Electronic Supplementary Information

Fluorinated mixed valence Fe(II)-Fe(III) phosphites with channels templated by linear tetramine chains. Structural and magnetic implications of partial replacement of Fe(II) by Co(II)

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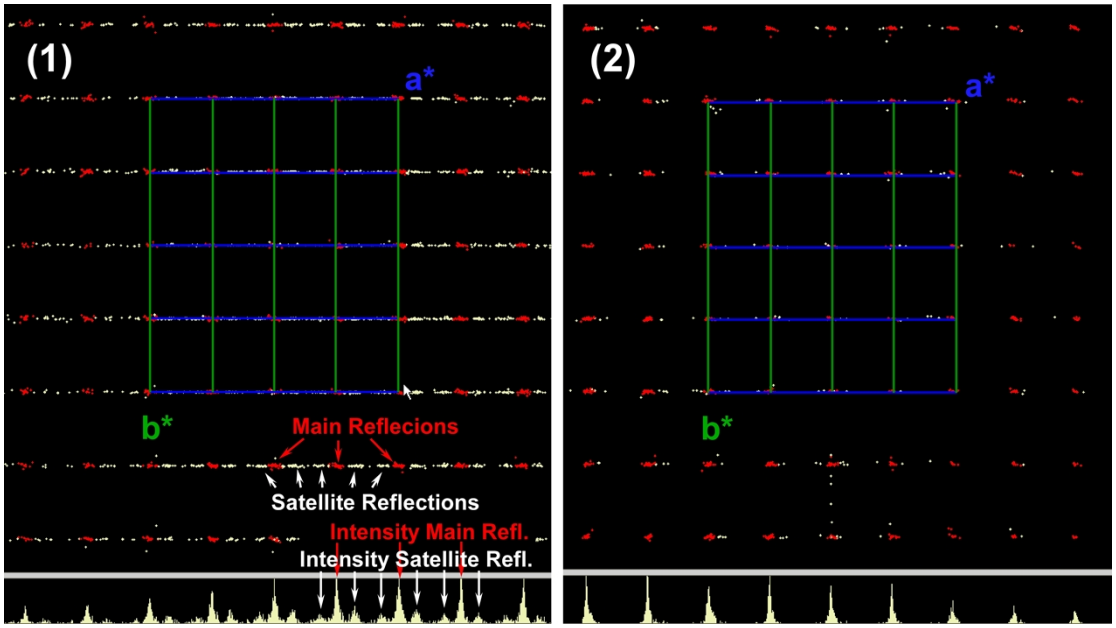


Figure S1. View of the unit cells of the compounds **1** and **2** along the c* axis.

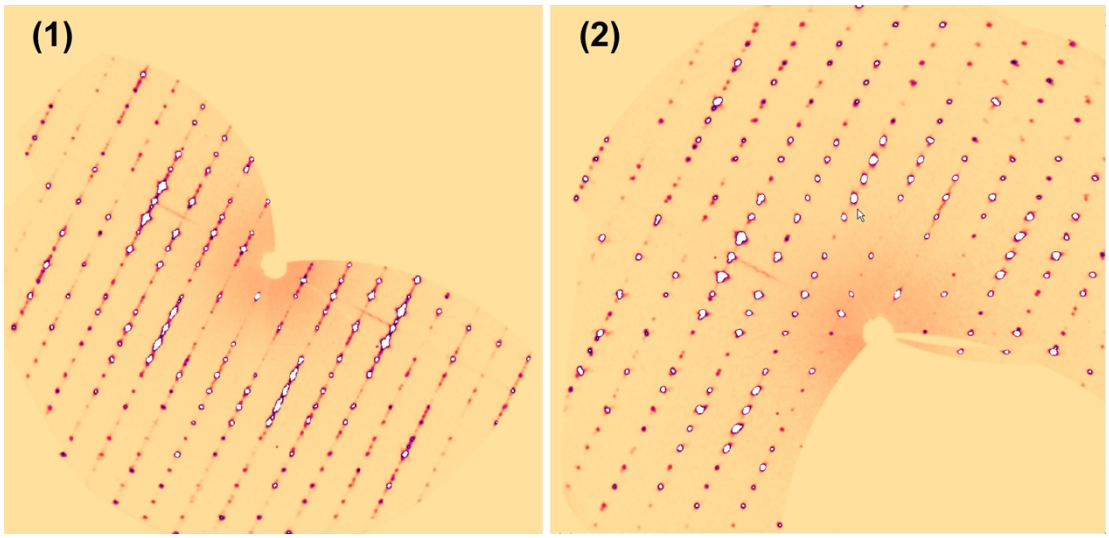


Figure S2. Reconstruction of the h0l layers of the diffraction patterns of **1** and **2**.

