Dalton Transactions

SUPPLEMENTARY INFORMATIONS

Magnetisation and Mössbauer study of triazole $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ weberites (M = Fe, Co, Mn, Zn, Ga, V)

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Fig. S1 Rietveld refinement of the X-ray patterns of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$.

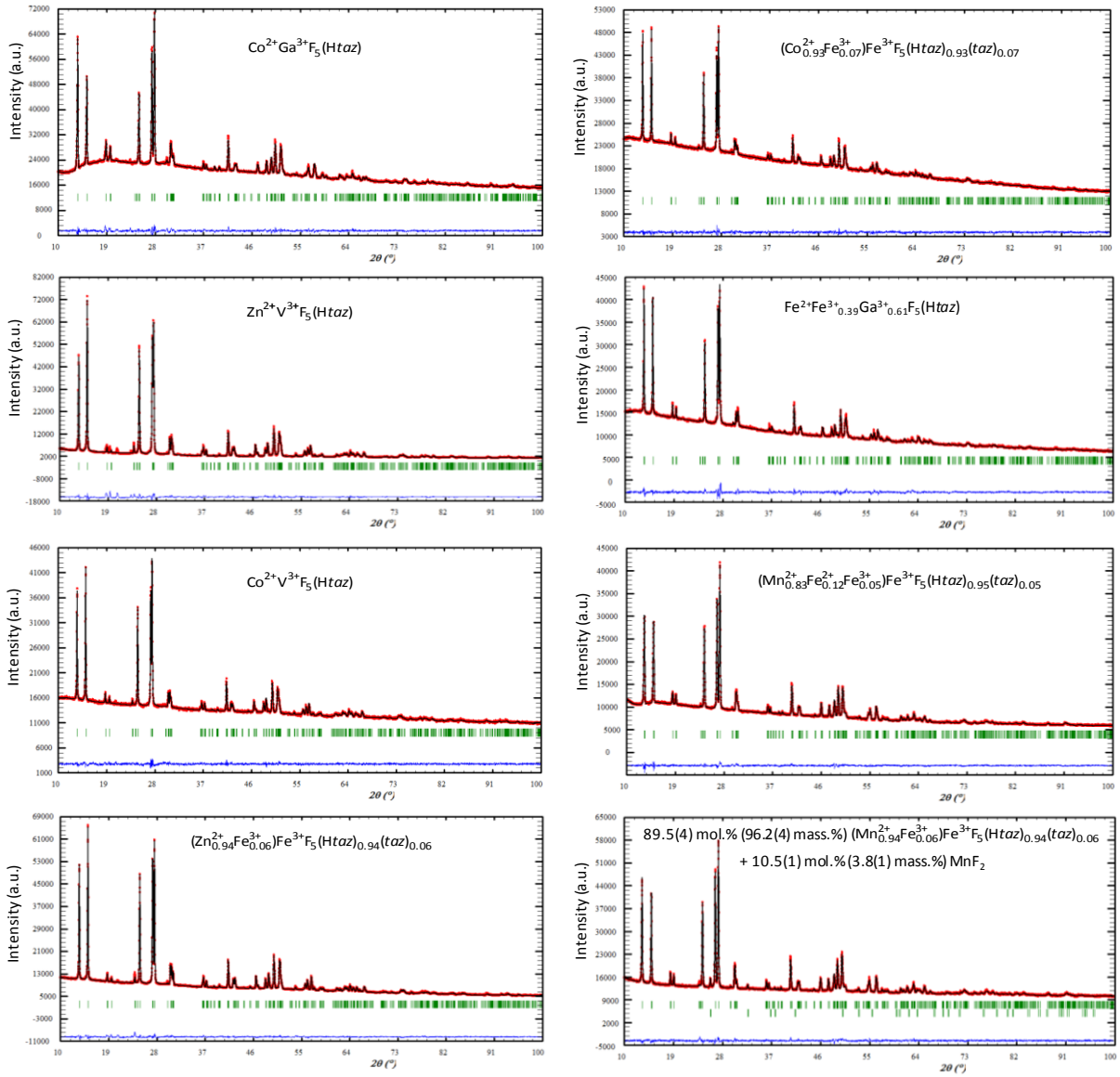

Table S1 Summary of crystallographic data for the structures of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(H\mathit{taz})_{1-x}(\mathit{taz})_x$.

	$Co^{2+}Ga^{3+}$	$Zn^{2+}V^{3+}$	$Co^{2+}V^{3+}$	$Zn^{2+}_{0.94}Fe^{3+}_{1.06}$	$Co^{2+}_{0.93}Fe^{3+}_{1.07}$
Formula	$CoGaF_5C_2H_3N_3$	$ZnVF_5C_2H_3N_3$	$CoVF_5C_2H_3N_3$	$Zn_{0.94}Fe_{1.06}F_5C_2H_{2.82}N_3$	$Co_{0.93}Fe_{1.07}F_5C_2H_{2.79}N_3$
Formula weight (g.mol^{-1})	292.71	280.39	273.93	284.65	278.55
Powder	Pink	Light green	Brown	Light green	Light pink
Temperature/K	296.2(2)				
Crystal system, SG	Orthorhombic, *Imma*				
a/Å	9.0194(4)	9.0595(4)	9.0738(4)	9.0753(2)	9.0882(5)
b/Å	7.3421(3)	7.4628(3)	7.4627(3)	7.4452(2)	7.4479(4)
c/Å	9.3901(4)	9.4321(4)	9.4407(4)	9.4607(2)	9.4689(5)
Volume/Å^3	621.8(1)	637.7(1)	639.3(1)	639.2(1)	640.9(1)
Z, $\rho_{calculated}$/g.cm^{-3}	4, 3.095	4, 2.889	4, 2.815	4, 2.927	4, 2.856
Θ range/°	5.015-99.994	5.015-99.994	5.015-99.994	5.015-99.994	5.015-99.994
Unique reflections	412	416	416	413	415
Parameters	56	50	50	52	56
R_p/R_{wp}	0.169/0.089	0.096/0.122	0.185/0.091	0.102/0.069	0.231/0.098
R_B/R_F	0.057/0.083	0.038/0.042	0.057/0.078	0.040/0.070	0.064/0.147

