O)_7(Z)$ ,  $Sr(H_2O)_7(Z)$ ,  $Ba(H_2O)_5(Z)$ , and  $Ba(H_2O)_4(Z)$ . Equivalent amounts of  $(H_3O)_2(H_2O)_6(Z)$ and the corresponding anhydrous MCO<sub>3</sub> salt were mixed in H<sub>2</sub>O. Slow evaporation afforded colorless crystals of  $Ca(H_2O)_7(Z)$ ,  $Sr(H_2O)_7(Z)$ , and  $Ba(H_2O)_5(Z)$  suitable for diffraction (these were kept in the mother liquor; for this reason a meaningful yield was not recorded). Evaporation of an aqueous solution to insipient dryness under an atmosphere containing 10 torr  $H_2O(g)$  afforded crystals of the tetrahydrate  $Ba(H_2O)_4(Z)$  suitabled for diffraction in ca. 50% yield.

 $Co(H_2O)_6(Z)$ . A solution of  $Ag_2(CH_3CN)_4(Z)$  (200 mg; 0.271 mmol) in CH<sub>3</sub>CN (5 mL) was added quickly to a solution of anhydrous CoCl<sub>2</sub> (35.2 mg; 0.271 mmol) in H<sub>2</sub>O (5 mL) and vigorously stirred for 10 min. Filtration followed by slow evaporation of the mixture of solvents afforded 100 mg of pink crystals of Co(H<sub>2</sub>O)<sub>6</sub>(Z) suitable for diffraction (70% yield). A photograph of the crystals is shown in Figure S1.

 $Ni(H_2O)_6(Z)$ . A solution of  $Ag_2(CH_3CN)_4B_{12}F_{12}$  (200 mg; 0.271 mmol) in CH<sub>3</sub>CN (5 mL) was added quickly to a solution of anhydrous NiCl<sub>2</sub> (35.1 mg; 0.271 mmol) in H<sub>2</sub>O (5 mL) and vigorously stirred for 10 min. Filtration followed by slow evaporation of the mixture of solvents afforded 85 mg of pale green crystals of Ni(H<sub>2</sub>O)<sub>6</sub>(Z) suitable for diffraction (60% yield). A photograph of the crystals is shown in Figure S1.

 $Zn(H_2O)_6Z$ . A solution of  $Ag_2(CH_3CN)_4B_{12}F_{12}$  (200 mg; 0.271 mmol) in  $CH_3CN$  (5 mL) was added quickly to a solution of anhydrous  $ZnCl_2$  (36.9 mg; 0.271 mmol) in  $H_2O$  (5 mL) and vigorously stirred for 10 min. Filtration followed by slow evaporation of the mixture of solvents afforded 72 mg of colorless crystals of  $Zn(H_2O)_6(Z)$  suitable for diffraction (50% yield).



Figure S1. Photographs of crystals of Co(H<sub>2</sub>O)<sub>6</sub>(B<sub>12</sub>F<sub>12</sub>) (left) and Ni(H<sub>2</sub>O)<sub>6</sub>(B<sub>12</sub>F<sub>12</sub>) (right).

compound	Mg(H <sub>2</sub> O) <sub>6</sub> (Z)	Ca(H <sub>2</sub> O) <sub>7</sub> (Z)	Sr(H <sub>2</sub> O) <sub>7</sub> (Z)	Ba(H <sub>2</sub> O) <sub>5</sub> (Z)	$Ba(H_2O)_4(Z)$	Co(H <sub>2</sub> O) <sub>6</sub> (Z)	Ni(H <sub>2</sub> O) <sub>6</sub> (Z)	$Zn(H_2O)_6(Z)$
M-F(B)			2.665(2) ×2	2.7927(10)-	2.652(7)-			
				3.2670(10) <sup>b</sup>	3.242(8) <sup>c</sup>			
М-О	2.0390(11),	2.3467(11)-	2.560(2)-	2.716(2)-	2.684(10)-	2.0663(4),	2.0290(7),	2.0611(4),
	2.0659(11)	2.4891(11)	2.674(3)	2.870(2)	2.851(10)	2.0907(4)	2.0515(7)	2.0926(4)
$\Sigma$ (M–F bond valences)			0.35	0.73	1.06 (Ba1),			
					0.95 (Ba2)			
$\Sigma$ (M–O bond valences)	2.27	2.23	1.81	1.29	1.12 (Ba1),	2.11	2.11	2.19
					1.18 (Ba2)			
$\Sigma$ (M bond valences)	2.27	2.23	2.16	2.02	2.18 (Ba1),	2.11	2.11	2.19
					2.13 (Ba2)			
⊙…⊙	7.535 × 3	7.467-8.392	$7.304 \times 2, 8.840$	6.943-7.720 <sup>d</sup>	6.857–9.048	$7.534 \times 3$	$7.510 \times 3$	7.534 × 3
$\odot \cdots \odot \cdots \odot$	88.3, 91.7	82.1, 83.3, 83.5	68.2, 76.1, 90	$90 \times 3$	57.2-82.5	87.9, 92.1	87.9, 92.1	87.9, 92.1
B-F	1.381(2)-	1.373(2)-	1.371(5)-	1.377(3)-	1.34(2)-	1.3793(6)-	1.3797(11)-	1.3810(6)-
	1.385(2)	1.390(2)	1.394(4)	1.391(2)	1.43(2)	1.3835(6)	1.3840(11)	1.3836(6)
В-В	1.785(2)-	1.783(2)-	1.785(6)-	1.773(3)-	1.74(2)-	1.7905(8)-	1.7917(14)-	1.7917(8)-
	1.796(2)	1.798	1.806(6)	1.809(3)	1.85(2)	1.8017(7)	1.7999(15)	1.8028(8)

Table S1. Selected Interatomic Distances (Å) and Angles (deg) for M(H<sub>2</sub>O)<sub>n</sub>B<sub>12</sub>F<sub>12</sub> Structures<sup>a</sup>

<sup>a</sup>  $Z^{2-} = B_{12}F_{12}^{2-}$ ;  $\Theta = B_{12}$  centroid; Bond valence parameters taken from ref. 1. (see Table S2). <sup>b</sup> There are 6 Ba–F distances. <sup>c</sup> There are 5 Ba–F distances for Ba1 and Ba2. <sup>d</sup> The 3  $\Theta \cdots \Theta$  distances are 6.943, 7.530, and 7.720 Å.