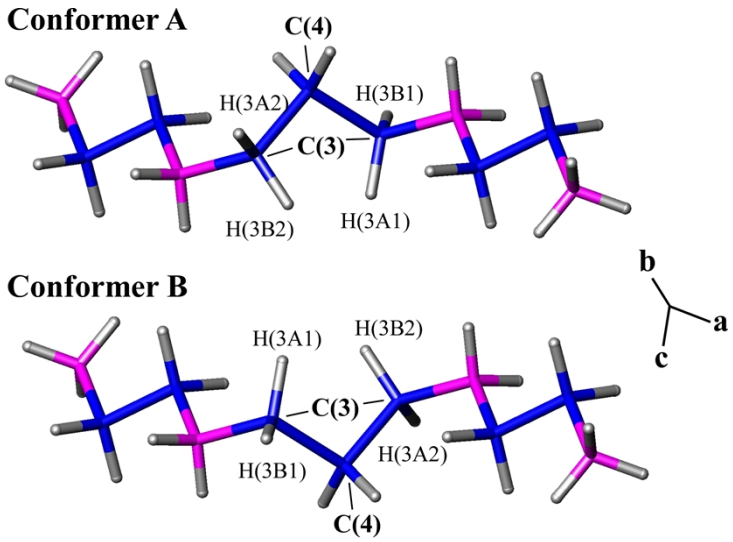


Figure S3. Conformers A and B of the organic molecule.

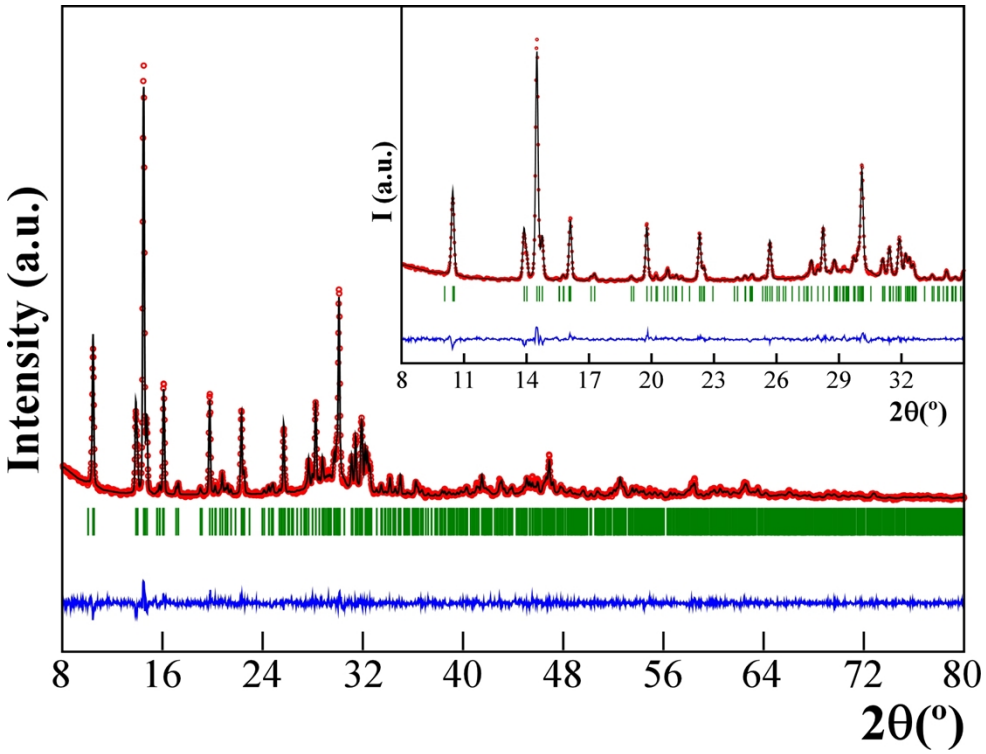


Figure S4. Observed (red dots), calculated (black line) and difference X-ray powder diffraction pattern (blue line) for the Rietveld structure analysis of **3**. Diffraction pattern recorded using a Bruker D8 Advance Vario powder diffractometer (Cu-$K_{\alpha 1}$ = 1.5406 Å).