	$Fe^{2+}_{0.99}Fe^{3+}_{0.40}Ga^{3+}_{0.61}$	$Fe^{2+}_{0.96}Fe^{3+}_{1.04}$	$Mn^{2+}_{0.83}Fe^{2+}_{0.12}Fe^{3+}_{1.05}$	$Mn^{2+}_{0.94}Fe^{3+}_{1.06}$
Formula	$Fe_{1.39}Ga_{0.61}F_5C_2H_{2.97}N_3$	$Fe_2F_5C_2H_{2.97}N_3$	$Mn_{0.83}Fe_{1.17}F_5C_2H_{2.85}N_3$	$Mn_{0.94}Fe_{1.06}F_5C_2H_{2.82}N_3$
Formula weight (g.mol^{-1})	284.20	275.71	274.94	274.83
Powder type	Purple	Purple	Light green	Light green
Temperature/K	296.2(2)			
Crystal system, SG	Orthorhombic, *Imma*			
a/Å	9.1404(4)	9.1583(3)	9.2723(4)	9.2919(4)
b/Å	7.4753(3)	7.4912(2)	7.5057(3)	7.5003(3)
c/Å	9.4629(4)	9.4607(3)	9.5831(3)	9.6020(3)
Volume/Å^3	646.6(1)	649.1(1)	666.9(1)	669.2(1)
Z, $\rho_{calculated}$/g.cm^{-3}	4, 2.889	4, 2.791	4, 2.709	4, 2.699
2Θ range/°	5.015-99.994	5.000-100.000	5.015-99.994	5.015-100.001
Unique reflections	417	418	440	439
Parameters	47	44	60	67
R_p/R_{wp}	0.184/0.105	0.160/0.080	0.143/0.083	0.144/0.082
R_B/R_F	0.052/0.097	0.048/0.084	0.047/0.065	0.040/0.052

Fig. S2 Evolution of cell parameters and volume as a function of M^{2+} and M^{3+} ionic radii of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$. The parameters corresponding to three novel compositions ($Zn^{2+}V^{3+}$, $Co^{2+}Ga^{3+}$ and $Co^{2+}V^{3+}$ represented by star) are compared with those previously reported in the literature.