cation	$R_{\rm MF}$	$R_{ m MO}$		effective ionic radius, Å <sup>b</sup>				
			6 coord.	8 coord.	9 coord.	11 coord.	12 coord.	
$Mg^{2+}$	1.581	1.693	0.71	0.89				
Ca <sup>2+</sup>	1.842	1.967	1.00	1.12	1.18	_	1.34	
$\mathrm{Sr}^{2+}$	2.019	2.118	1.18	1.26	1.31	—	1.44	
Ba <sup>2+</sup>	2.19	2.29	1.35	1.42	1.47	1.57	1.61	
Co <sup>2+</sup>	1.64	1.692	0.72 <sup>c</sup>					
		$(1.661)^{d}$						
Ni <sup>2+</sup>	1.599	1.654	0.690					
$Zn^{2+}$	1.62	1.704	0.740					

**Table S2.** Bond valence parameters for M–F and M–O distances<sup>a</sup> and effective ionic radii used in this work

<sup>a</sup> The bond valence contribution, *bv*, for each M–X distance is calculated using the formula  $bv(M-X) = \exp[(R_{MX} - d_{MX})/0.37]$ , where  $d_{MX}$  is the M–X distance. The  $R_{MX}$  values are from ref. 1. <sup>b</sup> From ref. 2. <sup>c</sup> High-spin d<sup>7</sup>. <sup>d</sup> Ref. 3.

$Ba(H_2O)_4(B_{12}F_{12})$	bond	distance, Å	<i>bv</i> param.	bv	bond	distance, Å	bv param.	bv
This work	Ba1-O	2.698	2.29	0.332	Ba2-O	2.685	2.29	0.344
	Ba1-O	2.783	2.29	0.264	Ba2-O	2.703	2.29	0.328
	Ba1-O	2.785	2.29	0.262	Ba2-O	2.750	2.29	0.288
	Ba1-O	2.786	2.29	0.262	Ba2-O	2.851	2.29	0.220
	Ba1-F	2.652	2.19	0.287	Ba2-F	2.741	2.19	0.226
	Ba1-F	2.657	2.19	0.283	Ba2-F	2.743	2.19	0.224
	Ba1-F	2.754	2.19	0.218	Ba2-F	2.757	2.19	0.216
	Ba1-F	2.767	2.19	0.210	Ba2-F	2.778	2.19	0.204
	Ba1-F	3.243	2.19	0.058	Ba2-F	3.116	2.19	0.082
			Σ( <i>bv</i> ) =	2.176			Σ( <i>bv</i> ) =	2.131
		Σ	(Ba-O bv) =	1.120		Σ	(Ba-O bv) =	1.179
				51.5%				55.3%

**Table S3.** Bond distances and bond valences for the SC-XRD structure of  $Ba(H_2O)_4(B_{12}F_{12})$ 

Table S4. Bond distances and bond valences for the SC-XRD structure of Ba(H<sub>2</sub>O)<sub>5</sub>(B<sub>12</sub>F<sub>12</sub>)

$Ba(H_2O)_5(B_{12}F_{12})$	bond	distance, Å	<i>bv</i> param.	bv
This work	Ba-O	2.7440	2.29	0.293
	Ba-O	2.7158	2.29	0.316
	Ba-O	2.8202	2.29	0.239
	Ba-O	2.8232	2.29	0.237
	Ba-O	2.8702	2.29	0.208
	Ba-F	2.7927	2.19	0.196
	Ba-F	3.2670	2.19	0.054
	Ba-F	2.9305	2.19	0.135
	Ba-F	3.0620	2.19	0.095
	Ba-F	3.1934	2.19	0.066
	Ba-F	2.8220	2.19	0.181
			Σ( <i>bv</i> ) =	2.021
		Σ	(Ba-O bv) =	1.293
				51.5%

$Sr(H_2O)_7(B_{12}F_{12})$	bond	distance, Å	bv param.	bv
This work	Sr-O	2.560	2.118	0.303
	Sr-O	2.650	2.118	0.237
	Sr-O	2.617	2.118	0.260
	Sr-O	2.674	2.118	0.223
	Sr-O	2.560	2.118	0.303
	Sr-O	2.617	2.118	0.260
	Sr-O	2.674	2.118	0.223
	Sr-F	2.665	2.019	0.174
	Sr-F	2.665	2.019	0.174
			$\Sigma(bv) =$	2.156
		Σ	(Sr-O bv) =	1.807
				83.8%

Table S5. Bond distances and bond valences for the SC-XRD structure of  $Sr(H_2O)_7(B_{12}F_{12})$ 

Table S6. Bond distances and bond valences for the SC-XRD structure of Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>F<sub>12</sub>)

$Ca(H_2O)_7(B_{12}F_{12})$	bond	distance, Å	bv param.	bv
This work	Ca-O	2.347	1.967	0.358
	Ca-O	2.360	1.967	0.346
	Ca-O	2.367	1.967	0.339
	Ca-O	2.389	1.967	0.319
	Ca-O	2.394	1.967	0.315
	Ca-O	2.403	1.967	0.308
	Ca-O	2.489	1.967	0.244
		Σ	(Ca-O( <i>bv</i> ) =	2.230
	ave. Ca-O =	2.393		

Mg(H <sub>2</sub> O) <sub>6</sub> (B <sub>12</sub> F <sub>12</sub> )	bond	distance, Å	<i>bv</i> param.	bv
This work	Mg-O	2.0390	1.693	0.393
	Mg-O	2.0390	1.693	0.393
	Mg-O	2.0390	1.693	0.393
	Mg-O	2.0659	1.693	0.365
	Mg-O	2.0659	1.693	0.365
	Mg-O	2.0659	1.693	0.365
		Σ(	Mg-O(bv) =	2.273
	ave. Mg-O =	2.052		

**Table S7.** Bond distances and bond valences for the SC-XRD structure of  $Mg(H_2O)_6(B_{12}F_{12})$ 

Table S8. Bond distances and bond valences for the SC-XRD structure of  $Co(H_2O)_6(B_{12}F_{12})$ 