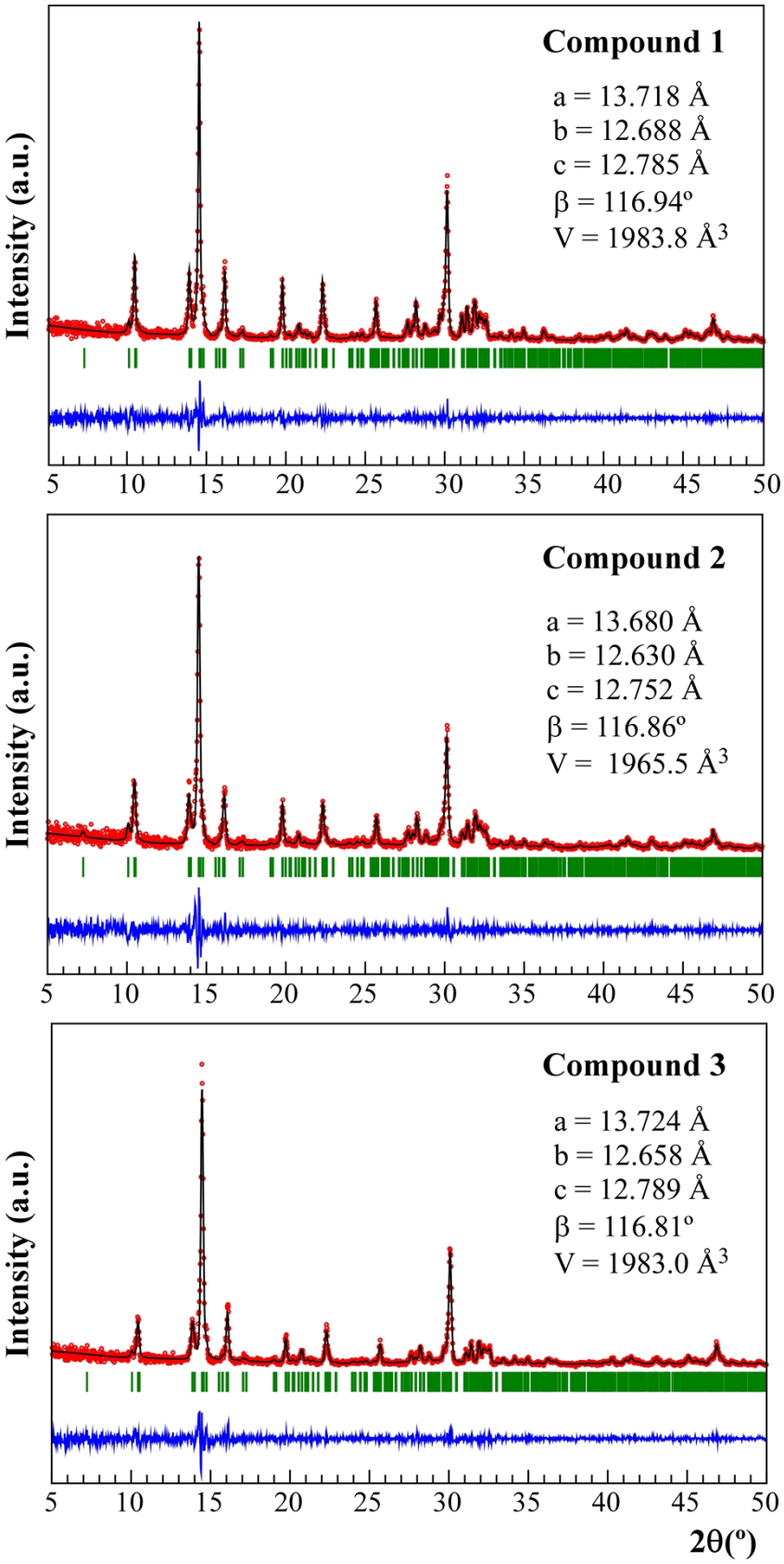


Figure S5. Observed, calculated and difference X-ray powder diffraction pattern for the pattern matching analysis of **1**, **2** and **3**. Diffraction patterns recorded using a PANalytical X´Pert PRO powder diffractometer (Cu-K_α radiation).