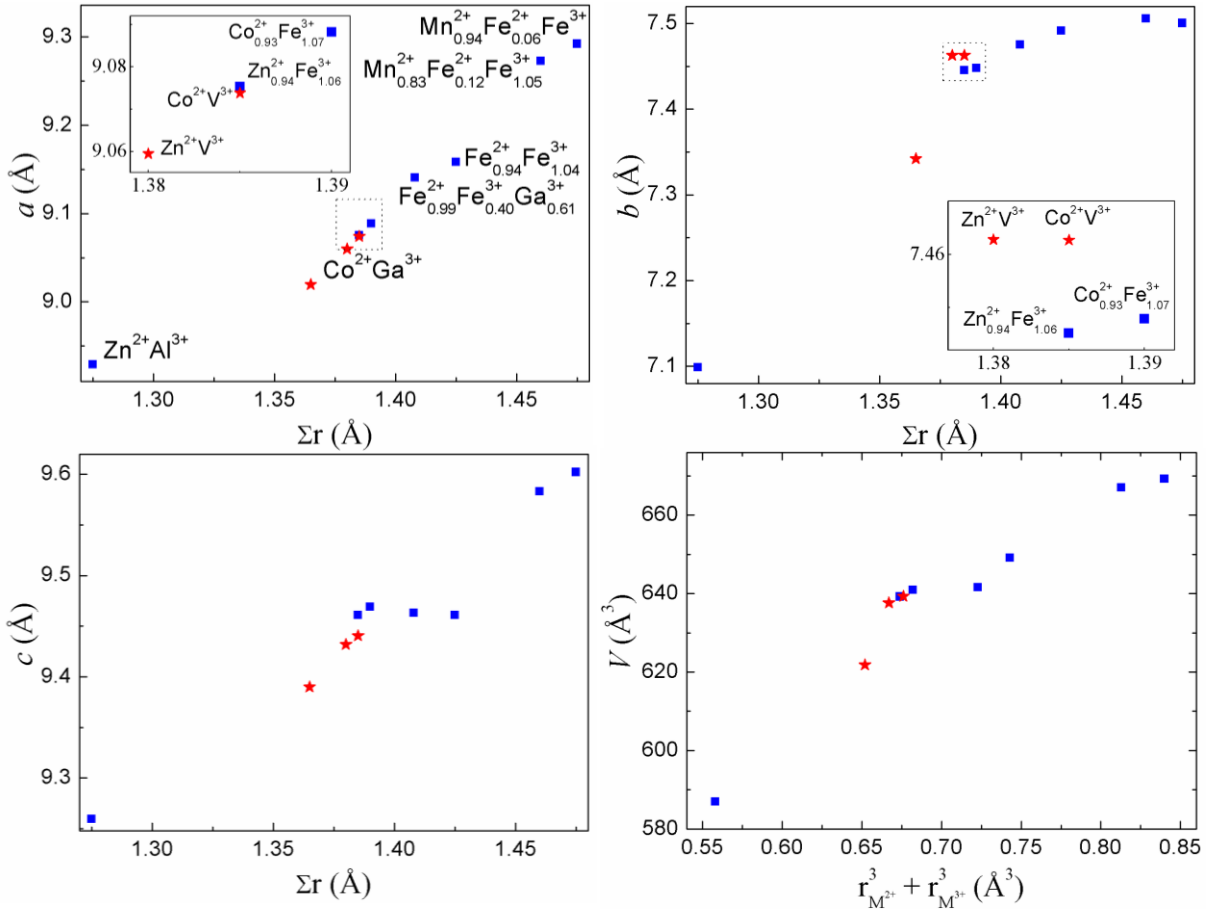

Table S2 Cell volumes of $M^{2+}M^{3+}F_5(H_2O)_2$ (values in italic) and $(M^{2+}_{1-x}M^{3+}_x)M^{3+}F_5(Htaz)_{1-x}(taz)_x$ (in bold), classified by the M^{2+} and M^{3+} ionic radii[1]. Undefined cell volumes and unsuccessful syntheses are represented by a question mark and a cross, respectively.

	Al^{3+} (0.535 Å)	Ga^{3+} (0.620 Å)	V^{3+} (0.640 Å)	Fe^{3+} (0.645 Å)	Mn^{3+} (0.645 Å)	Ti^{3+} (0.645 Å)
Ni^{2+} (0.690 Å)				*?* **X**		
Mg^{2+} (0.720 Å)	*485.7(2)*[2,3]					
Cu^{2+} (0.730 Å)			**X**	**X**	**X**	**X**
Zn^{2+} (0.740 Å)	*489.1(2)*[3] **586.9(1)**[4,5]	*515.1(2)*[3] **X**	*530.5(2)*[3] **637.7(1)**	*530.7(2)*[6] **639.2(1)**[4]	**X**	**X**
Co^{2+} (0.745 Å)	492.0(2)[3]	**621.8(1)**	**639.3(1)**	*?* **640.9(1)**[4]	**X**	**X**
Fe^{2+} (0.780 Å)	*499.7(2)*[7]	**646.6(1)**[4]	*544.7(2)*[7] **X**	*540.2(2)*[8,9] 649.1(1)[4]	**X**	
Mn^{2+} (0.830 Å)	*516.7(2)*[3]	*539.0(2)*[3] **X**	*558.5(2)*[3,10] **X**	*555.0(2)*[11] **666.9(1)**	**X**	
Cd^{2+} (0.950 Å)	*532.6(2)*[3]	*555.5(2)*[3]				

Table S3 Atomic positions, isotropic displacement parameters, selected inter-atomic distances (Å) and bond valence calculations of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$.

