Supporting Information for:

Polymorphisms in M2+AlF5(H2O)7 (M2+ = Fe2+, Co2+, or Ni2+): Syntheses, Crystal Structures, and Characterization of New Mixed Metal Fluoride Hydrates

Jun Min Seo [1], Hongil Jo [2], Myung Ho Choi [2], Kang Min Ok [2], Hong Young Chang [3] and Sun Woo Kim [1,*]

[1] Department of Chemistry Education, Chosun University, Gwangju 61452, Republic of Korea; rn298@naver.com
[2] Department of Chemistry, Sogang University, Seoul 04107, Republic of Korea; hongil.jo@liverpool.ac.uk (H.J.); narciachoi@gmail.com (M.-H.C.); kmok@sogang.ac.kr (K.M.O.)
[3] Department of Computer, Mathematical and Physical Sciences (CMPS), Sul Ross State University, Alpine, TX 79832, USA; hong.young.chang@sulross.edu
* Correspondence: swookim@chosun.ac.kr

Table S1. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) at RT.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) at 100 K.

Table S3. Bond valence calculation for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) at RT and 100 K, respectively.

Table S4. Out-of-center distortion of octahedral structures in $[Fe(H_2O)_6]^{2+}$ at RT and 100 K temperature.

Figure S1. Experimental and Calculated X-ray powder diffraction patterns for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}): (a) $FeAlF_5(H_2O)_7$, (b) $CoAlF_5(H_2O)_7$ and (c) $NiAlF_5(H_2O)$.

Figure S2. ORTEP representation (50% probability ellipsoid) for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}).

Figure S3. FT-IR Spectra of $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}): (a) $FeAlF_5(H_2O)_7$, (b) $CoAlF_5(H_2O)_7$ and (c) $NiAlF_5(H_2O)_7$.

Figure S4. Powder X-ray diffraction pattern for final residuals after TGA experiment: (a) $FeAlF_5(H_2O)_7$, (b) $CoAlF_5(H_2O)_7$ and (c) $NiAlF_5(H_2O)_7$.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) at RT.

$FeAlF_5(H_2O)_7$					
atom	sof	x	y	z	$U_{(iso)}$*/$U_{(eq)}$
Fe(1)	1	0.5	0.5	0.5	0.0160(3)
Fe(2)	1	0.5	0	0.5	0.0159(3)
Al(1)	1	0.25	0.25	0	0.0136(3)
O(1)	0.5	0.3789(3)	0.3260(3)	-0.0670(5)	0.0625(11)
H(1A)	0.5	0.464(4)	0.324(8)	-0.004(17)	0.094*
H(1B)	0.5	0.374(10)	0.344(10)	-0.208(6)	0.094*
O(2)	1	0.5	0.3484(3)	0.5	0.0524(15)
H(2)	1	0.446(4)	0.310(3)	0.409(6)	0.058(16)*
O(3)	1	0.3670(4)	0.5	0.2236(6)	0.0291(9)
H(3)	1	0.331(4)	0.4451(12)	0.157(6)	0.044*
O(4)	1	0.3575(4)	0.5	0.6842(6)	0.0367(10)
H(4)	1	0.353(5)	0.5560(13)	0.763(6)	0.055*
O(5)	1	0.5758(4)	0	0.8170(6)	0.0308(9)
H(5)	1	0.603(4)	0.0545(13)	0.899(5)	0.046*
O(6)	1	0.3667(3)	0.1054(2)	0.5494(4)	0.0301(7)
H(6A)	1	0.361(4)	0.125(3)	0.684(4)	0.045*
H(6B)	1	0.352(4)	0.159(2)	0.461(5)	0.045*
F(1)	0.5	0.3789(3)	0.3260(3)	-0.0670(5)	0.0625(11)
F(2)	1	0.3219(3)	0.1412(2)	-0.0669(4)	0.0534(8)
F(3)	1	0.3297(2)	0.24131(17)	0.2634(3)	0.0340(6)

$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

$CoAlF_5(H_2O)_7$					
atom	sof	x	y	z	$U_{(iso)}^*/U_{(eq)}$
Co(1)	1	0.5	0.5	0.5	0.0161(3)
Co(2)	1	0.5	0	0.5	0.0161(3)
Al(1)	1	0.25	0.25	0	0.0170(3)
O(1)	0.5	0.3778(3)	0.3268(3)	-0.0684(5)	0.0661(11)
H(1A)	0.5	0.462(4)	0.318(9)	0.000(17)	0.099*
H(1B)	0.5	0.381(10)	0.352(9)	-0.203(9)	0.099*
O(2)	1	0.5	0.3516(3)	0.5	0.0521(13)
H(2)	1	0.445(3)	0.313(2)	0.410(5)	0.050(14)*
O(3)	1	0.3675(3)	0.5	0.2250(6)	0.0296(8)
H(3)	1	0.329(3)	0.4445(12)	0.166(6)	0.044*
O(4)	1	0.3572(3)	0.5	0.6809(6)	0.0375(10)
H(4)	1	0.347(5)	0.5557(13)	0.763(6)	0.056*
O(5)	1	0.5751(4)	0	0.8141(5)	0.0313(8)
H(5)	1	0.597(4)	0.0549(12)	0.899(5)	0.047*
O(6)	1	0.3710(3)	0.10547(19)	0.5511(4)	0.0303(6)
H(6A)	1	0.368(4)	0.127(3)	0.686(3)	0.045*
H(6B)	1	0.355(4)	0.159(2)	0.464(5)	0.045*
F(1)	0.5	0.3778(3)	0.3268(3)	-0.0684(5)	0.0661(11)
F(2)	1	0.3238(3)	0.1418(2)	-0.0645(4)	0.0588(9)
F(3)	1	0.3306(2)	0.24300(15)	0.2649(3)	0.0351(6)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

$NiAlF_5(H_2O)_7$					
atom	sof	x	y	z	$U_{(iso)}^*/U_{(eq)}$
Ni(1)	1	0.5	0.5	0.5	0.0146(2)
Ni(2)	1	0.5	0	0.5	0.0148(2)
Al(1)	1	0.25	0.25	0	0.0152(3)
O(1)	0.5	0.3783(3)	0.3274(3)	-0.0694(6)	0.0730(13)
H(1A)	0.5	0.319(9)	0.374(8)	-0.05(2)	0.109*
H(1B)	0.5	0.458(5)	0.337(9)	0.01(2)	0.109*
O(2)	1	0.5	0.3526(3)	0.5	0.0452(13)
H(2)	1	0.443(3)	0.315(3)	0.411(6)	0.056(16)*
O(3)	1	0.3709(4)	0.5	0.2288(6)	0.0270(8)
H(3)	1	0.336(4)	0.4449(12)	0.161(6)	0.041*
O(4)	1	0.3576(3)	0.5	0.6791(6)	0.0299(9)
H(4)	1	0.358(5)	0.5560(13)	0.764(5)	0.045*
O(5)	1	0.5728(4)	0	0.8108(6)	0.0294(9)
H(5)	1	0.598(4)	0.0553(13)	0.891(5)	0.044*
O(6)	1	0.3704(3)	0.1037(2)	0.5495(4)	0.0278(6)
H(6A)	1	0.369(4)	0.126(3)	0.685(4)	0.042*
H(6B)	1	0.356(4)	0.158(2)	0.460(5)	0.042*
F(1)	0.5	0.3783(3)	0.3274(3)	-0.0694(6)	0.0730(13)
F(2)	1	0.3258(4)	0.1418(2)	-0.0634(4)	0.0670(11)
F(3)	1	0.3299(2)	0.24329(17)	0.2659(3)	0.0344(6)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) at 100 K.

$FeAlF_5(H_2O)_7$					
atom	sof	x	y	z	$U_{(iso)}$*/$U_{(eq)}$
Fe(1)	1	0.5	0.5	0.5	0.0108(2)
Fe(2)	1	0.5	0	1	0.0105(2)
Al(1)	1	0	0	0.5	0.0093(4)
Al(2)	1	1	0.5	1	0.0082(4)
O(1)	0.5	-0.0391(6)	0.2182(5)	0.5276(6)	0.0310(11)
H(1A)	0.5	0.032(18)	0.282(17)	0.626(10)	0.047*
H(1B)	0.5	-0.180(8)	0.239(18)	0.525(16)	0.047*
O(2)	0.5	0.8985(6)	0.5732(5)	1.1921(4)	0.0200(8)
H(2A)	0.5	0.819(19)	0.507(13)	1.243(13)	0.03*
H(2B)	0.5	0.97(2)	0.658(11)	1.276(10)	0.03*
O(3)	1	0.5308(8)	0.3243(5)	0.6254(5)	0.0292(12)
H(3A)	1	0.454(11)	0.398(6)	0.686(9)	0.044*
H(3B)	1	0.449(10)	0.225(4)	0.619(9)	0.044*
O(4)	1	0.2201(5)	0.3721(5)	0.3692(5)	0.0172(7)
H(4A)	1	0.115(7)	0.324(8)	0.414(7)	0.026*
H(4B)	1	0.164(9)	0.381(8)	0.268(4)	0.026*
O(5)	1	0.3122(6)	0.6270(5)	0.6596(5)	0.0210(9)
H(5A)	1	0.255(11)	0.709(6)	0.623(7)	0.032*
H(5B)	1	0.392(10)	0.669(7)	0.760(4)	0.032*
O(6)	1	0.1827(5)	-0.0693(5)	0.9190(5)	0.0173(8)
H(6A)	1	0.108(9)	-0.021(7)	0.849(7)	0.026*
H(6B)	1	0.091(8)	-0.148(6)	0.941(8)	0.026*
O(7)	1	0.5542(6)	-0.0354(5)	0.7631(5)	0.0184(9)