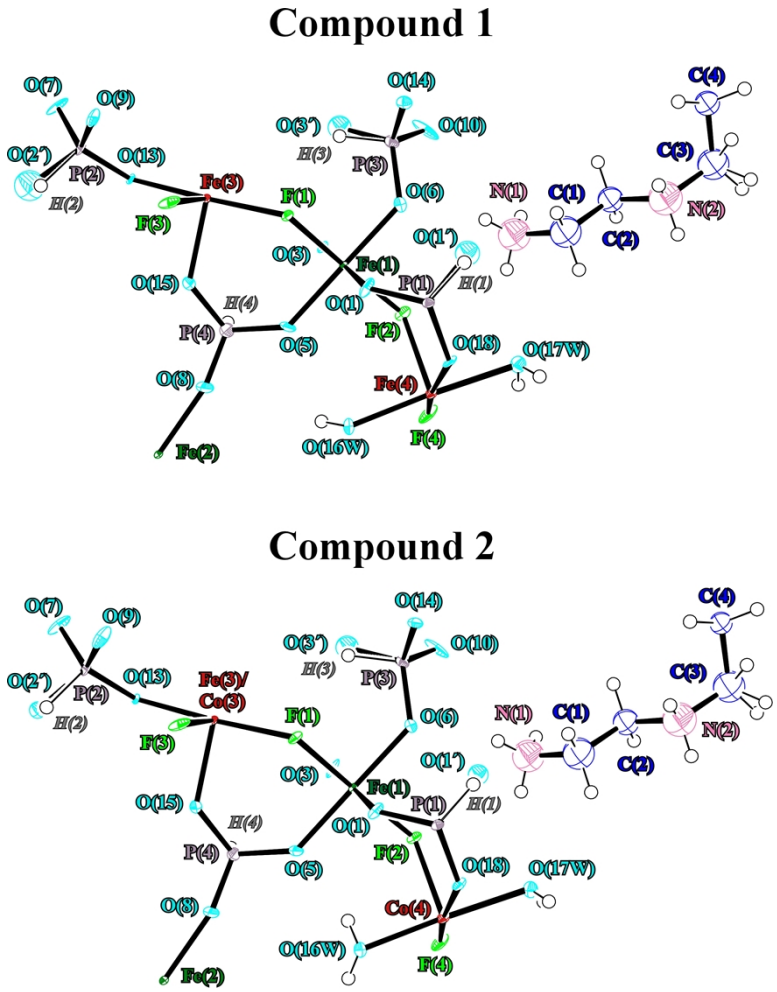


Figure S6. Thermal ellipsoid plots (50% probability) and atomic labelling schemes of compounds **1** and **2**.

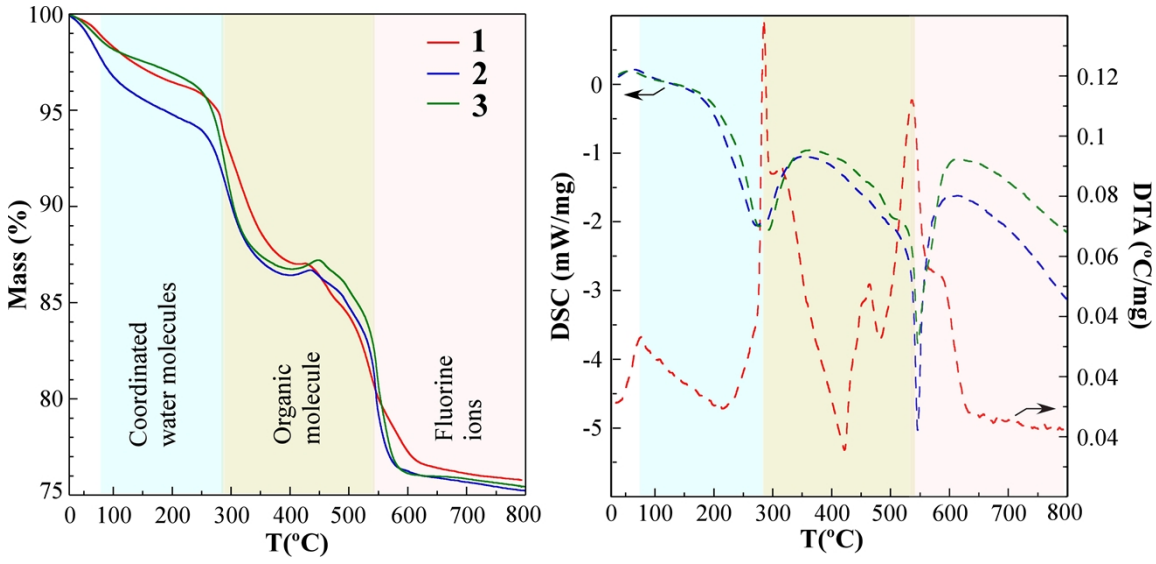


Figure S7. (a) TGA curves and **(b)** DSC and DTA curves of **1**, **2** and **3**.

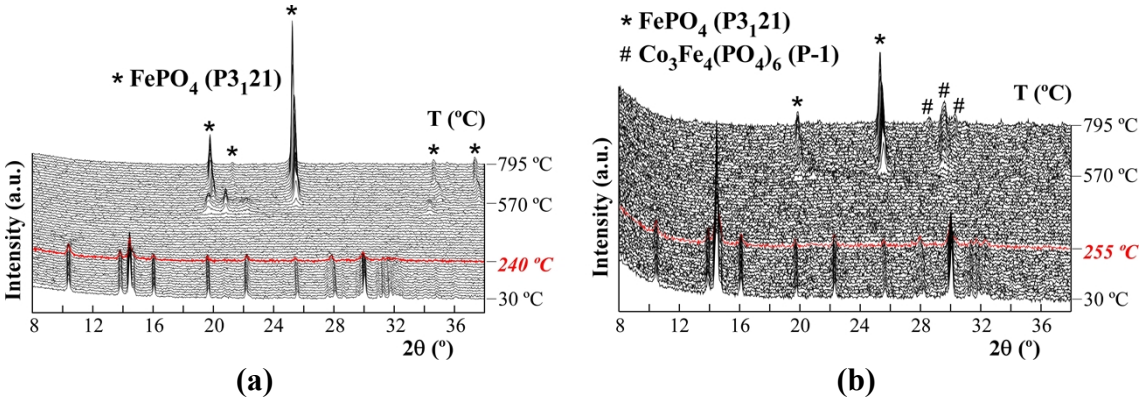


Figure S8. Thermodiffractograms of **(a) 1** and **(b) 3**.