	Atom, *site*	x	y	z	Site occupancy	B_{iso} (Å^2)
$Co^{2+}Ga^{3+}F_5(Htaz)$	Ga(1), *4a*	½	½	½	1	1.4(1)
	Co(1), *4c*	¾	¾	¾	1	1.5(1)
	F(1), *4e*	½	¾	0.4255(6)	1	1.4(1)
	F(2), *16j*	0.6489(3)	0.5496(4)	0.6346(3)	1	1.4(1)
	N(1), *8i*	0.9289(7)	¾	0.5776(6)	1	1
	N(2), *4e*	0	¾	0.3666(10)	1	1
	C(1), *8i*	0.8819(9)	¾	0.4547(9)	1	1
$Zn^{2+}V^{3+}F_5(Htaz)$	V(1), *4a*	½	½	½	1	1.6(1)
	Zn(1), *4c*	¾	¾	¾	1	2.3(1)
	F(1), *4e*	½	¾	0.4245(6)	1	1.9(1)
	F(2), *16j*	0.6470(3)	0.5563(4)	0.6332(3)	1	1.9(1)
	N(1), *8i*	0.9250(5)	¾	0.5796(6)	1	1.3(2)
	N(2), *4e*	0	¾	0.3704(9)	1	1.3(2)
	C(1), *8i*	0.8750(8)	¾	0.4509(8)	1	1.3(2)
$Co^{2+}V^{3+}F_5(Htaz)$	V(1), *4a*	½	½	½	1	0.4(1)
	Co(1), *4c*	¾	¾	¾	1	1.0(1)
	F(1), *4e*	½	¾	0.4231(6)	1	0.9(1)
	F(2), *16j*	0.6480(3)	0.5557(4)	0.6356(3)	1	0.9(1)
	N(1), *8i*	0.9248(6)	¾	0.5793(7)	1	1
	N(2), *4e*	0	¾	0.3658(9)	1	1
	C(1), *8i*	0.8777(9)	¾	0.4515(8)	1	1
$(Zn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$	Fe(2), *4a*	½	½	½	1	1.9(1)
	Zn(1)/Fe(1), *4c*	¾	¾	¾	0.94/0.06	2.2(1)
	F(1), *4e*	½	¾	0.4240(4)	1	2.4(1)
	F(2), *16j*	0.6476(2)	0.5583(3)	0.6342(2)	1	2.4(1)
	N(1), *8i*	0.9241(4)	¾	0.5818(4)	1	1
	N(2), *4e*	0	¾	0.3686(6)	1	1
	C(1), *8i*	0.8778(6)	¾	0.4500(5)	1	1
$(Co^{2+}_{0.93}Fe^{3+}_{0.07})Fe^{3+}F_5(Htaz)_{0.93}(taz)_{0.07}$	Fe(2), *4a*	½	½	½	1	1.7(1)
	Co(1)/Fe(1), *4c*	¾	¾	¾	0.93/0.07	2.3(1)
	F(1), *4e*	½	¾	0.4246(7)	1	2.0(1)
	F(2), *16j*	0.6487(4)	0.5567(5)	0.6355(3)	1	2.0(1)
	N(1), *8i*	0.9240(8)	¾	0.5838(8)	1	2.0(2)
	N(2), *4e*	0	¾	0.3676(11)	1	2.0(2)
	C(1), *8i*	0.8791(10)	¾	0.4510(11)	1	2.0(2)
$(Fe^{2+}_{0.99}Fe^{3+}_{0.01})(Fe^{3+}_{0.39}Ga^{3+}_{0.61})F_5(Htaz)_{0.99}(taz)_{0.01}$	Fe(2)/Ga(2) *4a*	½	½	½	0.39/0.61	3.3(1)
	Fe(1), *4c*	¾	¾	¾	1	1.6(1)
	F(1), *4e*	½	¾	0.4329(8)	1	1.4(1)
	F(2), *16j*	0.6504(4)	0.5568(5)	0.6385(3)	1	1.4(1)
	N(1), *8i*	0.9219(8)	¾	0.5812(8)	1	1.1(2)
	N(2), *4e*	0	¾	0.3682(10)	1	1.1(2)
	C(1), *8i*	0.8843(10)	¾	0.4504(11)	1	1.1(2)
$(Fe^{2+}_{0.96}Fe^{3+}_{0.04})Fe^{3+}F_5(Htaz)_{0.96}(taz)_{0.04}$	Fe(2), *4a*	½	½	½	1	1.3(1)
	Fe(1), *4c*	¾	¾	¾	1	1.8(1)
	F(1), *4e*	½	¾	0.4291(5)	1	1.5(1)
	F(2), *16j*	0.6473(3)	0.5507(4)	0.6363(2)	1	1.5(1)
	N(1), *8i*	0.9256(6)	¾	0.5778(6)	1	1
	N(2), *4e*	0	¾	0.3671(7)	1	1
	C(1), *8i*	0.8800(7)	¾	0.4540(7)	1	1
$(Mn^{2+}_{0.83}Fe^{2+}_{0.12}Fe^{3+}_{0.05})Fe^{3+}F_5(Htaz)_{0.95}(taz)_{0.05}$	Fe(2), *4a*	½	½	½	1	1.0(1)
	Mn(1)/Fe(1), *4c*	¾	¾	¾	0.83/0.17	1.3(1)
	F(1), *4e*	½	¾	0.4264(5)	1	1.7(1)
	F(2), *16j*	0.6462(2)	0.5512(3)	0.6338(2)	1	1.7(1)
	N(1), *8i*	0.9286(5)	¾	0.5729(5)	1	1
	N(2), *4e*	0	¾	0.3614(7)	1	1
	C(1), *8i*	0.8862(7)	¾	0.4492(7)	1	1
$(Mn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$	Fe(2), *4a*	½	½	½	1	1
	Mn(1)/Fe(1) *4c*	¾	¾	¾	0.94/0.06	1
	F(1), *4e*	½	¾	0.4289(5)	1	1
	F(2), *16j*	0.6456(2)	0.5505(3)	0.6354(2)	1	1
	N(1), *8i*	0.9293(5)	¾	0.5708(6)	1	1
	N(2), *4e*	0	¾	0.3591(8)	1	1
	C(1), *8i*	0.8844(7)	¾	0.4458(7)	1	1

$Co^{2+}Ga^{3+}F_5(Htaz)$		
	d_{ij} (Å)	s_{ij}
Ga(1)-F(1) x 2	1.964(2)	0.39
Ga(1)-F(2) x 4	1.880(3)	0.50
Co(1)-F(2) x 4	2.042(3)	0.34
Co(1)-N(1) x 2	2.286(6)	0.30
N(1)-N(1)	1.283(9)	1.53
N(1)-C(1)	1.229(10)	1.78
Σs_{ij}		
ΣGa(1)=2.77	ΣF(1)=0.79	ΣN(1)=3.61
ΣCo(1)=1.95	ΣF(2)=0.83	

$Zn^{2+}V^{3+}F_5(Htaz)$		
	d_{ij} (Å)	s_{ij}
V(1)-F(1) x 2	1.997(2)	0.45
V(1)-F(2) x 4	1.878(3)	0.62
Zn(1)-F(2) x 4	2.043(3)	0.32
Zn(1)-N(1) x 2	2.258(5)	0.27
N(1)-N(1)	1.359(6)	1.24
N(1)-C(1)	1.296(9)	1.48
Σs_{ij}		
ΣV(1)=3.39	ΣF(1)=0.90	ΣN(1)=3.00
ΣZn(1)=1.81	ΣF(2)=0.94	