Co(H <sub>2</sub> O) <sub>6</sub> (B <sub>12</sub> F <sub>12</sub> )	bond	distance, Å	bv param.	bv	bond	distance, Å	bv param.	bv
This work	Co-O	2.0663	1.692	0.364	Co-O	2.0663	1.661	0.334
	Co-O	2.0663	1.692	0.364	Co-O	2.0663	1.661	0.334
	Co-O	2.0663	1.692	0.364	Co-O	2.0663	1.661	0.334
	Co-O	2.0907	1.692	0.340	Co-O	2.0907	1.661	0.313
	Co-O	2.0907	1.692	0.340	Co-O	2.0907	1.661	0.313
	Co-O	2.0907	1.692	0.340	Co-O	2.0907	1.661	0.313
		Σ	(Co-O( <i>bv</i> ) =	2.112		Σ	Co-O( <i>bv</i> ) =	1.942
	ave. Co-O =	2.079						

$Ni(H_2O)_6(B_{12}F_{12})$	bond	distance, Å	bv param.	bv
This work	Ni-O	2.0290	1.654	0.363
	Ni-O	2.0290	1.654	0.363
	Ni-O	2.0290	1.654	0.363
	Ni-O	2.0515	1.654	0.342
	Ni-O	2.0515	1.654	0.342
	Ni-O	2.0515	1.654	0.342
		Σ	(Ni-O( <i>bv</i> ) =	2.113
	ave. Ni-O =	2.040		

Table S9. Bond distances and bond valences for the SC-XRD structure of Ni(H<sub>2</sub>O)<sub>6</sub>(B<sub>12</sub>F<sub>12</sub>)

**Table S10.** Bond distances and bond valences for the SC-XRD structure of  $Zn(H_2O)_6(B_{12}F_{12})$ 

$Zn(H_2O)_6(B_{12}F_{12})$	bond	distance, Å	bv param.	bv
This work	Zn-O	2.0611	1.704	0.381
	Zn-O	2.0611	1.704	0.381
	Zn-O	2.0611	1.704	0.381
	Zn-O	2.0926	1.704	0.350
	Zn-O	2.0926	1.704	0.350
	Zn-O	2.0926	1.704	0.350
		Σ	(Zn-O( <i>bv</i> ) =	2.192
	ave. Zn-O =	2.077		



**Figure S2.** The O(H)…F (2.880(6)–2.902(6) Å) and O(H)…O (3.016(6) Å) hydrogen bonding distances in the structure of  $Sr(H_2O)_7(B_{12}F_{12})$ . Note that one of the H<sub>2</sub>O molecules is hidden from view behind the Sr atom.





**Figure S3.** A hypothetical structure transformation for the putative dehydration reaction Ba(H<sub>2</sub>O)<sub>5</sub>(B<sub>12</sub>F<sub>12</sub>)  $\rightarrow$  Ba(H<sub>2</sub>O)<sub>4</sub>(B<sub>12</sub>F<sub>12</sub>) + H<sub>2</sub>O.



**Figure S4.** The tricapped square antiprism  $BaO_5F_6$  coordination sphere in  $Ba(H_2O)_5(B_{12}F_{12})$  (50% probability ellipsoids except for H atoms). The Ba–OH<sub>2</sub> distances range from 2.716(2) to 2.870(2) Å. The two "capping" Ba–F distances are 3.062(1) and 3.267(1). The other Ba–F distances range from 2.793(1) to 3.193(1) Å. The individual Ba–OH<sub>2</sub> and Ba–F distances are listed in Table S4.



**Figure S5.** The two unique monocapped square antiprism  $BaO_4F_5$  coordination spheres in  $Ba(H_2O)_4(B_{12}F_{12})$  (50% probability ellipsoids except for H atoms). The Ba–OH<sub>2</sub> and Ba–F distances are listed in Tables S1 and S3.



**Figure S6.** The structure of  $Ba(H_2O)_6(B_{12}H_{12})$ , which contains  $BaO_6H_4$  coordination spheres (ref. 4; the H atoms in H<sub>2</sub>O molecules were not located). The  $\odot \cdots \odot$  distances are 7.018 and 7.516  $\times 2$  Å (cf. 6.943, 7.530, and 7.720 Å in  $Ba(H_2O)_5(B_{12}F_{12})$ ;  $\odot = B_{12}$  centroid). The Ba–O distances in  $Ba(H_2O)_6(B_{12}H_{12})$  are 2.813 Å  $\times 4$  and 2.951 Å  $\times 2$  (uncertainties were not reported), which can be compared with the ranges of Ba–O distances in  $Ba(H_2O)_5(B_{12}F_{12})$  and  $Ba(H_2O)_4(B_{12}F_{12})$ , 2.716(2)– 2.870(2) and 2.68(1)–2.85(1) Å, respectively. The displacement of the Ba atom from the centroid of the  $[B_{12}H_{12}^{2-}]_8$  parallelpiped is 1.40 Å.



**Figure S7.** Two perpendicular views of the distorted monocapped square antiprism  $SrO_7F_2$  coordination sphere in  $Sr(H_2O)_7(B_{12}F_{12})$  (50% probability ellipsoids except for H atoms in the drawing on the left). The orientation of the drawing on the right is looking down the [010] direction (the crystallographic  $C_2$  axis). The Sr–OH<sub>2</sub> and Sr–F distances are listed in Tables S1 and S5.



**Figure S8.** Top. The offset stacks of corrugated pseudo-close-packed layers of  $Z^{2-}$  anion centroids in the structure of Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>F<sub>12</sub>). Bottom. Two perpendicular views of the monocapped triangular antiprism (monocapped octahedral) CaO<sub>7</sub> coordination sphere in Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>F<sub>12</sub>) (50% probability ellipsoids except for H atoms in the drawing on the left). The Ca–OH<sub>2</sub> distances are listed in Tables S1 and S6.



**Figure S9.** The O–H…F hydrogen bonding in Ca(H<sub>2</sub>O)<sub>7</sub>(Z). The O(H)…F distances range from 2.833(3) to 3.034(3) Å. There are no interionic O–H…O hydrogen bonds between H<sub>2</sub>O molecules in different Ca(H<sub>2</sub>O)<sub>7</sub><sup>2+</sup> complexes in this structure.