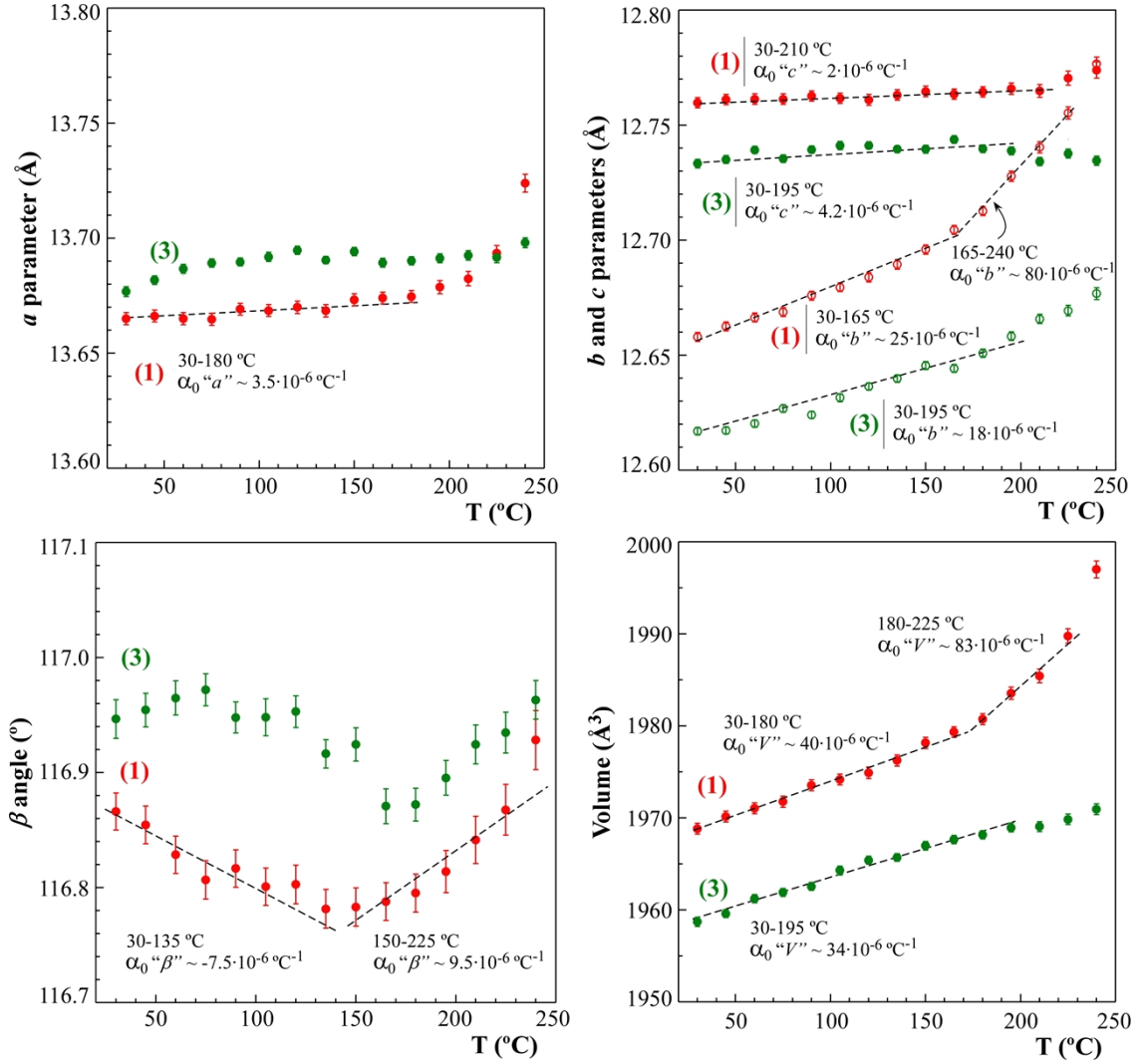


Figure S9. Thermal evolution of the parameters and volume of the unit cells for **1** and **3** in the 30 to 250 ºC temperature range.