H(7A)	1	0.462(8)	0.004(9)	0.697(7)	0.028*
H(7B)	1	0.687(5)	-0.020(9)	0.732(8)	0.028*
O(8)	1	0.4577(7)	0.2447(5)	1.0255(5)	0.0185(9)
H(8A)	1	0.331(6)	0.284(8)	1.000(8)	0.028*
H(8B)	1	0.561(7)	0.308(7)	0.992(8)	0.028*
F(1)	0.5	-0.0391(6)	0.2182(5)	0.5276(6)	0.0310(11)
F(2)	0.5	0.8985(6)	0.5732(5)	1.1921(4)	0.0200(8)
F(3)	1	0.0565(6)	-0.0056(6)	0.3066(4)	0.0326(10)
F(4)	1	0.2721(5)	0.0568(4)	0.5744(4)	0.0166(7)
F(5)	1	0.7450(5)	0.3992(4)	0.9127(4)	0.0169(7)
F(6)	1	0.9310(5)	0.6755(4)	0.9406(4)	0.0166(7)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

$CoAlF_5(H_2O)_7$					
atom	sof	x	y	z	$U_{(iso)}$*/$U_{(eq)}$
Co(1)	1	0.5	0.5	0.5	0.00844(17)
Co(2)	1	0.5	0	1	0.00797(17)
Al(1)	1	0	0	0.5	0.0107(3)
Al(2)	1	1	0.5	1	0.0096(3)
O(1)	0.5	-0.0407(4)	0.2184(3)	0.5335(4)	0.0273(7)
H(1A)	0.5	0.039(11)	0.288(10)	0.627(7)	0.041*
H(1B)	0.5	-0.183(5)	0.216(12)	0.552(10)	0.041*
O(2)	0.5	0.8938(4)	0.5718(3)	1.1895(3)	0.0193(6)
H(2A)	0.5	0.835(14)	0.498(7)	1.242(9)	0.029*
H(2B)	0.5	0.893(15)	0.675(4)	1.259(8)	0.029*
O(3)	1	0.5275(5)	0.3286(4)	0.6242(4)	0.0293(8)

H(3A)	1	0.586(8)	0.351(6)	0.730(3)	0.044*
H(3B)	1	0.443(7)	0.229(4)	0.604(6)	0.044*
O(4)	1	0.2194(4)	0.3727(3)	0.3695(3)	0.0159(6)
H(4A)	1	0.118(6)	0.321(5)	0.415(5)	0.024*
H(4B)	1	0.156(6)	0.367(5)	0.268(3)	0.024*
O(5)	1	0.3207(4)	0.6267(3)	0.6607(3)	0.0229(7)
H(5A)	1	0.244(7)	0.674(5)	0.592(5)	0.034*
H(5B)	1	0.389(7)	0.698(5)	0.751(4)	0.034*
O(6)	1	0.1849(4)	-0.0697(3)	0.9223(3)	0.0164(6)
H(6A)	1	0.110(6)	-0.033(5)	0.845(4)	0.025*
H(6B)	1	0.105(6)	-0.155(4)	0.944(5)	0.025*
O(7)	1	0.5542(4)	-0.0356(3)	0.7662(3)	0.0160(6)
H(7A)	1	0.460(5)	0.008(5)	0.704(5)	0.024*
H(7B)	1	0.686(4)	-0.036(5)	0.735(5)	0.024*
O(8)	1	0.4546(4)	0.2384(3)	1.0174(3)	0.0173(6)
H(8A)	1	0.323(4)	0.275(5)	1.013(5)	0.026*
H(8B)	1	0.549(5)	0.300(5)	0.976(5)	0.026*
F(1)	0.5	-0.0407(4)	0.2184(3)	0.5335(4)	0.0273(7)
F(2)	0.5	0.8938(4)	0.5718(3)	1.1895(3)	0.0193(6)
F(3)	1	0.0555(4)	0.0003(4)	0.3072(3)	0.0280(6)
F(4)	1	0.2734(3)	0.0591(3)	0.5748(3)	0.0158(5)
F(5)	1	0.7447(3)	0.3977(3)	0.9098(3)	0.0161(5)
F(6)	1	0.9308(3)	0.6758(3)	0.9408(3)	0.0153(5)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

$NiAlF_5(H_2O)_7$					
atom	sof	x	y	z	$U_{(iso)}{}^*/U_{(eq)}$
Ni(1)	1	0.5	0.5	0.5	0.0078(3)
Ni(2)	1	0.5	0	1	0.0074(3)
Al(1)	1	0	0	0.5	0.0096(5)
Al(2)	1	1	0.5	1	0.0090(5)
O(1)	0.5	-0.0374(6)	0.2204(5)	0.5313(6)	0.0272(11)
H(1A)	0.5	-0.138(18)	0.20(2)	0.596(17)	0.041*
H(1B)	0.5	-0.10(2)	0.282(19)	0.466(16)	0.041*
O(2)	0.5	0.8861(6)	0.5748(5)	1.1875(5)	0.0162(8)
H(2A)	0.5	0.88(2)	0.487(9)	1.236(13)	0.024*
H(2B)	0.5	0.93(2)	0.666(9)	1.276(9)	0.024*
O(3)	1	0.5355(7)	0.3246(5)	0.6178(5)	0.0205(10)
H(3A)	1	0.456(10)	0.386(7)	0.691(8)	0.031*
H(3B)	1	0.453(10)	0.221(4)	0.590(9)	0.031*
O(4)	1	0.2212(6)	0.3793(5)	0.3734(5)	0.0135(9)
H(4A)	1	0.119(9)	0.322(7)	0.416(7)	0.02*
H(4B)	1	0.191(10)	0.338(8)	0.262(2)	0.02*
O(5)	1	0.3220(6)	0.6250(5)	0.6603(5)	0.0175(9)
H(5A)	1	0.224(9)	0.697(7)	0.641(8)	0.026*
H(5B)	1	0.418(9)	0.687(7)	0.748(6)	0.026*
O(6)	1	0.1886(6)	-0.0665(5)	0.9246(5)	0.0150(9)
H(6A)	1	0.116(9)	-0.013(7)	0.857(7)	0.023*
H(6B)	1	0.097(9)	-0.150(6)	0.942(8)	0.023*
O(7)	1	0.5540(6)	-0.0391(5)	0.7678(5)	0.0135(9)
H(7A)	1	0.458(8)	-0.004(9)	0.698(6)	0.02*

H(7B)	1	0.677(7)	-0.062(9)	0.722(7)	0.02*
O(8)	1	0.4580(7)	0.2388(5)	1.0191(5)	0.0147(9)
H(8A)	1	0.330(6)	0.283(8)	1.029(9)	0.022*
H(8B)	1	0.549(8)	0.301(7)	0.975(8)	0.022*
F(1)	0.5	-0.0374(6)	0.2204(5)	0.5313(6)	0.0272(11)
F(2)	0.5	0.8861(6)	0.5748(5)	1.1875(5)	0.0162(8)
F(3)	1	0.0554(6)	-0.0041(6)	0.3034(4)	0.0262(9)
F(4)	1	0.2755(5)	0.0568(4)	0.5732(4)	0.0139(7)
F(5)	1	0.7461(5)	0.3959(4)	0.9065(4)	0.0133(7)
F(6)	1	0.9318(5)	0.6765(4)	0.9379(4)	0.0133(7)

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S3. Bond valence calculation for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) at RT and 100 K, respectively.

$FeAlF_5(H_2O)_7$ at RT										
Atoms	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	F(1)	F(2)	F(3)	**$\Sigma_{cations}$**
Fe(1)		$0.358^{[x2]}$	$0.347^{[x2]}$	$0.327^{[x2]}$						**2.06**
Fe(2)					$0.364^{[x2]}$	$0.330^{[x4]}$				**2.05**
Al(1)	0.558						0.419	$0.524^{[x2]}$	$0.520^{[x2]}$	**3.06**
H(1A)	0.653						0.326			**0.98**
H(1B)	0.658	$^{[x2]}0.009$		$^{[x2]}0.018$			0.327			**1.01**
H(2)		$^{[x2]}0.693$							0.160	**0.85**
H(3)	0.016		$^{[x2]}0.693$				0.006	0.090		**0.81**
H(4)	0.042			$^{[x2]}0.677$			0.017			**0.74**
H(5)					$^{[x2]}0.667$			0.160		**0.83**
H(6A)						0.683		0.152	0.168	**1.00**
H(6B)						0.677				**0.68**

Σ_{anions}	**1.87**	**1.76**	**1.73**	**1.72**	**1.70**	**1.69**	**1.09**	**0.93**	**0.85**	

[a] Bond valences sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "*i*", R_0 is a constant dependent on the bonded elements, R_i is the bond length of bond *i* and B=0.37 or 0.558 (H-F only). Left and right superscripts indicate the # of equivalent bonds for anions and cations, respectively.