**Figure S10.** The structure of  $Sr(H_2O)_8(B_{12}H_{12})$ , which contains  $SrO_8$  coordination spheres (ref. 4; the H atoms in H<sub>2</sub>O molecules were not located). All of the  $\odot \cdots \odot$  distances are 7.614 Å (cf. 7.304 × 2 and 8.840 Å in  $Sr(H_2O)_7(B_{12}F_{12})$ ;  $\odot = B_{12}$  centroid). The Sr–O distances in  $Sr(H_2O)_8(B_{12}H_{12})$  are 2.588 Å × 2 and 2.636 Å × 6 (uncertainties were not reported), which can be compared with the Sr–O distances in  $Sr(H_2O)_7(B_{12}F_{12})$ , 2.650(4), 2.560(2) × 2, 2.617(3) × 2, and 2.674(3) × 2 Å.



**Figure S11.** The structure of Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>H<sub>12</sub>)·H<sub>2</sub>O, which contains CaO<sub>7</sub> coordination spheres (ref. 4; H atoms on the H<sub>2</sub>O molecules were not located). The  $\odot \cdots \odot$  distances within the close-packed layers are 8.456, 8.466, and 8.704 Å (cf. 7.467–8.392 Å in Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>F<sub>12</sub>);  $\odot = B_{12}$  centroid). The Ca–O distances in Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>H<sub>12</sub>)·H<sub>2</sub>O range from 2.349 to 2.446 Å (uncertainties were not reported), which can be compared with the 2.347(1)–2.489(1) Å range of Ca–O distances in Ca(H<sub>2</sub>O)<sub>7</sub>(B<sub>12</sub>F<sub>12</sub>).



**Figure S12.** Plots of M–OH<sub>2</sub> distance vs. O(H)…F or O(H)…O distance plots for the single-crystal X-ray structures of  $Mg(H_2O)_6(UO_2(EtCO_2)_3)_2$  (ref. 5),  $K_2Zn(H_2O)_6(SO_4)_2$  (ref. 6), Ni(H<sub>2</sub>O)<sub>6</sub>(VOF<sub>4</sub>(H<sub>2</sub>O)) (ref. 7), and M(H<sub>2</sub>O)<sub>6</sub>(B<sub>12</sub>F<sub>12</sub>) (this work; M = Mg, Co, Ni, Zn). The dotted lines are visual aids to highlight the trend that within a given structure the coordinated H<sub>2</sub>O molecules with shorter M–OH<sub>2</sub> bonds have shorter O(H)…F or O(H)…O hydrogen bond distances than the coordinated H<sub>2</sub>O molecules with longer M–OH<sub>2</sub> bonds. Note that there are both O–H…F and O–H…O types of hydrogen bonds in Ni(H<sub>2</sub>O)<sub>6</sub>(VOF<sub>4</sub>(H<sub>2</sub>O)).

compound	M–O, Å	O(H)…X, Å	reference	
$Mg(H_2O)_6(B_{12}F_{12})^b$	2.0390(11) × 3, 2.0659(11) × 3; ave. 2.053	2.723(2), 2.749(2), 2.904(2), 2.914(2) <sup>f</sup>	this work	
$Mg(H_2O)_6(B_{12}H_{12})^{c,d}$	$2.094 \times 2, 2.100 \times 2,$ $2.146(5) \times 2;$ ave. 2.113	$\times 2, 2.100 \times 2,$ — ) $\times 2;$ ave. 2.113 —		
$Mg(H_2O)_6(B_{12}H_{12})\cdot 6H_2O^b$	2.045(2) × 6	8		
$Mg(H_2O)_6(B_{10}H_{10})\cdot 4H_2O^b$	Mg1: $2.019(1) \times 2$ , $2.056(1) \times 2$ , $2.019(1) \times 2$ ; Mg2: $2.043(1) \times 2$ , $2.050(1) \times 2$ , $2.056(1) \times 2$ ; ave. $2.045$	—	9	
Mg(H <sub>2</sub> O) <sub>6</sub> (SiF <sub>6</sub> ) <sup>b</sup>	2.0480(8), 2.0550(7), 2.0571(8); ave. 2.053	2.792(1)-2.899(1) <sup>f</sup>	10	
$\overline{Mg(H_2O)_6(B(CN)_4)_2}^b$	2.0373(9)-2.0910(10); ave. 2.061	2.821(2)-3.040(2) <sup>h</sup>	11	
$Mg(H_2O)_6(UO_2(EtCO_2)_3)_2^b$	Mg1: 2.034(2) × 6; Mg2: 2.045(2) × 2, 2.059(2) × 2, 2.067(2) × 2; ave. 2.046	2.688(4)-2.921(4) <sup>g</sup>	5	
$Mg(H_2O)_6(SO_4)^b$	Mg1: 2.0385(15) × 2, 2.0485(15) × 2, 2.0601(15) × 2; Mg2: 2.0409(16) × 2, 2.0491(14) × 2, 2.0804(16) × 2; ave. 2.053	2.685(2)–2.874(2) <sup>g</sup>	12	
Mg(H <sub>2</sub> O) <sub>6</sub> (SO <sub>3</sub> ) <sup>e</sup>	2.0552(7) × 3, 2.1063(7) × 3; ave. 2.081	2.675(3)-2.835(3) <sup>g</sup>	13	
$Co(H_2O)_6(B_{12}F_{12})^b$	2.0663(4) × 3, 2.0907(4) × 3; ave. 2.079	2.734(1), 2.739(1), 2.886(1), 2.919(1) <sup>f</sup>	this work	
$Co(H_2O)_6(SnF_6)^b$	2.077(5) × 6	2.727(5), 2. 755(4) <sup>f</sup>	14	