$Co^{2+}V^{3+}F_5(Htaz)$		
	d_{ij} (Å)	s_{ij}
V(1)-F(1) x 2	2.002(2)	0.44
V(1)-F(2) x 4	1.901(3)	0.58
Co(1)-F(2) x 4	2.031(3)	0.35
Co(1)-N(1) x 2	2.261(6)	0.32
N(1)-N(1)	1.365(8)	1.22
N(1)-C(1)	1.280(10)	1.55
Σs_{ij}		
ΣV(1)=3.23	ΣF(1)=0.89	ΣN(1)=3.09
ΣCo(1)=2.03	ΣF(2)=0.93	

$(Zn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$		
	d_{ij} (Å)	s_{ij}
Fe(2)-F(1) x 2	1.995(2)	0.43
Fe(2)-F(2) x 4	1.896(2)	0.56
M(1)-F(2) x 4	2.025(2)	0.34
M(1)-N(1) x 2	2.242(4)	0.28
N(1)-N(1)	1.378(5)	1.18
N(1)-C(1)	1.316(6)	1.41
Σs_{ij}		
ΣFe(1)=3.08	ΣF(1)=0.85	ΣN(1)= 2.87
ΣM(1)=1.90	ΣF(2)=0.89	

$(Co^{2+}_{0.93}Fe^{3+}_{0.07})Fe^{3+}F_5(Htaz)_{0.93}(taz)_{0.07}$		
	d_{ij} (Å)	s_{ij}
Fe(2)-F(1) x 2	1.994(2)	0.43
Fe(2)-F(2) x 4	1.911(3)	0.53
M(1)-F(2) x 4	2.024(3)	0.35
M(1)-N(1) x 2	2.231(7)	0.34
N(1)-N(1)	1.381(10)	1.17
N(1)-C(1)	1.322(13)	1.38
Σs_{ij}		
ΣFe(1)=2.99	ΣF(1)=0.85	ΣN(1)=2.90
ΣM(1)=2.11	ΣF(2)=0.89	

$(Fe^{2+}_{0.99}Fe^{3+}_{0.01})(Fe^{3+}_{0.39}Ga^{3+}_{0.61})F_5(Htaz)_{0.99}(taz)_{0.01}$		
	d_{ij} (Å)	s_{ij}
M(2)-F(1) x 2	1.974(2)	0.41
M(2)-F(2) x 4	1.946(3)	0.44
Fe(1)-F(2) x 4	2.007(3)	0.38
Fe(1)-N(1) x 2	2.240(9)	0.28
N(1)-N(1)	1.430(10)	1.03
N(1)-C(1)	1.284(13)	1.53
Σsij		
ΣM(2)=2.59	ΣF(1)=0.82	ΣN(1)=2.84
ΣFe(1)=2.08	ΣF(2)=0.82	

$(Fe^{2+}_{0.96}Fe^{3+}_{0.04})Fe^{3+}F_5(Htaz)_{0.96}(taz)_{0.04}$		
	d_{ij} (Å)	s_{ij}
Fe(2)-F(1) x 2	1.989(2)	0.43
Fe(2)-F(2) x 4	1.904(2)	0.54
Fe(1)-F(2) x 4	2.067(3)	0.32
Fe(1)-N(1) x 2	2.289(6)	0.25
N(1)-N(1)	1.363(8)	1.23
N(1)-C(1)	1.243(9)	1.71
Σs_{ij}		
ΣFe(2)=3.04	ΣF(1)=0.87	ΣN(1)=3.19
ΣFe(1)=1.79	ΣF(2)=0.87	

$(Mn^{2+}_{0.83}Fe^{2+}_{0.12}Fe^{3+}_{0.05})Fe^{3+}F_5(Htaz)_{0.95}(taz)_{0.05}$		
	d_{ij} (Å)	s_{ij}
Fe(2)-F(1) x 2	2.005(2)	0.41
Fe(2)-F(2) x 4	1.905(2)	0.54
M(1)-F(2) x 4	2.096(2)	0.31
M(1)-N(1) x 2	2.371(5)	0.24
N(1)-N(1)	1.324(7)	1.37
N(1)-C(1)	1.249(8)	1.68
Σs_{ij}		
ΣFe(2)=3.00	ΣF(1)=0.83	ΣN(1)=3.29
ΣM(1)=1.70	ΣF(2)=0.85	

$(Mn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$		
	d_{ij} (Å)	s_{ij}
Fe(2)-F(1) x 2	1.996(2)	0.42
Fe(2)-F(2) x 4	1.914(2)	0.53
M(1)-F(2) x 4	2.095(2)	0.31
M(1)-N(1) x 2	2.395(5)	0.23
N(1)-N(1)	1.314(7)	1.41
N(1)-C(1)	1.271(9)	1.59
Σs_{ij}		
ΣFe(2)=2.97	ΣF(1)=0.85	ΣN(1)=3.22
ΣM(1)=1.68	ΣF(2)= 0.84	

Fig. S3 TGA under air atmosphere of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$. The relative proportions of the final oxides are given.