$CoAlF_5(H_2O)_7$ at RT										
Atoms	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	F(1)	F(2)	F(3)	$\Sigma_{cations}$
Co(1)		$0.378^{[x2]}$	$0.343^{[x2]}$	$0.318^{[x2]}$						**2.08**
Co(2)					$0.368^{[x2]}$	$0.336^{[x4]}$				**2.08**
Al(1)	0.564						0.423	$0.531^{[x2]}$	$0.521^{[x2]}$	**3.09**
H(1A)	0.655						0.326			**0.98**
H(1B)	0.648	$^{[x2]}0.009$		$^{[x2]}0.024$			0.324			**1.00**
H(2)		$^{[x2]}0.694$							0.164	**0.86**
H(3)	0.015		$^{[x2]}0.701$				0.006	0.090		**0.81**
H(4)	0.044			$^{[x2]}0.645$			0.017			**0.71**
H(5)					$^{[x2]}0.665$			0.160		**0.83**
H(6A)						0.691		0.146		**0.84**
H(6B)						0.684			0.164	**0.85**
Σ_{anions}	**1.93**	**1.78**	**1.75**	**1.66**	**1.70**	**1.71**	**1.07**	**0.93**	**0.85**	

[a] Bond valences sum calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "*i*", R_0 is a constant dependent on the bonded elements, R_i is the bond length of bond *i* and B=0.37 or 0.558 (H-F only). Left and right superscripts indicate the # of equivalent bonds for anions and cations, respectively.

$NiAlF_5(H_2O)_7$ at RT										
Atoms	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	F(1)	F(2)	F(3)	$\Sigma_{cations}$
Ni(1)		$0.373^{[x2]}$	$0.356^{[x2]}$	$0.317^{[x2]}$						**2.09**
Ni(2)					$0.371^{[x2]}$	$0.336^{[x4]}$				**2.09**
Al(1)	0.569						0.427	$0.537^{[x2]}$	$0.527^{[x2]}$	**3.12**
H(1A)	0.689						0.326			**0.90**
H(1B)	0.686						0.324			**1.01**
H(2)		$^{[x2]}0.694$							0.164	**0.86**
H(3)	0.017		$^{[x2]}0.706$				0.007	0.080		**0.81**
H(4)	0.048			$^{[x2]}0.663$			0.019			**0.73**
H(5)					$^{[x2]}0.684$			0.160		**0.84**
H(6A)						0.687		0.146	0.168	**1.00**
H(6B)						0.671				**0.67**
Σ_{anions}	**2.01**	**1.76**	**1.77**	**1.64**	**1.74**	**1.70**	**1.10**	**0.92**	**0.86**	

[a] Bond valences sum calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "*i*", R_0 is a constant dependent on the bonded elements, R_i is the bond length of bond *i* and B=0.37 or 0.558 (H-F only). Left and right superscripts indicate the # of equivalent bonds for anions and cations, respectively.

$FeAlF_5(H_2O)_7$ at 100K															
Atoms	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	F(1)	F(2)	F(3)	F(4)	F(5)	F(6)	$\Sigma_{cations}$
Fe(1)			$0.349^{[x2]}$	$0.352^{[x2]}$	$0.317^{[x2]}$										**2.04**
Fe(2)						$0.367^{[x2]}$	$0.347^{[x2]}$	$0.317^{[x2]}$							**2.06**
Al(1)	0.505								0.379		$0.546^{[x2]}$	$0.512^{[x2]}$			**3.00**
Al(2)		0.550								0.413			$0.510^{[x2]}$	$0.490^{[x2]}$	**2.96**
H(1A)	0.654	0.071							0.326	0.028					**1.08**
H(1B)	0.648		$0.018^{[x2]}$		$0.015^{[x2]}$				0.324						**1.04**
H(2A)		0.647			$0.063^{[x2]}$					0.323					**1.09**
H(2B)	0.067	0.635							0.027	0.319					**1.05**
H(3A)		0.007	0.651		0.016					0.003					**0.68**
H(3B)			0.635									0.165			**0.80**
H(4A)	0.061			0.670					0.024						**0.76**
H(4B)		0.007		0.654						0.003				0.141	**0.81**
H(5A)	0.032				0.665				0.013						**0.71**
H(5B)					0.661			0.042							**0.70**
H(6A)						0.676					0.164				**0.84**
H(6B)						0.663								0.149	**0.81**
H(7A)							0.651					0.166			**0.82**
H(7B)							0.635				0.157				**0.79**
H(8A)								0.651						0.124	**0.78**
H(8B)								0.635					0.175		**0.81**
Σ_{anions}	**1.97**	**1.92**	**1.65**	**1.68**	**1.74**	**1.71**	**1.63**	**1.65**	**1.09**	**1.09**	**0.87**	**0.84**	**0.69**	**0.90**	

[a] Bond valences sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "*i*", R_0 is a constant dependent on the bonded elements, R_i is the bond length of bond *i* and B=0.37 or 0.558 (H-F only). Left and right superscripts indicate that the # of equivalent bonds for anions and cations, respectively.

$CoAlF_5(H_2O)_7$ at 100K															
Atoms	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	F(1)	F(2)	F(3)	F(4)	F(5)	F(6)	$\Sigma_{cations}$
Co(1)			$0.368^{[x2]}$	$0.341^{[x2]}$	$0.327^{[x2]}$										**2.07**
Co(2)						$0.372^{[x2]}$	$0.343^{[x2]}$	$0.339^{[x2]}$							**2.11**
Al(1)	0.521								0.391		$0.536^{[x2]}$	$0.519^{[x2]}$			**3.02**
Al(2)		0.559								0.420			$0.514^{[x2]}$	$0.499^{[x2]}$	**3.01**
H(1A)	0.649	0.074							0.324	0.077					**1.12**
H(1B)	0.649		$0.018^{[x2]}$						0.324						**1.01**
H(2A)		0.649			$0.060^{[x2]}$					0.324					**1.09**
H(2B)	0.047	0.649							0.056	0.324					**1.08**
H(3A)			0.679										0.165		**0.84**
H(3B)			0.667									0.169			**0.84**
H(4A)	0.028			0.658					0.064						**0.75**
H(4B)				0.689										0.143	**0.83**
H(5A)	0.017				0.683				0.045						**0.75**
H(5B)					0.711		0.012	0.030							**0.75**
H(6A)						0.691					0.168				**0.86**
H(6B)						0.679								0.153	**0.84**
H(7A)							0.678					0.163			**0.84**
H(7B)							0.691				0.151				**0.84**
H(8A)								0.683						0.142	**0.83**
H(8B)								0.672					0.172		**0.84**
Σ_{anions}	**1.91**	**1.93**	**1.73**	**1.69**	**1.78**	**1.74**	**1.72**	**1.72**	**1.20**	**1.15**	**0.86**	**0.85**	**0.85**	**0.94**	

[a] Bond valences sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "*i*", R_0 is a constant dependent on the bonded elements, R_i is the bond length of bond *i* and B=0.37 or 0.558 (H-F only). Left and right superscripts indicate that the # of equivalent bonds for anions and cations, respectively.

$NiAlF_5(H_2O)_7$ at 100K															
Atoms	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	F(1)	F(2)	F(3)	F(4)	F(5)	F(6)	$\Sigma_{cations}$
Ni(1)			$0.353^{[x2]}$	$0.353^{[x2]}$	$0.330^{[x2]}$										**2.07**
Ni(2)						$0.378^{[x2]}$	$0.338^{[x2]}$	$0.336^{[x2]}$							**2.10**
Al(1)	0.533								0.400		$0.512^{[x2]}$	$0.517^{[x2]}$			**2.99**
Al(2)		0.558								0.419			$0.517^{[x2]}$	$0.499^{[x2]}$	**3.01**
H(1A)	0.668								0.330						**1.00**
H(1B)	0.651				$0.035^{[x2]}$				0.325						**1.05**
H(2A)		0.644			$0.040^{[x2]}$					0.322					**1.05**
H(2B)	0.074	0.644							0.078	0.322					**1.12**
H(3A)		0.008	0.648		0.015					0.018					**0.71**
H(3B)			0.638									0.168			**0.81**
H(4A)	0.031			0.659					0.068						**0.76**
H(4B)				0.649										0.140	**0.79**
H(5A)	0.014				0.664				0.041						**0.72**
H(5B)					0.653		0.013	0.036							**0.70**
H(6A)						0.666					0.161				**0.83**
H(6B)						0.665								0.157	**0.82**
H(7A)							0.667					0.166			**0.83**
H(7B)							0.667				0.137				**0.80**
H(8A)								0.667						0.146	**0.81**
H(8B)								0.667					0.173		**0.84**
Σ_{anions}	**1.97**	**1.85**	**1.64**	**1.66**	**1.74**	**1.71**	**1.69**	**1.71**	**1.24**	**1.08**	**0.81**	**0.85**	**0.69**	**0.94**	

[a] Bond valences sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond "*i*", R_0 is a constant dependent on the bonded elements, R_i is the bond length of bond *i* and B=0.37 or 0.558 (H-F only). Left and right superscripts indicate that the # of equivalent bonds for anions and cations, respectively.