Table S11. Comparisons of M–O and O(H)…X distances in some metal salt hexahydrates

compound	M–O, Å	O(H)···X, Å	reference
$(NH_2Me_2)_2Co(H_2O)_6(SO_4)_2\cdot 2H_2O^b$	2.069(4) × 2, 2.081(4) × 2, 2.116(4) × 2; ave. 2.089	2.724(6)–2.975(7) <sup>g</sup>	15
Cs <sub>2</sub> (Co(H <sub>2</sub> O) <sub>6</sub> ) <sub>3</sub> (HPO <sub>3</sub> ) <sub>4</sub> <sup>b</sup>	Co1: $2.076(5) \times 2$ , $2.078(3) \times 4$ ; Co2: $2.072(4) \times 2$ , $2.081(5)$ , $2.104(3) \times 2$ , $2.106(5)$ ; ave. $2.084$	2.680(9)–2.685(9) <sup>g</sup>	16
Ni(H <sub>2</sub> O) <sub>6</sub> (B <sub>12</sub> F <sub>12</sub> ) <sup>b</sup>	2.0290(7) × 3, 2.0515(7) × 3; ave. 2.040	2.732(1), 2.735(1), 2.859(1), 2.919(1) <sup>f</sup>	this work
$\overline{Ni(H_2O)_6(B_{12}H_{12})\cdot 6H_2O^b}$	$2.026  imes 6^{i}$		17
Ni(H <sub>2</sub> O) <sub>6</sub> (SnF <sub>6</sub> ) <sup>b</sup>	2.045(3) × 6	2.730(3), 2.750(3) <sup>f</sup>	14
Ni(H <sub>2</sub> O) <sub>6</sub> (TiF <sub>6</sub> ) <sup>b</sup>	2.044(5) × 6	2.709(7), 2.760(7) <sup>f</sup>	18
$Ni(H_2O)_6(VOF_4(H_2O))^b$	2.0097(9) × 2, 2.0321(9) × 2, 2.0866(9) × 2; ave. 2.043	$2.615(1), 2.641(1), 2.664(1);^{f}$ $2.775(1), 2.863(1)^{g}$	7
$Zn(H_2O)_6(B_{12}F_{12})^b$	2.0611(4) × 3, 2.0926(4) × 3; ave. 2.077	2.733(1), 2.734(1), 2.869(1), 2.894(1) <sup>f</sup>	this work
$Zn(H_2O)_6(B_{12}H_{12}) \cdot 6H_2O^b \qquad Zn1: 2.050(7) \times 3, 2.089(7) \\Zn2: 2.068(2) \times 6; \text{ ave. } 2.068$			19
$(Zn(H_2O)_6)_2(ZrF_8)^b$	$2O_{6}_{2}(ZrF_{8})^{b}$ 2.0367(6)-2.1638(6); ave. 2.093		20
$\overline{K_2Zn(H_2O)_6(SO_4)_2}^b$	2.031(1) × 2, 2.123(2) × 2, 2.131(1) × 2; ave. 2.095	2.651(1)–2.806(1) <sup>g</sup>	6

Table S11. (continued) Comparisons of M–O and O(H)…X distances in some metal salt hexahydrates

# Table S11. (continued) Comparisons of M–O and O(H)…X distances in some metal salt hexahydrates

<sup>a</sup> All structures at low temperature ( $\leq 150$  K) unless otherwise indicated. <sup>b</sup> Single-crystal X-ray diffraction. <sup>c</sup> Powder X-ray diffraction. <sup>d</sup> T = 295 K. <sup>e</sup> Single-crystal neutron diffraction. <sup>f</sup> X = F. <sup>g</sup> X = O. <sup>h</sup> X = N. <sup>i</sup> Standard uncertainties for bond distances were not listed in this paper.



**Figure S13.** Part of the structures of  $(Zn(H_2O)_6)_2(ZrF_8)$ , showing the network of O–H···F and O–H···O hydrogen bonds (top: ref. 20) and  $Zn(H_2O)_6(B_{12}F_{12})$  (bottom; this work). The Zn–O distances in  $(Zn(H_2O)_6)_2(ZrF_8)$  range from 2.0367(6) to 2.1638(6) Å (cf.  $Zn(H_2O)_6(B_{12}F_{12})$ , 2.0611(4) and 2.0926(4) Å). Some of the O(H)···F hydrogen bond distances in  $(Zn(H_2O)_6)_2(ZrF_8)$ , which range from 2.580(1) to 2.973(1) Å, are bifurcated (cf.  $Zn(H_2O)_6(B_{12}F_{12})$ , 2.733(1)–2.894(1) Å, none of which are bifurcated). The O(H)···O distances in  $(Zn(H_2O)_6)_2(ZrF_8)$  range from 2.852(1) to 2.889(1) Å. There are no O–H···O hydrogen bonds in  $Zn(H_2O)_6(B_{12}F_{12})$ .



**Figure S14.** The structure of Ni(H<sub>2</sub>O)<sub>6</sub>(TiF<sub>6</sub>) (left; the H atoms were not located; ref. 18). This is an example of the Co(H<sub>2</sub>O)<sub>6</sub>(SiF<sub>6</sub>) structure type (space group  $R\overline{3}$ ). The unique Ni–O and Ti–F distances are 2.044(5) and 1.791(5) Å, respectively. The unique Ti···Ti distance is 6.372 Å and the unique acute Ti···Ti···Ti angle is 83.8°. The two O(H)···F hydrogen bond distances for each of the six coordinated H<sub>2</sub>O molecules are 2.709(7) and 2.760(7) Å, and the F···O···F angle is 115.0°. For comparison, in Ni(H<sub>2</sub>O)<sub>6</sub>(B<sub>12</sub>F<sub>12</sub>) (right) the Ni–O distances are 2.0290(7) and 2.0515(7) Å and the O(H)···F hydrogen bond distances are 2.732(1), 2.735(1), 2.859(1), and 2.910(1) Å.



**Figure S15.** The low-temperature structure of Mg(H<sub>2</sub>O)<sub>6</sub>(SiF<sub>6</sub>) (left; ref. 10; space group  $P2_1/c$ ). The Mg–O1, Mg–O2, and Mg–O3 distances are 2.0571(8), 2.0550(7), and 2.0480(8) Å, respectively. The Si···Si distances are  $6.354 \times 2$  and 6.790 Å, and the acute Si···Si···Si angles are  $83.5 \times 2$  and  $83.3^{\circ}$ . The six unique O(H)···F distances are 2.792(1), 2.808(1), 2.815(1), 2.822(1), 2.832(1), and 2.899(1) Å. (Note: these are the correct O(H)···F distances in this structure, generated using the CIF deposited with the ICSD, but they are different than the values listed in Table 3 in ref. 10, which range from 2.763(1) to 2.798(1) Å). For comparison, in Mg(H<sub>2</sub>O)<sub>6</sub>(B<sub>12</sub>F<sub>12</sub>) (right) the Mg–O distances are 2.0390(11) and 2.0659(11) Å and the O(H)···F hydrogen bond distances are 2.723(2), 2.749(2), 2.904(2), and 2.914(2) Å (the crystallographic 3-fold axis is indicated with triangles, and only 4 of the anions that make up the  $(B_{12}F_{12}^{2-})_8$  parallelpiped in which the Mg(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> cation is centered are shown for clarity).