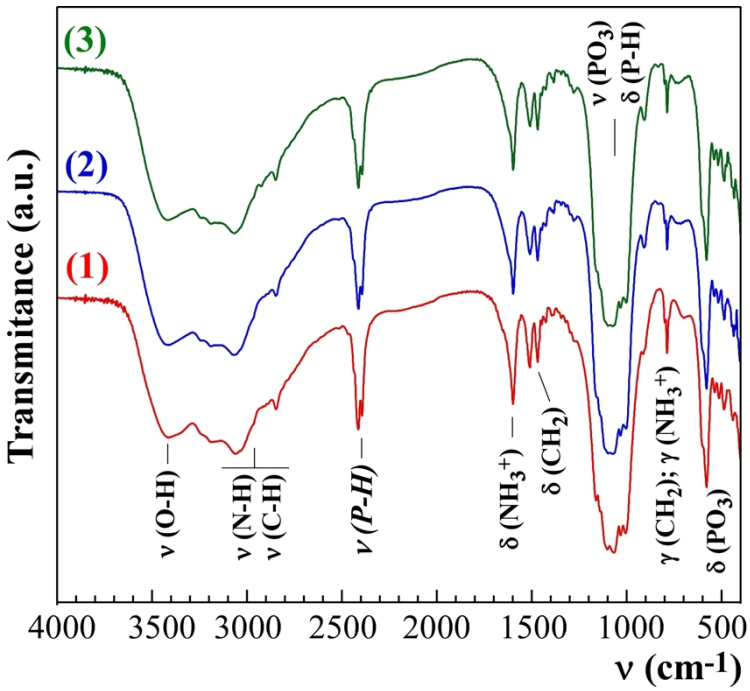


Figure S10. Infrared spectra of the compounds **1**, **2** and **3** in the 400 to 4000 cm^{-1} frequency range.

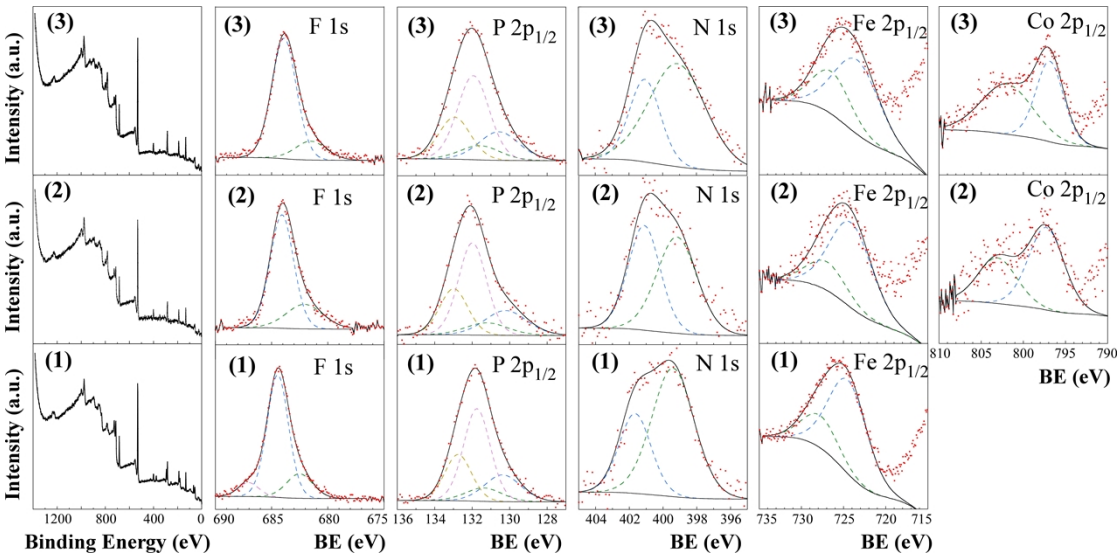


Figure S11. XPS spectra of compounds **1**, **2** and **3**.

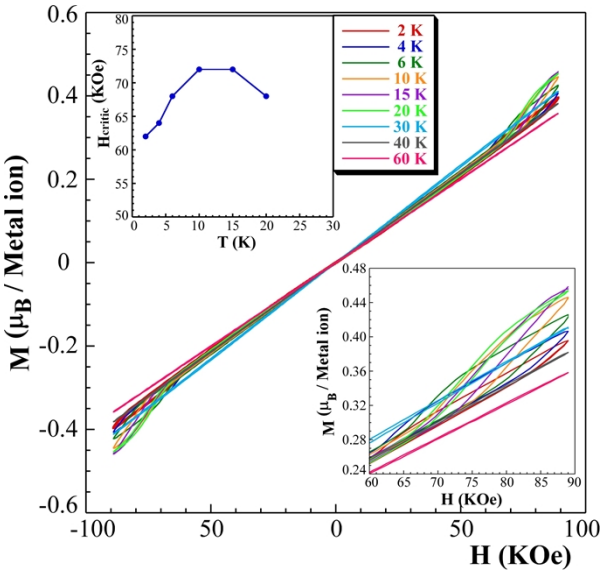


Figure S12. Magnetization *vs* applied magnetic field at different temperatures for **3**. The lower inset shows the detail of the metamagnetic transition and the upper inset the thermal evolution of the critical field of the metamagnetic transition.