Table S4. Out-of-center distortion of octahedral structures in $[Fe(H_2O)_6]^{2+}$ at RT and 100 K temperature.

	Octahedra	Bond distance (Å)		Bond difference b/w M-O and M-O'	Cosine (θ) for ∠O-M-O'	Δ_d
RT	$[Fe(1)(H_2O)_6]^{2+}$	Fe(1)-O(2)	2.093	0	1 (for 180°)	0
		Fe(1)-O(2)'	2.093			
		Fe(1)-O(3)	2.105	0	1 (for 180°)	
		Fe(1)-O(3)'	2.105			
		Fe(1)-O(4)	2.126	0	1 (for 180°)	
		Fe(1)-O(4)'	2.126			
	$[Fe(2)(H_2O)_6]^{2+}$	Fe-O(5)	2.087	0	1 (for 180°)	0
		Fe-O(5)'	2.087			
		Fe-O(6)	2.123	0	1 (for 180°)	
		Fe-O(6)'	2.123			
		Fe-O(6)''	2.123	0	1(for 180°)	
		Fe-O(6)'''	2.123			
	$[Al(1)F_5(H_2O)]^{2-}$	Al(1)-O(1)/F(1)	1.867	0	1(for 180°)	0
		Al(1)-O(1)'/F(1)'	1.867			
		Al(1)-F(2)	1.784	0	1(for 180°)	
		Al(1)-F(2)'	1.784			
		Al(1)-F(3)	1.787	0	1(for 180°)	
		Al(1)-F(3)'	1.787			

	Octahedral	Bond distance (Å)		Bond difference b/w M-O and M-O'	Cosine (θ) for ∠O-M-O'	Δ_d
100 K	$[Fe(1)(H_2O)_6]^{2+}$	Fe(1)-O(3)	2.102	0	1 (for 180°)	0
		Fe(1)-O(3)'	2.102			
		Fe(1)-O(4)	2.099	0	1 (for 180°)	
		Fe(1)-O(4)'	2.099			
		Fe(1)-O(5)	2.138	0	1 (for 180°)	
		Fe(1)-O(5)'	2.138			
	$[Fe(2)(H_2O)_6]^{2+}$	Fe-O(6)	2.084	0	1 (for 180°)	0
		Fe-O(6)'	2.084			
		Fe-O(7)	2.105	0	1 (for 180°)	
		Fe-O(7)'	2.105			
		Fe-O(8)'	2.138	0	1(for 180°)	
		Fe-O(8)'	2.138			
	$[Al(1)F_5(H_2O)]^{2-}$	Al(1)-O(1)/F(1)	1.904	0	1(for 180°)	0

		Al(1)-O(1)'/F'(1)'	1.904			
		Al(1)-F(3)	1.769	0	1(for 180°)	
		Al(1)-F(3)'	1.769			
		Al(1)-F(4)	1.793	0	1(for 180°)	
		Al(1)-F(4)'	1.793			
	$[Al(2)F_5(H_2O)]^{2-}$	Al(1)-O(2)/F(2)	1.872	0	1(for 180°)	0
		Al(1)-O(2)'/F'(2)'	1.872			
		Al(1)-F(5)	1.794	0	1(for 180°)	
		Al(1)-F(5)'	1.794			
		Al(1)-F(6)	1.809	0	1(for 180°)	
		Al(1)-F(6)'	1.809			

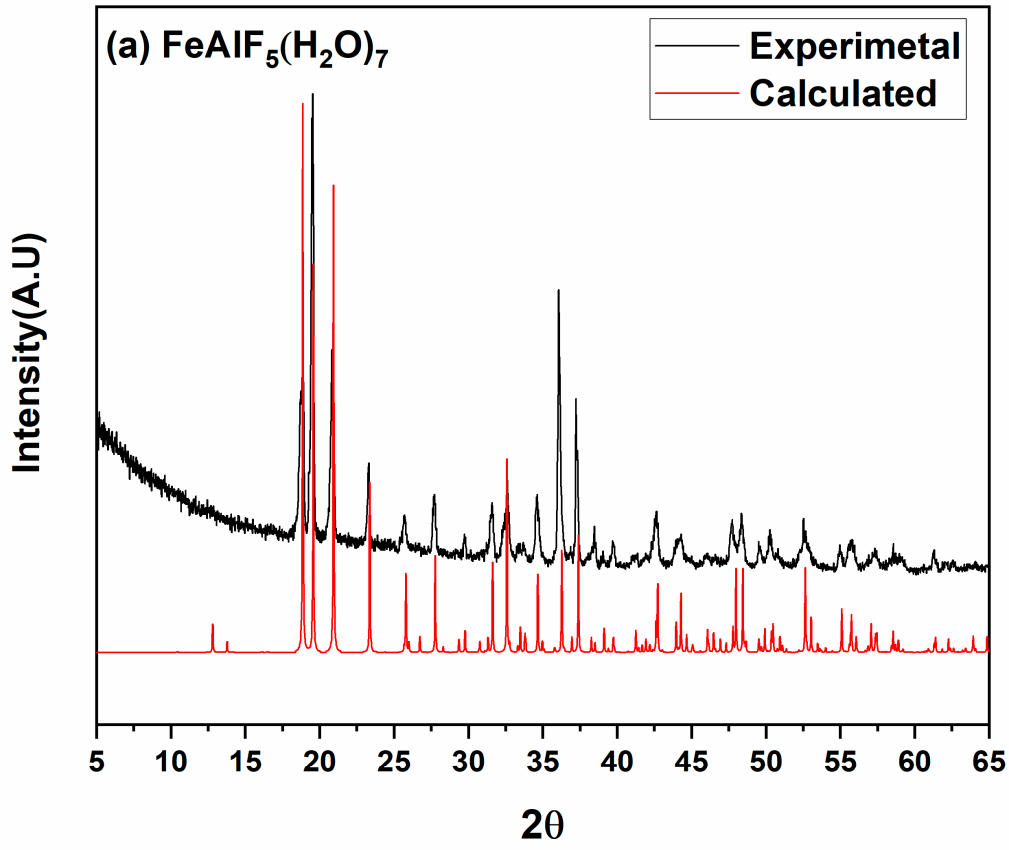
The out-of-center distortion is defined by Δ_d parameter as below.

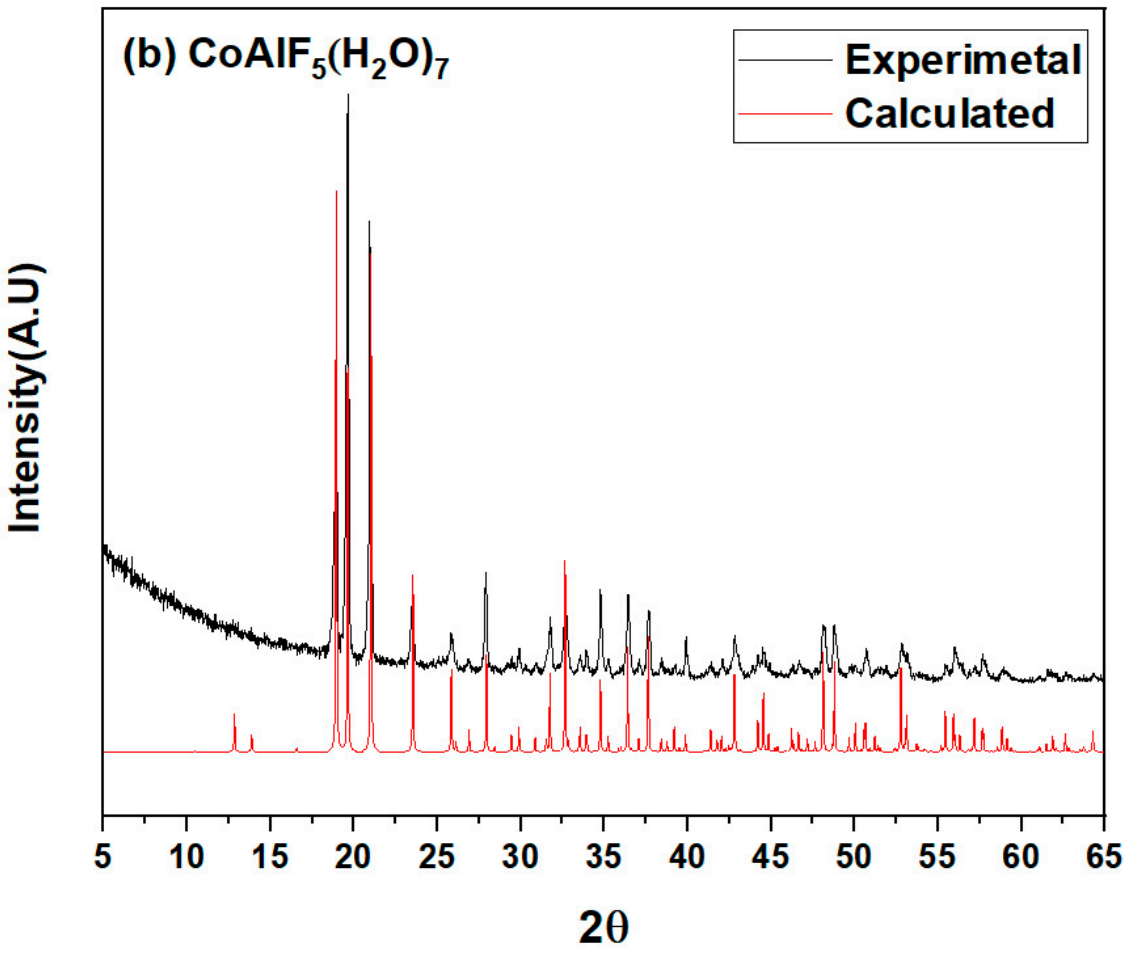
$$\Delta_d = \frac{|(M-O)-(M-O')|}{|\cos\theta 1|} + \frac{|(M-O)-(M-O')|}{|\cos\theta 2|} + \frac{|(M-O)-(M-O')|}{|\cos\theta 3|}$$