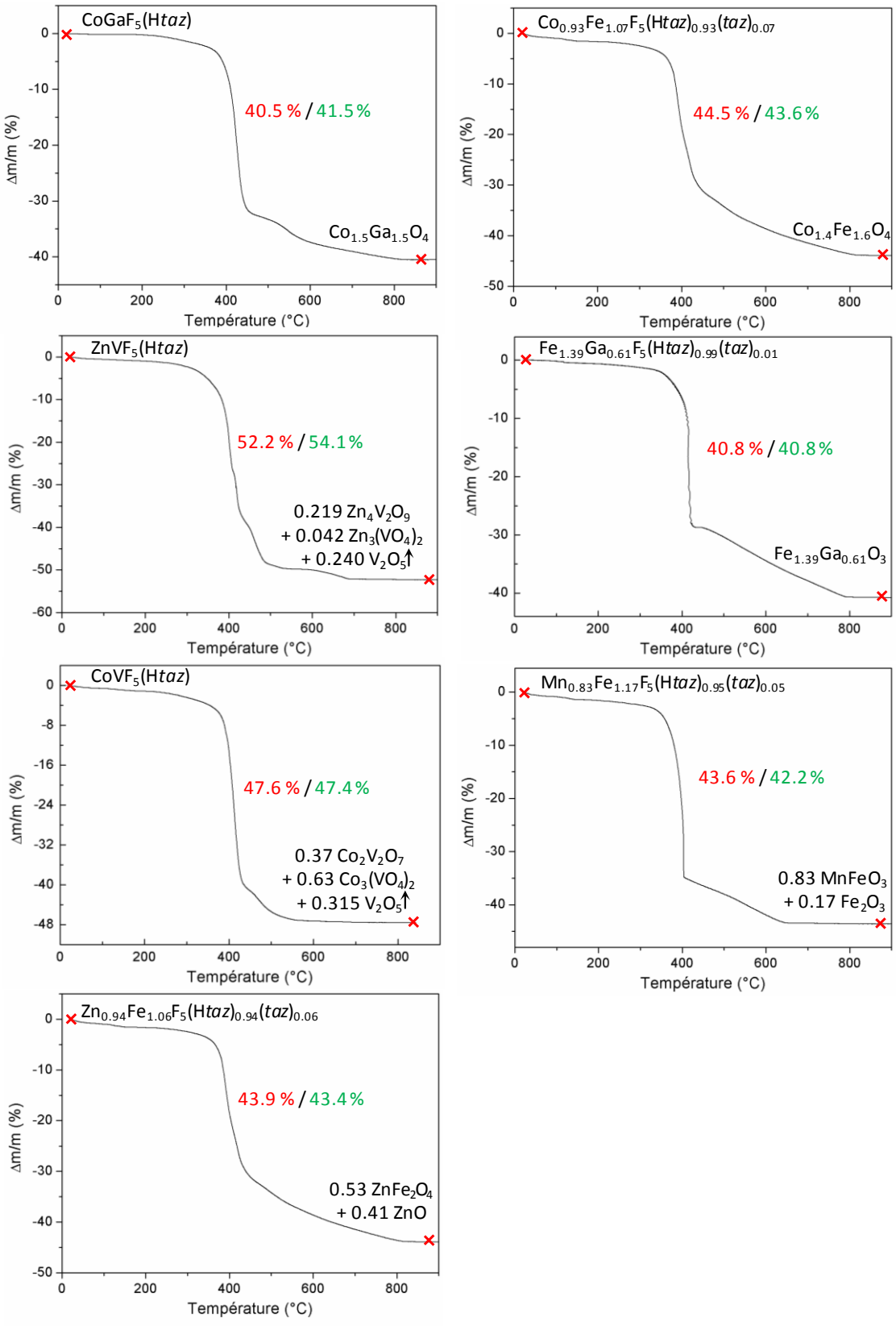

Figure S4. IR spectra of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$.