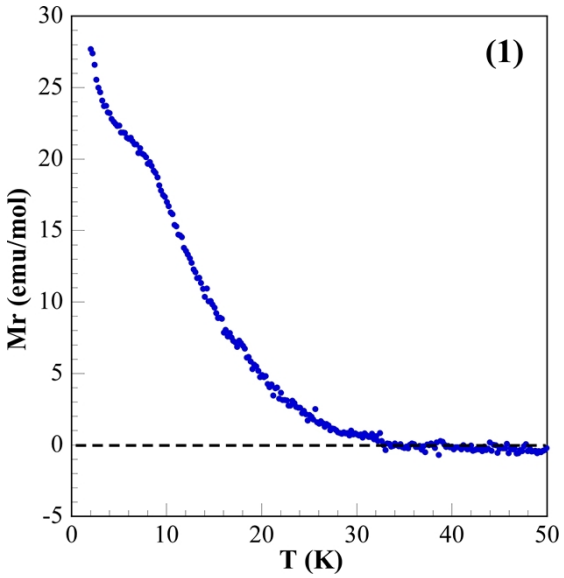


Figure S13. Temperature dependence of the thermoremanent magnetization (TRM) between 2 and 50 K for **1**.

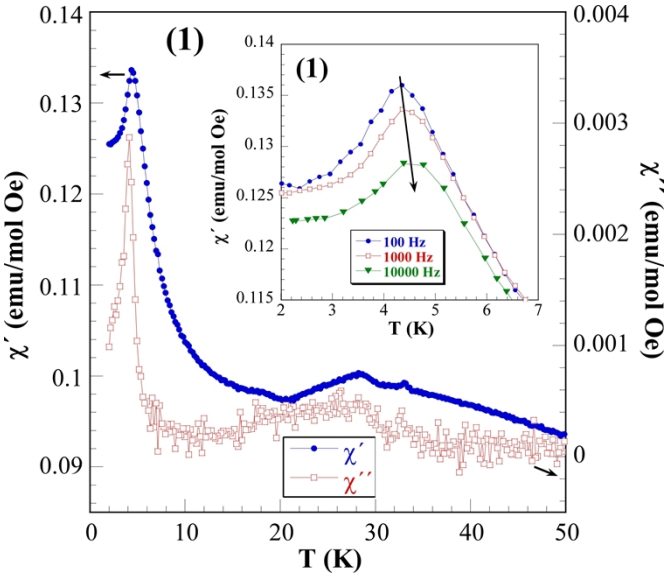
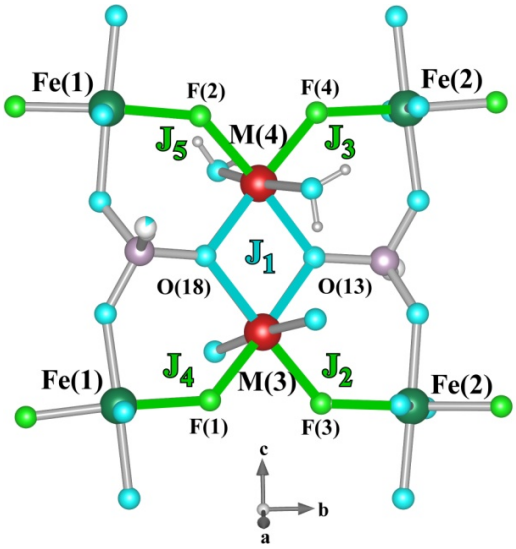
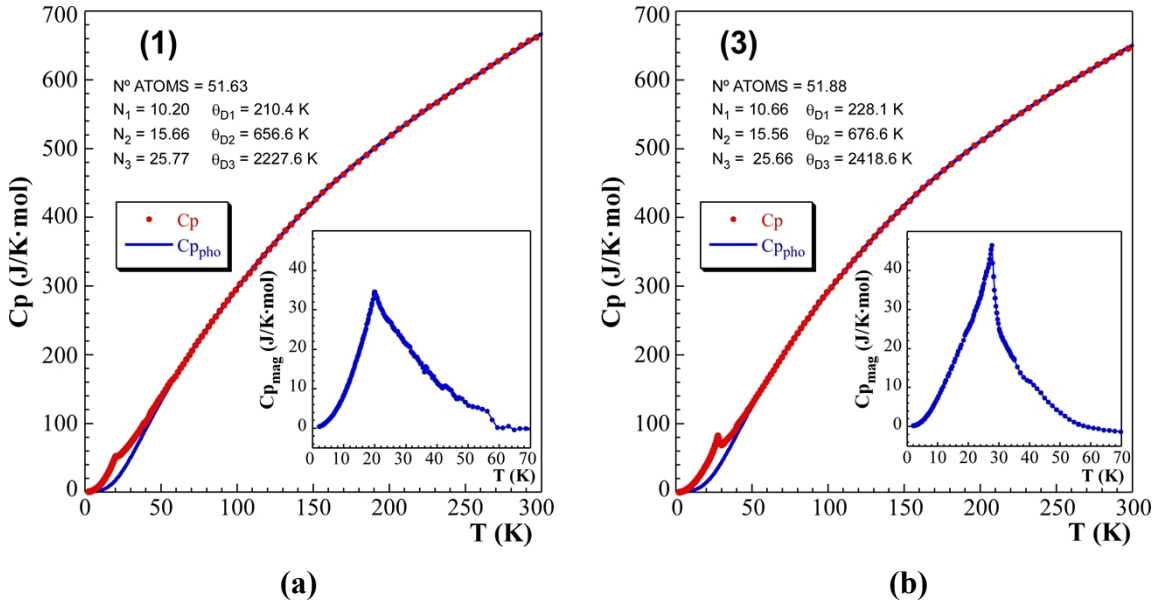