where the oxygen atom pairs (O and O') of six H_2O molecules which constitute the octahedral is used. The oxygen atoms are located in opposite positions from each other and Θ is represented by the angle, ∠O-M-O'. Two axial positions in the octahedral $[AlF_5(H_2O)]^{2-}$ is occupied by oxygen and fluorine, respectively, which attributes to the crystallographic disorder for the oxygen and fluorine in $[AlF_5(H_2O)]^{2-}$.

As an example, Δ_d parameters calculated for $FeAlF_5(H_2O)_7$ at RT and ~100K are depicted in the table above. Other Δ_d parameters for $CoAlF_5(H_2O)_7$ and $NiAlF_5(H_2O)_7$ are also shown as zero values, respectively. It means that the tilting and distortion of octahedral structures does NOT exist in $[M(H_2O)_6]^{2+}$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}) and $[AlF_5(H_2O)]^{2-}$.

Figure S1. Experimental and Calculated X-ray powder diffraction patterns for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}): (a) $FeAlF_5(H_2O)_7$, (b) $CoAlF_5(H_2O)_7$ and (c) $NiAlF_5(H_2O)$.




(b) CoAlF5(H2O)7
Experimetal
Calculated
Intensity(A.U)
5
10
15
20
25
30
35
40
45
50
55
60
65
2θ

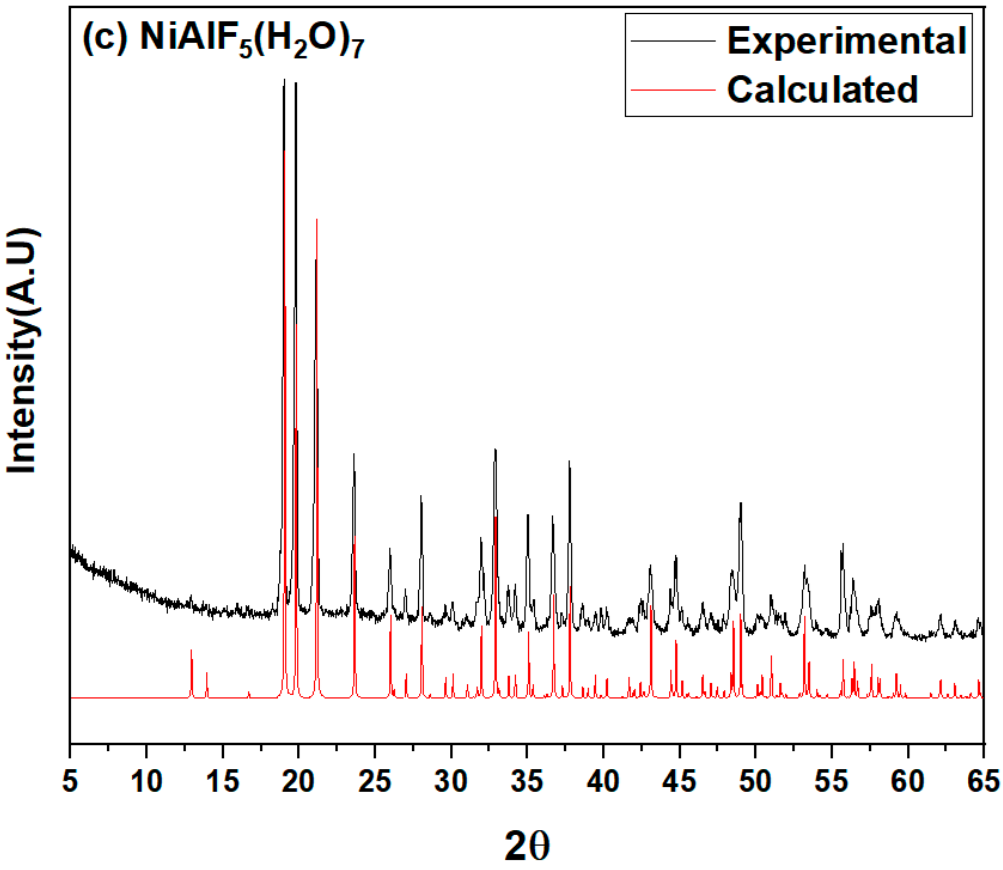
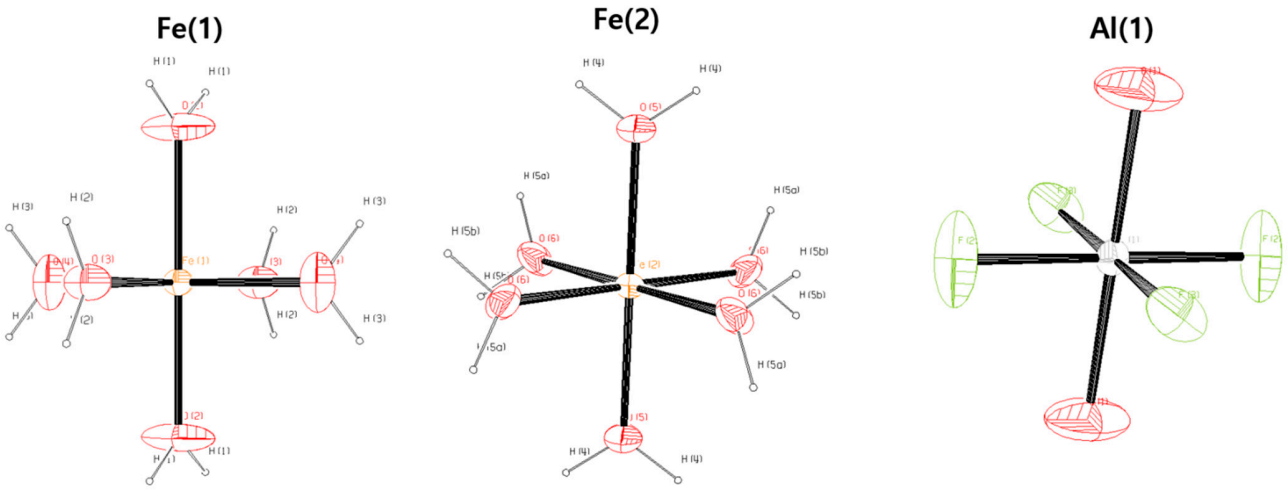


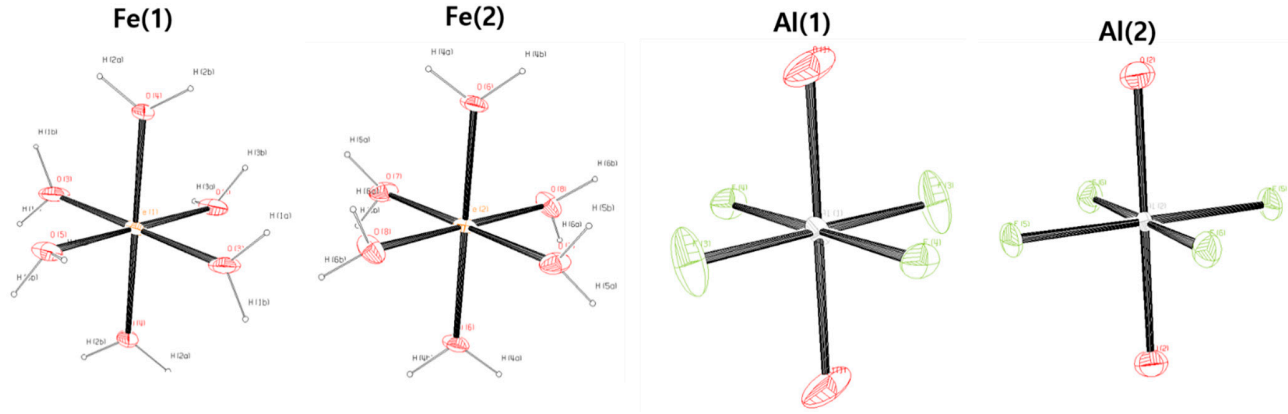
Figure S2. ORTEP representation (50% probability ellipsoid) for $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}).