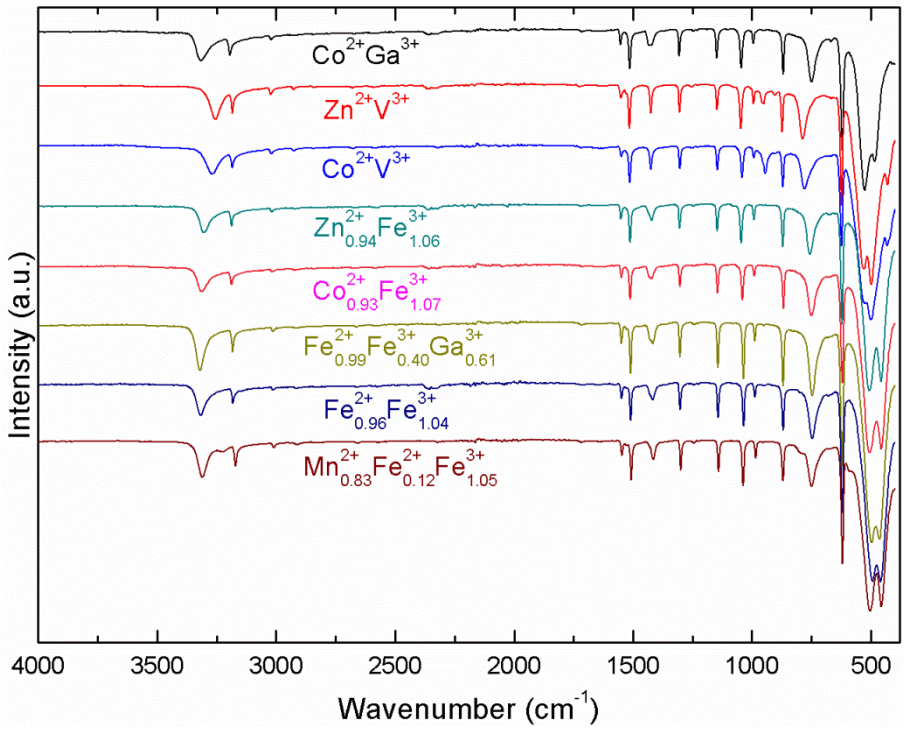

Table S4 Vibrational modes assignment, with stretching (υ) and deformation vibrations (β, γ), of infrared spectra of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$.

Mode	$Co^{2+}Ga^{3+}$	$Zn^{2+}V^{3+}$	$Co^{2+}V^{3+}$	$Zn^{2+}_{0.94}Fe^{3+}_{1.06}$	$Co^{2+}_{0.93}Fe^{3+}_{1.07}$	$Fe^{2+}_{0.99}Fe^{3+}_{0.40}Ga^{3+}_{0.61}$	$Fe^{2+}_{0.96}Fe^{3+}_{1.04}$	$Mn^{2+}_{0.83}Fe^{2+}_{0.12}Fe^{3+}_{1.05}$
υ_{N-H}	3317	3256	3270	3305	3314	3321	3317	3311
υ_{C-H}	3195	3184	3184	3187	3188	3183	3181	3171
$\upsilon_{C=N}$	1553 1514 1424	1551 1516 1426	1550 1514 1426	1551 1513 1421	1549 1512 1423	1549 1511 1417	1549 1510 1417	1547 1508 1414
υ_{N-C}, υ_{N-N}	1306	1305	1303	1304	1303	1303	1302	1300
β_{C-H}	1149	1148	1146	1147	1146	1144	1144	1142
β_{ring}	1046	1048	1042	1046	1041	1037	1036	1038
β_{N-H}	994	993	992	992	990	988	988	984
γ_{C-H}	869 750	874 788	871 781	871 757	868 752	870 748	869 747	870 750
γ_{ring}	621	624	623	621	621	621	620	620

Table S5 Isomer shift and quadrupole splitting values of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ phases at 300 K and 77 K RP or vacuum.

			δ (mm.s^{-1}) ± 0.01	ΔE_Q (mm.s^{-1}) ± 0.01	B_{hf} (T) ± 0.5	τ ± 0.02
$(Zn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$	300 K (1 bar)	Fe^{3+}	0.45	1.08	—	0.80
		Fe^{3+}	0.44	0.58	—	0.20
	300 K (vacuum)	Fe^{3+}	0.44	1.08	—	0.80
		Fe^{3+}	0.43	0.58	—	0.20
	77 K (1 bar)	Fe^{3+}	0.54	1.16	—	0.79
		Fe^{3+}	0.54	0.78	—	0.21
$(Mn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$	300 K (1 bar)	Fe^{3+}	0.45	1.05	—	0.80
		Fe^{3+}	0.45	0.68	—	0.20
	300 K (vacuum)	Fe^{3+}	0.45	1.05	—	0.86
		Fe^{3+}	0.43	0.63	—	0.14
	77 K (1 bar)	Fe^{3+}	0.55	<1.06>	<32.7>	0.87
		Fe^{3+}	0.54	0.98	—	0.13
	77 K (vacuum)	Fe^{3+}	0.54	1.09	—	0.84
		Fe^{3+}	0.53	0.69	—	0.16
$(Mn^{2+}_{0.83}Fe^{2+}_{0.12}Fe^{3+}_{0.05})Fe^{3+}F_5(Htaz)_{0.95}(taz)_{0.05}$	300 K (1 bar)	Fe^{3+}	0.45	1.04	—	0.75
		Fe^{3+}	0.45	0.65	—	0.14
		Fe^{2+}	1.27	2.84	—	0.11
	300 K (vacuum)	Fe^{3+}	0.45	1.03	—	0.74
		Fe^{3+}	0.45	0.61	—	0.17
		Fe^{2+}	1.28	2.85	—	0.09
	77 K (1 bar)	Fe^{3+}	<0.55>	<0.98>	<34.4>	0.86
		Fe^{2+}	<1.35>	<0.03>	<16.4>	0.14
	77 K (vacuum)	Fe^{3+}	<0.55>	<0.91>	<18.5>	0.57
		Fe^{3+}	0.55	0.99	—	0.34
		Fe^{2+}	1.35	2.99	—	0.09
$(Co^{2+}_{0.93}Fe^{3+}_{0.07})Fe^{3+}F_5(Htaz)_{0.93}(taz)_{0.07}$	300 K (1 bar)	Fe^{3+}	0.46	1.06	—	0.78
		Fe^{3+}	0.44	0.60	—	0.22
	300 K (vacuum)	Fe^{3+}	0.46	1.06	—	0.78
		Fe^{3+}	0.44	0.63	—	0.22
	77 K (1 bar)	Fe^{3+}	0.55	1.09	—	0.49
		Fe^{3+}	<0.52>	<0.36>	<18.3>	0.34
		Fe^{3+}	0.58	0.65	—	0.17
	77 K (vacuum)	Fe^{3+}	0.54	1.10	—	0.78
		Fe^{3+}	0.54	0.62	—	0.22
$(Fe^{2+}_{0.99}Fe^{3+}_{0.01})(Fe^{3+}_{0.39}Ga^{3+}_{0.61})F_5(Htaz)_{0.99}(taz)_{0.01}$	300 K (1 bar)	Fe^{3+}	0.46	1.02	—	0.26
		Fe^{3+}	0.46	0.48	—	0.02
		Fe^{2+}	1.27	3.00	—	0.72
	300 K (vacuum)	Fe^{3+}	0.46	1.01	—	0.21
		Fe^{3+}	0.43	0.60	—	0.08
		Fe^{2+}	1.27	2.99	—	0.71
	77 K (1 bar)	Fe^{3+}	0.54	1.07	—	0.26
		Fe^{2+}	1.38	3.56	—	0.74
$(Fe^{2+}_{0.96}Fe^{3+}_{0.04})Fe^{3+}F_5(Htaz)_{0.96}(taz)_{0.04}$	300 K (1 bar)	Fe^{3+}	0.45	1.02	—	0.46
		Fe^{3+}	0.45	0.64	—	0.07
		Fe^{2+}	1.26	2.93	—	0.47
	300 K (vacuum)	Fe^{3+}	0.45	1.05	—	0.39
		Fe^{3+}	0.43	0.63	—	0.14
		Fe^{2+}	1.26	2.93	—	0.47
	77 K (1 bar)	Fe^{3+}	<0.59>	<0.76>	<25.5>	0.54
		Fe^{2+}	<1.38>	<3.67>	<14.4>	0.46
	77 K (vacuum)	Fe^{3+}	0.52	1.07	—	0.42
		Fe^{3+}	0.52	0.64	—	0.10
		Fe^{2+}	1.345	3.26	—	0.48