**Figure S16.** Thermogravimetric trace for a 13.687 mg sample of  $Co(H_2O)_6(Z)$ . The two temperature ramps were 2.0 °C min<sup>-1</sup> (15–175 min) and 1.0 °C min<sup>-1</sup> (175–270 min;  $Z^{2-} = B_{12}F_{12}^{2-}$ ). The experimental mass ratio 0.8605 (11.778 mg/13.687 mg) and the  $Co(H_2O)_2(Z)/Co(H_2O)_6(Z)$  molar mass ratio 0.8627 ((452.677 g mol<sup>-1</sup>)/524.738 g mol<sup>-1</sup>) are the same to within the uncertainty of the experiment. Attempts to remove the last two coordinated H<sub>2</sub>O molecules without the thermal decomposition of the  $B_{12}F_{12}^{2-}$  anion were not successful for this compound or for the Mg, Ni, and Zn homologues.



**Figure S17.** FTIR spectra of Mg(H<sub>2</sub>O)<sub>6</sub>(BrO<sub>3</sub>)<sub>2</sub> (ref. 21), Al(H<sub>2</sub>O)<sub>6</sub>F<sub>3</sub> (ref. 22), the Tutton salt  $K_2Zn(H_2O)_6(SO_4)_2$  (ref. 23), and  $(NH_4)_2M(H_2O)_6(SO_4)_2$  (ref. 24; M = 50:50 Co:Ni). The v(OH) bands at 3000–3300 cm<sup>-1</sup> are significantly redshifted relative to  $v_{asym}$ (OH) and  $v_{sym}$ (OH) for  $H_2O(g)$  (3756 and 3655 cm<sup>-1</sup>, respectively<sup>25</sup>). The first three figures were adapted from figures in the respective references. The authors thank Prof. Santunu Ghosh for kindly supplying a digital data file with which the spectrum of (NH<sub>4</sub>)<sub>2</sub>M(H<sub>2</sub>O)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub> was prepared.



**Figure S18.** ATR-FTIR spectra of  $M(H_2O)_6(B_{12}F_{12})$  (M = Mg, Co, Ni, Zn). The samples were evaporated on the ZnSe ATR crystal and collected using 2 cm<sup>-1</sup> resolution. The small peaks at ca. 3250 cm<sup>-1</sup> marked with asterisks are assigned to  $2\delta(HOH)$ .<sup>25</sup> Expansions of the v(OH) regions are shown in Figure S19.



**Figure S19.** The v(OH) regions of ATR-FTIR spectra of microcrystalline  $M(H_2O)_6(B_{12}F_{12})$  (M = Mg, Co, Ni, Zn). The samples were evaporated from aqueous solutions on the ZnSe ATR crystal. The small peaks at ca. 3250 cm<sup>-1</sup> are assigned to  $2\delta(HOH)$ .



**Figure S20.** Expansions of the v(OH) regions of ATR-FTIR spectra of  $M(H_2O)_6(Z)$  (this work; M = Mg, Co, Ni, Zn). The samples were evaporated on the ZnSe ATR crystal from aqueous solutions.



**Figure S21.** Top: Experimental ATR-FTIR spectrum of  $Co(H_2O)_6(B_{12}F_{12})$  (sample evaporated on the ZnSe ATR crystal from aqueous solution). Bottom: Deconvolution of a portion of the experimental spectrum (black trace) into four Lorentzian peaks. The positions of the four blue fitted peaks are (left to right) 3617, 3580, 3546, and 3524 cm<sup>-1</sup>. The full-widths at half-max (FWHM) are (left to right) 19.4(2), 26.6(2), 13.8(3), and 16.0(2) cm<sup>-1</sup>. The relative areas are (left to right) 2.0, 3.7, 1.0, 2.1. The resultant of the four fitted peaks is the red trace. Note that the wavenumber axes are scaled equally and are aligned.



**Figure S22.** Room-temperature ATR-FTIR spectra of microcrystalline samples of  $Mg(H_2O)_6(B_{12}F_{12})$  and  $Mg(D_2O)_6(B_{12}F_{12})$  evaporated on the ZnSe ATR crystal from H<sub>2</sub>O or D<sub>2</sub>O solutions, respectively. The two  $\delta$ (HOH) angle-deformation bands at 1640 and 1624 cm<sup>-1</sup> and the two  $\delta$ (DOD) bands at 1206 and 1196 cm<sup>-1</sup> can be compared with the corresponding bands at 1595 and 1179 cm<sup>-1</sup> for monomeric H<sub>2</sub>O(*g*) and D<sub>2</sub>O(*g*), respectively.<sup>25</sup>



**Figure S23.** Experimental ATR-FTIR spectra (black traces) of  $Mg(H_2O)_6(B_{12}F_{12})$  (top) and  $Mg(D_2O)_6(B_{12}F_{12})$  (bottom) and their deconvolution into four Lorentzian peaks (blue). The fitted peak positions and full-widths at half-max are shown. The resultants of the four fitted peaks are the red traces. Note that the wavenumber axes both span 200 cm<sup>-1</sup>. Both samples were evaporated on the ZnSe ATR crystal from H<sub>2</sub>O or D<sub>2</sub>O solutions.



**Figure S24.** The v(OD) regions of ATR-FTIR spectra of Mg(HOD)(H<sub>2</sub>O)<sub>5</sub>(B<sub>12</sub>F<sub>12</sub>) (top) and Co(HOD)(H<sub>2</sub>O)<sub>5</sub>(B<sub>12</sub>F<sub>12</sub>) (bottom). Both samples were prepared by evaporation to dryness of 90:10 (v:v) H<sub>2</sub>O:D<sub>2</sub>O solutions on the ZnSe ATR crystal. On average, ca. 15% of all of the hexaaqua 2+ complex cations will have one HOD ligand and five H<sub>2</sub>O ligands, ca. 2% will have two HOD ligands and four H<sub>2</sub>O ligands, and ca. 1% will have one D<sub>2</sub>O ligand and five H<sub>2</sub>O ligands. A negligible percentage will have more than two HOD ligands, and a D<sub>2</sub>O ligand simultaneously, or more than one D<sub>2</sub>O ligand. However, since H<sub>2</sub>O evaporates faster than D<sub>2</sub>O,<sup>26,27</sup> the actual percentages in the dried samples may be higher than the above-mentioned values.