$FeAlF_5(H_2O)_7$
*C*2/m (No. 12), 300 K



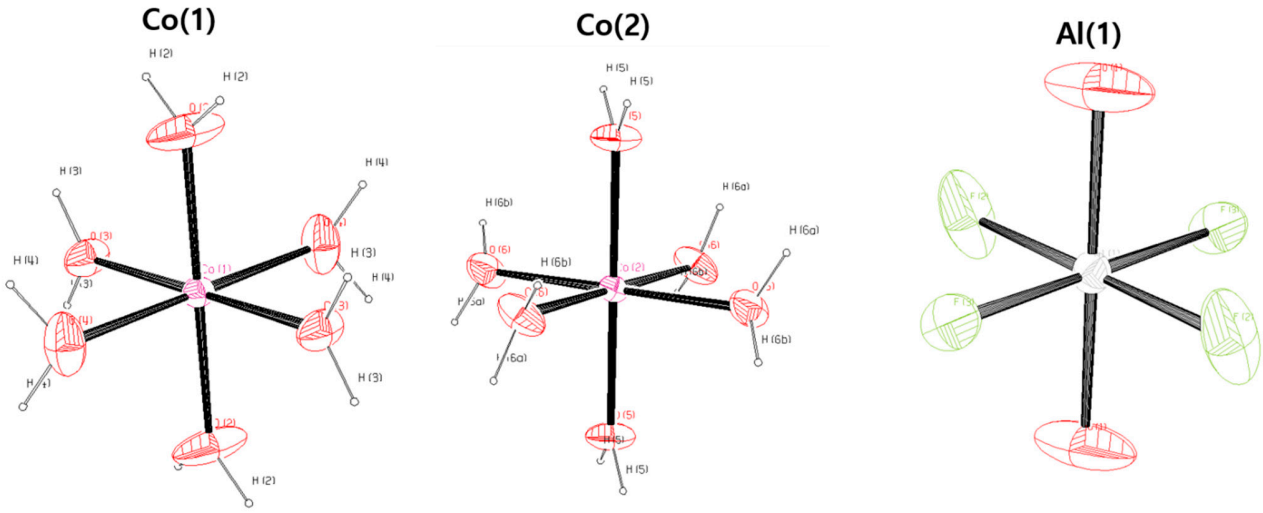
(Hydrogen atoms bonded to disordered O/F sites were excluded to enhance clarity)

$FeAlF_5(H_2O)_7$
P-1 (No. 2), 100 K



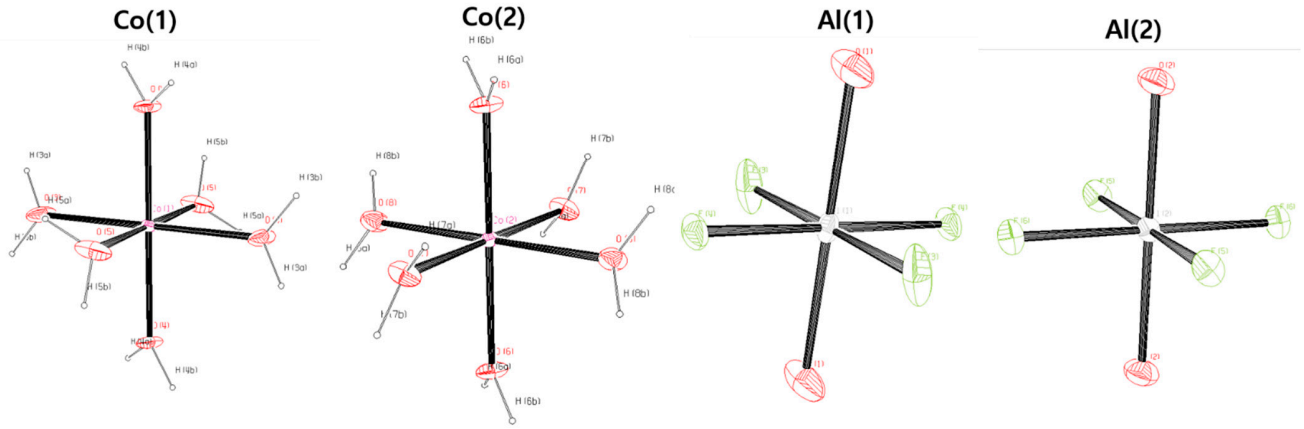
(Hydrogen atoms bonded to disordered O/F sites were excluded to enhance clarity)

$CoAlF_5(H_2O)_7$
*C*2/m (No. 12), 300 K



(Hydrogen atoms bonded to disordered O/F sites were excluded to enhance clarity)

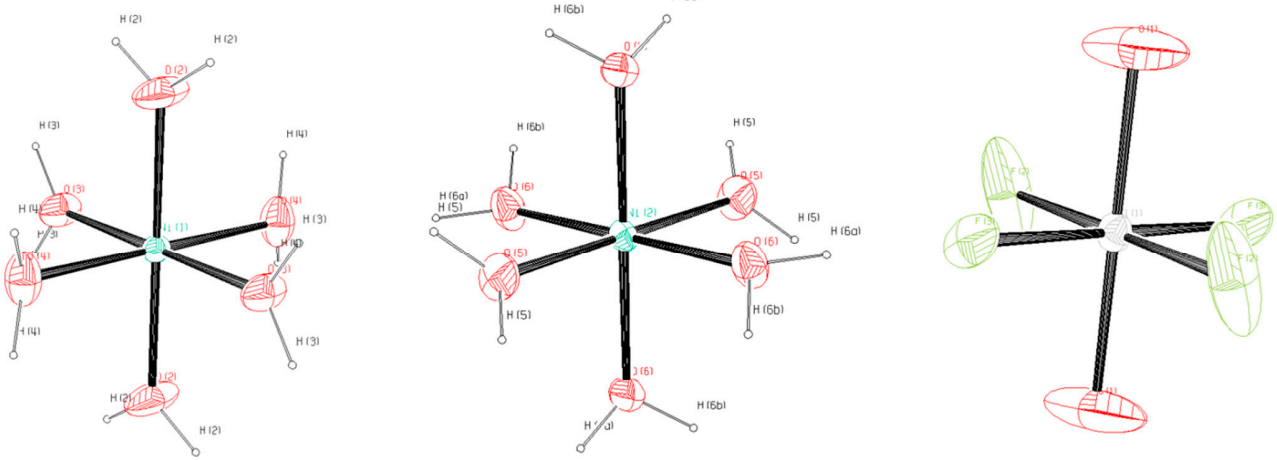
$CoAlF_5(H_2O)_7$
P-1 (No. 2), 100 K



(Hydrogen atoms bonded to disordered O/F sites were excluded to enhance clarity)

$NiAlF_5(H_2O)_7$
*C*2/m (No. 12), 300 K

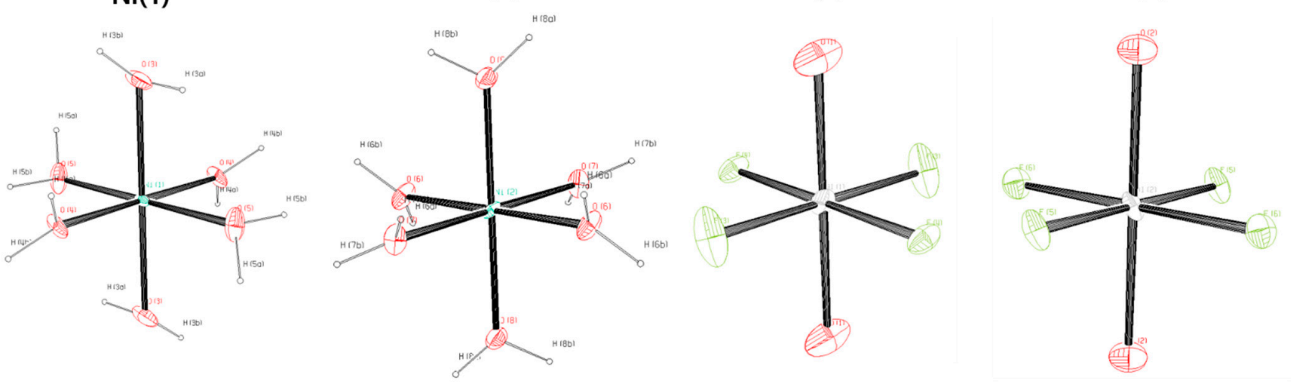
Ni(1) Ni(2) Al(1)



(Hydrogen atoms bonded to disordered O/F sites were excluded to enhance clarity)