Table S6 Superexchange M-F-M angles, metal-metal distances and magnetic ordering temperatures of $(M^{2+}_{1-x}M^{3+}_{x})M^{3+}F_5(Htaz)_{1-x}(taz)_x$ compared with $M^{2+}M^{3+}F_5(H_2O)_2$ previously reported in the literature. Undefined angles and distances are represented by a question mark.

$Co^{2+}V^{3+}F_5(Htaz)$, T_N = 18(1) K			
V^{3+}-$F_{ax.}$-V^{3+}	137.5(1)°		
V^{3+}-$F_{eq.}$-Co^{2+}	146.7(1)°		
V^{3+}-V^{3+}	3.7313(2) Å		
V^{3+}-Co^{2+}	3.7679(1) Å		
$(Zn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$, T_N = 27(1) K		$Zn^{2+}Fe^{3+}F_5(H_2O)_2$, T_N = 9(2) K [6]	
Fe^{3+}-$F_{ax.}$-Fe^{3+}	137.8(1)°	Fe^{3+}-$F_{ax.}$-Fe^{3+}	146.0(1)°
Fe^{3+}-$F_{eq.}$-Zn^{2+},Fe^{3+}	148.0(1)°	Fe^{3+}-$F_{eq.}$-Zn^{2+}	134.7(1)°
Fe^{3+}-Fe^{3+}	3.7226(1) Å	Fe^{3+}-Fe^{3+}	3.737(7) Å
Fe^{3+}-Zn^{2+},Fe^{3+}	3.7691(1) Å	Fe^{3+}-Zn^{2+}	3.668(7) Å
$(Co^{2+}_{0.93}Fe^{3+}_{0.07})Fe^{3+}F_5(Htaz)_{0.93}(taz)_{0.07}$, T_N = 82(1) K		$Co^{2+}Fe^{3+}F_5(H_2O)_2$, T_N = 27(1) K [12]	
Fe^{3+}-$F_{ax.}$-Fe^{3+}	138.0(1)°	Fe^{3+}-$F_{ax.}$-Fe^{3+}	?
Fe^{3+}-$F_{eq.}$-Co^{2+},Fe^{3+}	147.0(1)°	Fe^{3+}-$F_{eq.}$-Co^{2+}	?
Fe^{3+}-Fe^{3+}	3.7239(2) Å	Fe^{3+}-Fe^{3+}	?
Fe^{3+}-Co^{2+},Fe^{3+}	3.7727(1) Å	Fe^{3+}-Co^{2+}	?
$(Mn^{2+}_{0.94}Fe^{3+}_{0.06})Fe^{3+}F_5(Htaz)_{0.94}(taz)_{0.06}$, T_N = 100(1) K		$Mn^{2+}Fe^{3+}F_5(H_2O)_2$, T_N = 39(1) K [6]	
Fe^{3+}-$F_{ax.}$-Fe^{3+}	140.0(1)°	Fe^{3+}-$F_{ax.}$-Fe^{3+}	150.6(1)°
Fe^{3+}-$F_{eq.}$-Mn^{2+},Fe^{3+}	145.6(1)°	Fe^{3+}-$F_{eq.}$-Mn^{2+}	134.8(1)°
Fe^{3+}-Fe^{3+}	3.7501(1) Å	Fe^{3+}-Fe^{3+}	3.782(7) Å
Fe^{3+}-Mn^{2+},Fe^{3+}	3.8307(1) Å	Fe^{3+}-Mn^{2+}	3.719(7) Å

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