compd	v <sub>asym</sub> (OH)	v <sub>sym</sub> (OH)	$v_{asym}(OD)$	$v_{sym}(OD)$	v(OH)/v(OD) ratios	ref.
$H_2O(g)$	3756	3655			3756/2789 = 1.347	25
$D_2O(g)$			2789	2666	3655/2666 = 1.371	25
H <sub>2</sub> O(Ar, 11 K)	3734	3638			3734/2771 = 1.348	28
D <sub>2</sub> O(Ar, 11 K)			2771	2658	3638/2658 = 1.369	28
$Mg(H_2O)_6(Z)(s)$	3628, 3596	3561, 3544			3628/2699 = 1.344;	this work
					3596/2674 = 1.345	this work
$Mg(D_2O)_6(Z)(s)$			2699, 2674	2604, 2593	3561/2604 = 1.368;	this work
					3544/2593 = 1.367	this work
$Co(H_2O)_6(Z)(s)$	3617, 3581	3544, 3524			3617/2690 = 1.345;	this work
					3581/2663 = 1.345	this work
$Co(D_2O)_6(Z)(s)$			2690, 2663	2593, 2580	3544/2593 = 1.367;	this work
					3524/2580 = 1.366	this work

<sup>a</sup> All  $\nu(OH)$  and  $\nu(OD)$  values in cm<sup>-1</sup>. The  $\nu_{asym}$  and  $\nu_{sym}$  assignments for the  $M(H_2O)_6(Z)$  and  $M(D_2O)_6(Z)$  compounds are based on the peak ratios.



**Figure S25.** Comparison of ATR-FTIR spectra of microcrystalline samples of  $Ni(H_2O)_6(B_{12}F_{12})$  (top; this work) and  $Ni(H_2O)_6(VOF_4(H_2O))$  (bottom; ref. 7; the peaks marked with asterisks are artifacts). The authors thank Drs. Martin Donakowski and Romain Gautier for kindly supplying a digital data file with which the spectrum of  $Ni(H_2O)_6(VOF_4(H_2O))$  shown in this figure was prepared (it was shown in %transmittance mode in ref. 7).



**Figure S26.** Comparison of room temperature FTIR spectra of  $Mg(H_2O)_6(UO_2(EtCO_2)_3)_2$  (top; ref. 5; KBr pellet) and microcrystalline  $Mg(H_2O)_6(B_{12}F_{12})$  (bottom; this work; sample prepared by evaporation of an aqueous solution on the ZnSe ATR crystal). The spectra are scaled equally (1000 cm<sup>-1</sup>) but are intentially offset to highlight the larger redshift of the v(OH) bands in the spectrum of  $Mg(H_2O)_6(UO_2(EtCO_2)_3)_2$ . The authors thank Prof. Viktor Serezhkin for kindly supplying a digital data file with which the spectrum of  $Mg(H_2O)_6(UO_2(EtCO_2)_3)_2$  shown in this figure was prepared (the spectrum in the supporting information for ref. 5 was plotted in %transmittance mode).



**Figure S27.** Comparison of room temperature FTIR spectra of microcrystalline  $Mg(H_2O)_6(B_{12}F_{12})$  (top; this work; sample prepared by evaporation on the ZnSe ATR crystal of an aqueous solution),  $Mg(H_2O)_6(BF_4)_2$  (middle; ref. 29), and  $Mg(H_2O)_6(B(CN)_4)_2$  (bottom; ref. 11). Note that the wavenumber axes are scaled equally and are aligned. The authors thank Dr. Joanna Hetmańczyk and Prof. Eduard Bernhardt, respectively, for kindly supplying digital data files with which the spectra of  $Mg(H_2O)_6(BF_4)_2$  and  $Mg(H_2O)_6(B(CN)_4)_2$ , respectively, shown in this figure were prepared.



Figure S28. The v(OH) regions of ATR-FTIR and transmission FTIR spectra of crystalline  $Ni(H_2O)_6(B_{12}F_{12})$ .



**Figure S29.** Comparison of FTIR spectra of  $Mg(H_2O)_6(BF_4)_2$  at 295 K and 8.5 K (top and bottom panels; ref. 29; Nujol mull between KBr windows) and microcrystalline  $Mg(H_2O)_6(B_{12}F_{12})$  at 294(1) K (middle panel; this work; sample evaporated from an aqueous solution on the ZnSe ATR crystal). The authors thank Dr. Joanna Hetmańczyk for kindly supplying digital data files with which the spectra of  $Mg(H_2O)_6(BF_4)_2$  shown in this figure were prepared.



**Figure S30.** FTIR spectra of  $Mg(H_2O)_6(BF_4)_2$  at 295 K and 8.5 K (ref. 29; Nujol mull between KBr windows). The authors thank Dr. Joanna Hetmańczyk for kindly supplying digital data files with which the spectra shown in this figure were prepared.



**Figure S31.** Comparison of FTIR spectra of  $Mg(H_2O)_6(B_{12}F_{12})$  at 294(1) K (top; this work) and  $Mg(H_2O)_6(SiF_6)_2$  at 77 K (bottom; ref. 30). Note that the wavenumber axes are scaled equally and are aligned.



**Figure S32.** ATR-FTIR spectrum of microcrystalline  $Co(H_2O)_6(B_{12}F_{12})$  (top; this work; sample prepared by evaporation of an aqueous solution on the ZnSe ATR crystal), IR photodissociation spectrum of the gas-phase cation  $[Ar-Na(H_2O)_2]^+$  (middle; ref. 31), and FTIR spectrum of monomeric H<sub>2</sub>O absorbed in a thin film of poly(vinylidene fluoride) (bottom; ref. 32). Note that the wavenumber axes are scaled equally and are aligned.



**Figure S33.** ATR-FTIR spectrum of microcrystalline  $Co(H_2O)_6(B_{12}F_{12})$  (top; this work) and  $H_2O$  in a frozen N<sub>2</sub> matrix at 11 K (bottom; ref. 28). In the bottom spectrum only the bands labelled as  $v_{asym}(OH)$  and  $v_{sym}(OH)$  are due to monomeric H<sub>2</sub>O molecules. The other bands are due to dimers and higher oligomers. Note that the wavenumber axes are scaled equally and are aligned.