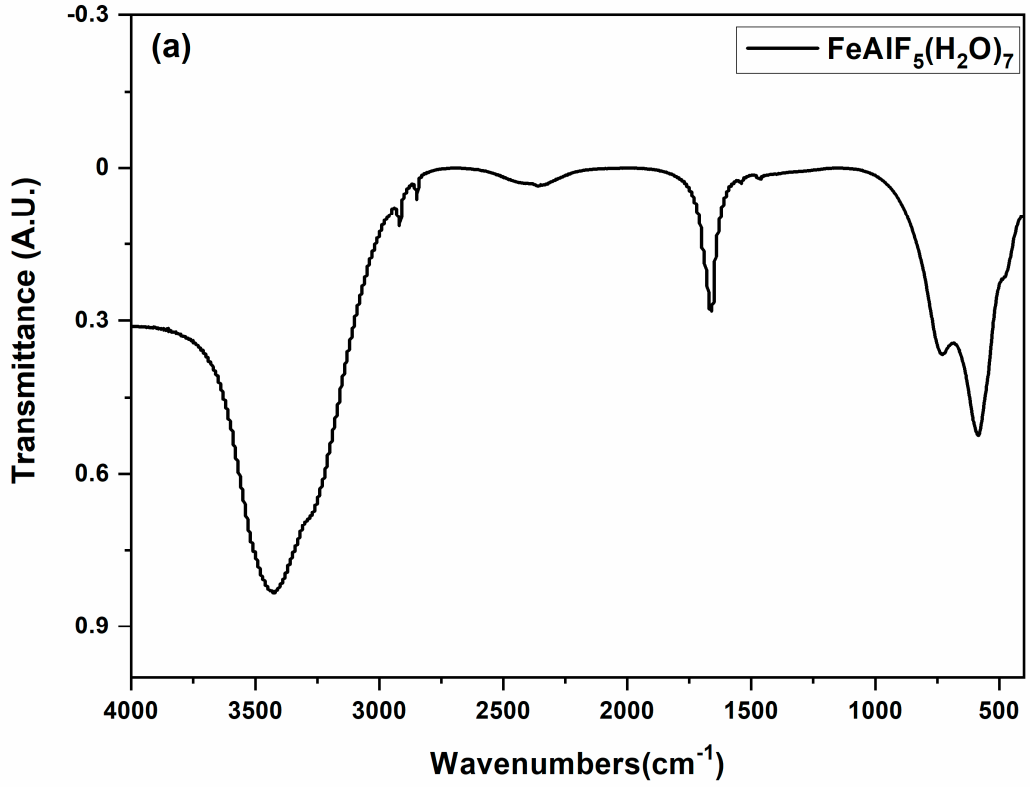
$NiAlF_5(H_2O)_7$
P-1 (No. 2), 100 K

Ni(1) Ni(2) Al(1) Al(2)

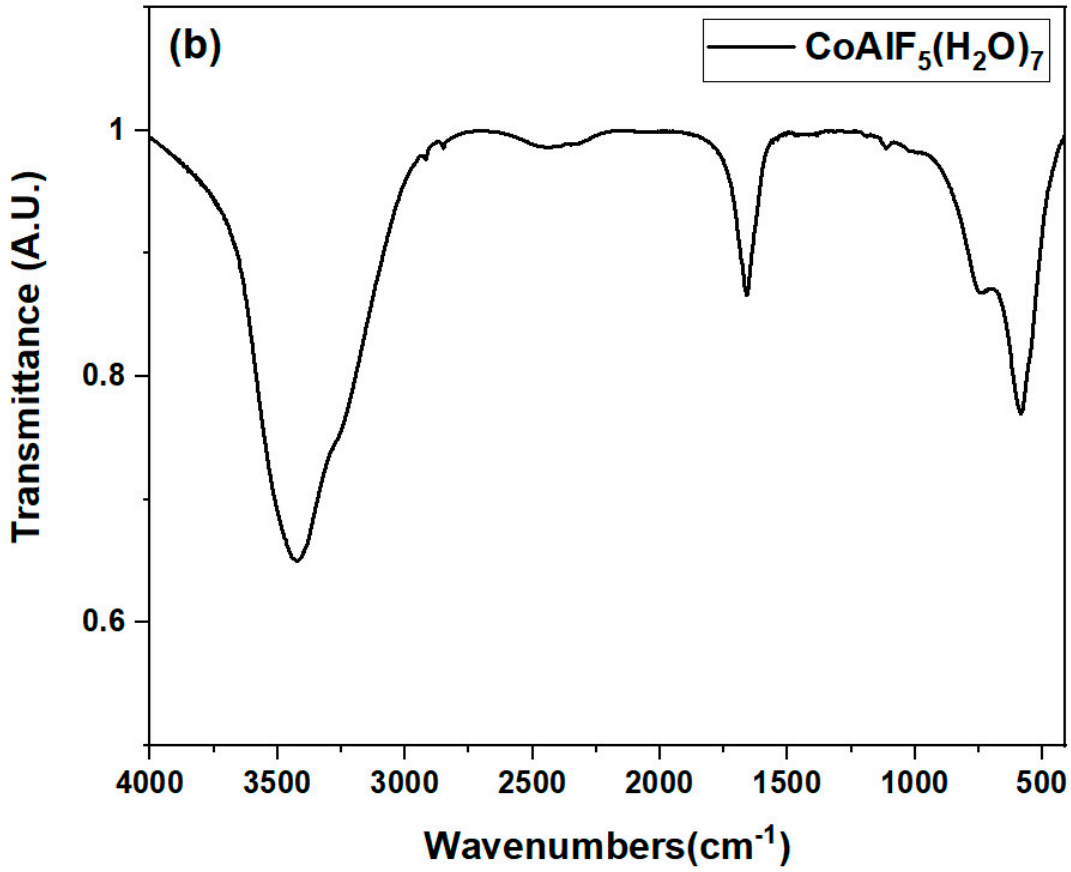


(Hydrogen atoms bonded to disordered O/F sites were excluded to enhance clarity)

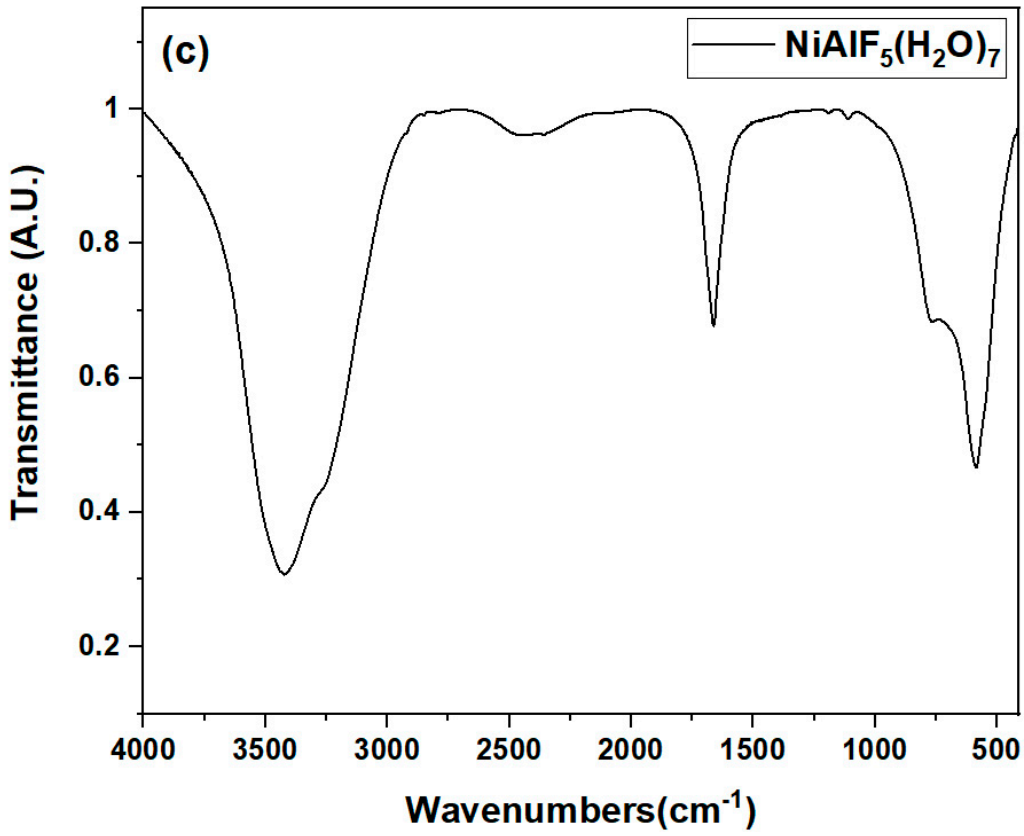
Figure S3. FT-IR Spectra of $M^{2+}AlF_5(H_2O)_7$ (M^{2+} = Fe^{2+}, Co^{2+}, or Ni^{2+}): (a) $FeAlF_5(H_2O)_7$, (b) $CoAlF_5(H_2O)_7$ and (c) $NiAlF_5(H_2O)_7$.



$FeAlF_5(H_2O)_7$			
υ(O-H)	**δ(H-O-H)**	**υ(Fe-O)**	**υ(Al-F) or υ(Al-O/F)**
3430	1660	580	730
		465	

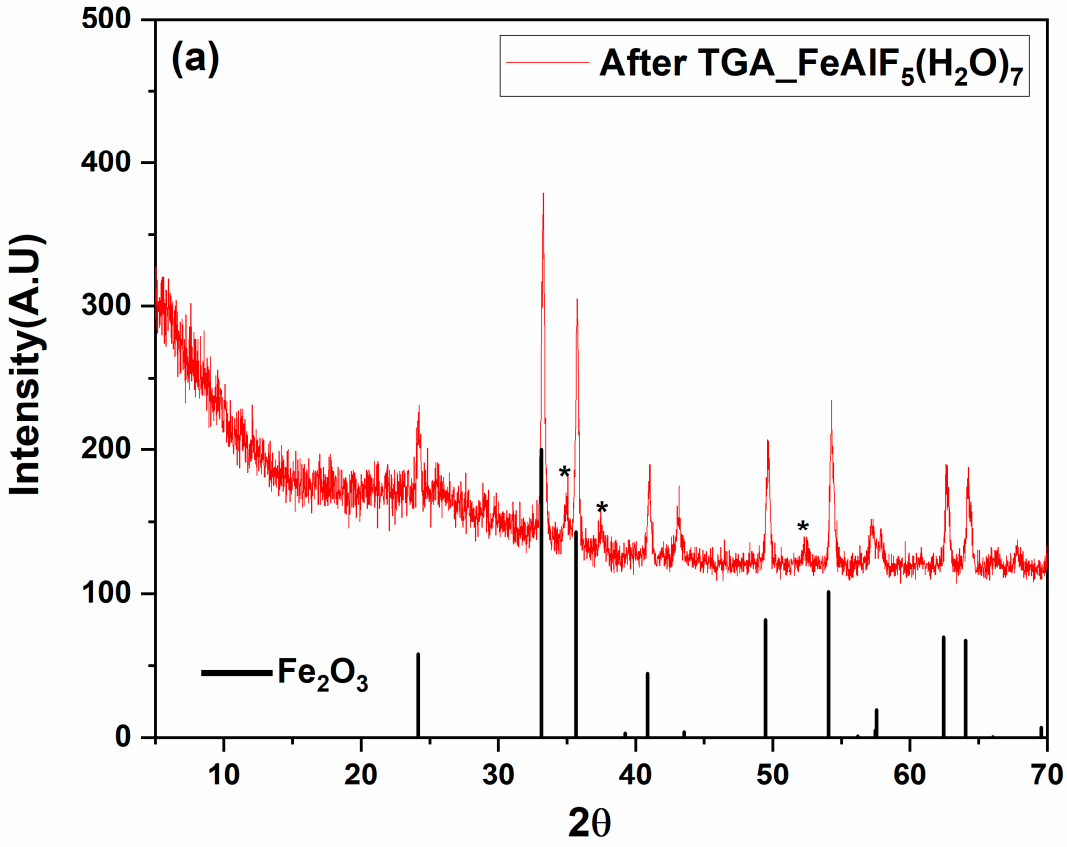


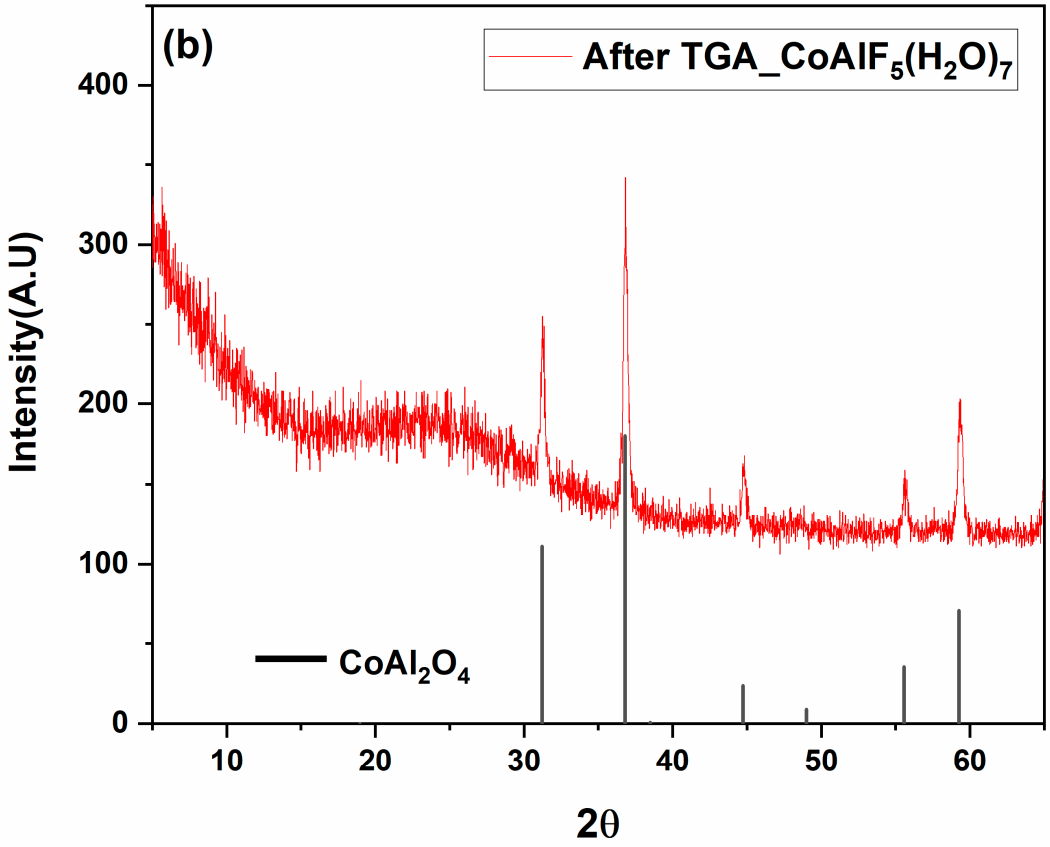
$CoAlF_5(H_2O)_7$			
υ(O-H)	**δ(H-O-H)**	**υ(Co-O)**	**υ(Al-F) or υ(Al-O/F)**
3260	1660	583	750

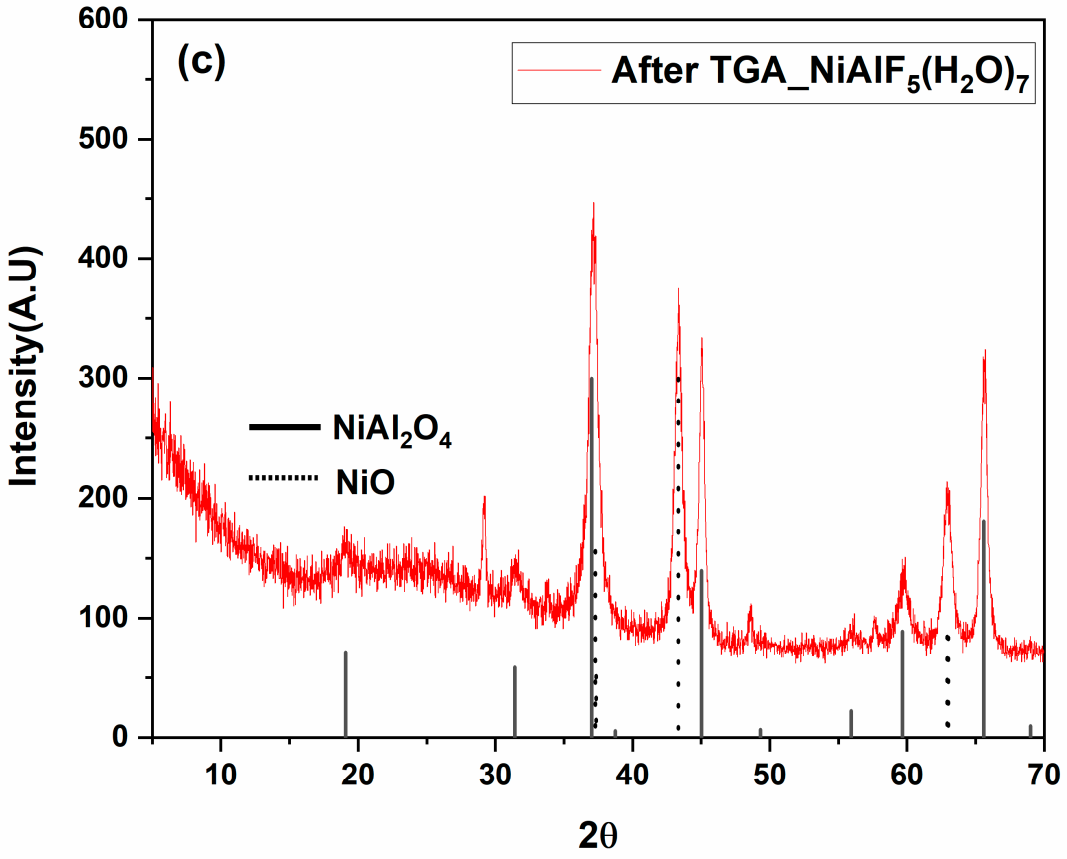


$NiAlF_5(H_2O)_7$			
υ(O-H)	**δ(H-O-H)**	**υ(Ni-O)**	**υ(Al-F) or υ(Al-O/F)**
3260	1650	580	770

Figure S4. Powder X-ray diffraction pattern for final residuals after TGA experiment: (a) $FeAlF_5(H_2O)_7$, (b) $CoAlF_5(H_2O)_7$ and (c) $NiAlF_5(H_2O)_7$.




(b)
After TGA_CoAlF5(H2O)7
CoAl2O4
Intensity(A.U)
2θ
0
100
200
300
400
10
20
30
40
50
60


(c)
After TGA_NiAlF5(H2O)7
NiAl2O4
NiO
Intensity(A.U)
2θ
0
100
200
300
400
500
600
10
20
30
40
50
60
70