**Figure S34.** ATR-FTIR spectra of  $Co(D_2O)_6(Z)$  (prepared by evaporation of a D<sub>2</sub>O solution on the ATR crystal) undergoing D<sub>2</sub>O/H<sub>2</sub>O exchange at 50 °C under 10 and 17 torr H<sub>2</sub>O(*g*).



**Figure S35.** Comparison of the room temperature FTIR spectra of microcrystalline  $Sr(H_2O)_n(B_{12}F_{12})$  (top; this work; sample prepared by evaporation from aqueous solution on the ZnSe ATR crystal) and  $Sr(H_2O)_3(C_8H_4O_4)_2$  (bottom; ref. 33;  $C_8H_4O_4^{2^-}$  = terephthalate(2–)). The spectrum of  $Sr(H_2O)_3(C_8H_4O_4)_2$  was adapted from a figure in the miscellaneous information for ref. 33.



(figure caption on the next page)

**Figure S36.** (Previous page) ATR-FTIR spectra of a microcrystalline  $Ca(H_2O)_n(Z)$  dried from aqueous solution on the ATR crystal under various conditions of temperature and humidity. The compositions indicated for the sample in spectrum 8 (Ca(H<sub>2</sub>O)<sub>4</sub>(Z)) and in spectrum 9 (Ca(H<sub>2</sub>O)<sub>6</sub>(Z)) are commensurate with the 50 °C gravimetric experiment shown in Figure 6 in the main text. The compositions indicated for the samples in spectra 1, 2, 3, and 7 are based on the similarity of those spectra with either spectrum 8 or 9. These spectra show that Ca(H<sub>2</sub>O)<sub>4</sub>(Z) is hydrated to Ca(H<sub>2</sub>O)<sub>6</sub>(Z) at 22 °C under 6 torr H<sub>2</sub>O(*g*) in only 7 min, and is dehydrated back to Ca(H<sub>2</sub>O)<sub>4</sub>(Z) at 22 °C under dry N<sub>2</sub> in about 1 h. This experiment demonstrates room-temperature latent porosity for Ca(H<sub>2</sub>O)<sub>4</sub>(Z). Comparison of the spectra of Ca(H<sub>2</sub>O)<sub>6</sub>(Z) (spectra 3 and 9) with the spectrum of Mg(H<sub>2</sub>O)<sub>6</sub>(Z) suggests that (i) the Ca(H<sub>2</sub>O)<sub>6</sub>(Z) and (ii) none of the O(H)…F hydrogen bond distances in Ca(H<sub>2</sub>O)<sub>6</sub>(Z) are as short as the 2.72 and 2.75 O(H)…F hydrogen bond distances in Mg(H<sub>2</sub>O)<sub>6</sub>(Z). Note that the range of O(H)…F distances in Ca(H<sub>2</sub>O)<sub>7</sub>(Z) is 2.83–3.03 Å.



**Figure S37.** The Ca(H<sub>2</sub>O)<sub>7</sub><sup>2+</sup> coordination sphere in Ca(H<sub>2</sub>O)<sub>7</sub>(Z), showing the long Ca–OH<sub>2</sub> bond (2.489(1) Å) in relation to an incipient Ca(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> complex in the Ca(H<sub>2</sub>O)<sub>6</sub>(Z) compound formed at 22 °C under 6 or 8 torr H<sub>2</sub>O(*g*) or at 50 °C under 17 or 18 torr H<sub>2</sub>O(*g*).



**Figure S38.** Comparison of the FTIR spectra of microcrystalline  $Ba(H_2O)_8(B_{12}F_{12})$  at 25 °C in  $N_2/15(1)$  torr  $H_2O(g)$  (top; spectrum 1),  $Ba(H_2O)_n(B_{12}F_{12})$  at 25 °C in dry  $N_2$  (top right and middle left; spectra 2 and 3; n = 4-5),  $Ba(H_2O)(B_{12}F_{12})$  at 80 °C in dry  $N_2$  (middle right; spectrum 4), and  $Ba(H_2O)_3(ClO_4)_2(s)$  at various temperatures (bottom set of spectra; ref. 34. The composition  $Ba(H_2O)_8(B_{12}F_{12})$  in spectrum 1 is based on the 25 °C gravimetric experiment shown in Figure 5 in the main text. The four relatively sharp peaks in spectrum 1 are at (left to right) 3626, 3590, 3570, and 3553 cm<sup>-1</sup>. The bottom set of spectra were adapted from a figure in the supporting information for ref. 34.



**Figure S39.** Deconvolution of the experimental spectrum of  $Ba(H_2O)(B_{12}F_{12})$  at 80 °C in dry N<sub>2</sub> (black trace; see Figure S38) into two Lorentzian peaks. The positions of the two blue fitted peaks are (left to right) 3650 and 3558 cm<sup>-1</sup>. The full widths at half-max (FWHM) are (left to right) 8.9(8) and 23(1) cm<sup>-1</sup>. The resultant of the two fitted peaks is the red trace, which almost exactly superimposes most of the two individual blue peaks. The ratio of integrated intensities of the fitted peaks is 3:1. The peak positions in the experimental spectrum are 3652 and 3557 cm<sup>-1</sup>.



**Figure S40.** FTIR spectra of  $Al_3(H_2O)_7(PO_4)_2F_3$  and partially deuterated  $Al_3(D_2O)_7(PO_4)_2F_3$  (ref. 35). This figure was adapted from Figure 4 in ref. 35.



**Figure S41.** Plot of the longest and shortest M–OH<sub>2</sub> distances in  $M_2(H_2O)_n(Z)$  and  $M(H_2O)_m(Z)$  compounds and whether or not they exhibit latent porosity at ambient temperature. The error bars shown are three times the standard uncertainties for the distances in the respective single-crystal X-ray structures and are smaller than the diamond-shaped data points. The alkali metal salt hydrates are  $Li_2(H_2O)_4(Z)$ ,<sup>36</sup>  $Na_2(H_2O)_3(Z)$ ,<sup>36</sup>  $K(H_2O)_2(Z)$ ,<sup>37</sup>  $Rb(H_2O)_2(Z)$ ,<sup>36</sup> and  $Cs(H_2O)(Z)$ .<sup>38</sup> The divalent metal salt hydrate distances are from this work. The lines are visual aids and have no other significance.

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