Figure S14. Temperature dependence of the real (χ′) and imaginary (χ″) components of the ac magnetic susceptibility for compound **1** measured with applied field h_{ac} = 10 Oe and at a frequency ν = 1000 Hz. The insets show the in-phase (χ′) component of **1** under different excitation frequencies at driving field of 10Oe.



		Intralayer Super magnetic exchange			
		M-O-M		distance M-M	
Pathway		(1)	(2)	(1)	(2)
J_1	M(4)-O(13)-M(3)	97.8(3)	97.8(2)	3.21	3.18
	M(4)-O(18)-M(3)	100.1(3)	99.3(2)		
J_2	Fe(2)-F(3)-M(3)	124.5(3)	125.6(2)	3.57	3.56
J_3	Fe(2)-F(4)-M(4)	132.0(3)	132.7(2)	3.61	3.61
J_4	Fe(1)-F(1)-M(3)	126.8(3)	127.5(2)	3.63	3.62
J_5	Fe(1)-F(2)-M(4)	126.5(3)	127.3(2)	3.69	3.69

Figure S15. Schematic view of the most important magnetic exchange pathways for compounds **1** to **3.** Bond lengths (Å) and angles (º) obtained from single crystal X-ray diffraction for **1** and **2** and related to the possible magnetic exchange pathways.



(a) **(b)**

Figure S16. Thermal evolution of Cp, Cphon, and Cmag of phases **(a) 1** and **(b) 3**. The lower insets show a detail of the magnetic contribution, Cmag.

Table S1. Bond distances (Å) and angles (°) for **1**.

[Fe(1)O_4F_2] octahedron

Fe(1)	F(1)	O(3)	O(6)	F(2)	O(5)	O(1)
O(1)	86.1(3)	178.5(3)	88.8(3)	90.4(3)	89.7(3)	***2.011(7)***
O(5)	89.3(3)	89.0(3)	178.4(3)	92.7(3)	***1.986(7)***	
F(2)	176.0(3)	89.1(3)	87.5(3)	***1.983(6)***		
O(6)	90.4(3)	92.6(3)	***1.975(7)***			
O(3)	94.5(3)	***1.962(7)***				
F(1)	***1.944(6)***					

[Fe(2)O_4F_2] octahedron

Fe(2)	F(3)^{iv}	O(8)	O(9)^{iv}	F(4)^{iii}	O(10)^{ix}	O(7)^{ii}
O(7)^{ii}	87.0(3)	92.2(4)	177.4(3)	94.2(3)	87.3(4)	***1.997(7)***
O(10)^{ix}	89.8(3)	177.8(4)	90.3(3)	85.0(3)	***1.993(8)***	
F(4)^{iii}	174.7(3)	92.9(4)	86.5(3)	***1.960(6)***		
O(9)^{iv}	92.2(3)	90.3(4)	***1.950(7)***			
O(8)	92.3(4)	***1.938(9)***				
F(3)^{iv}	***1.929(6)***					

[M(3)O_4F_2] octahedron

Fe(3)	O(15)	O(14)^{vii}	F(3)	F(1)	O(18)^{viii}	O(13)
O(13)	92.7(3)	88.7(3)	96.2(3)	175.7(2)	79.8(3)	***2.149(7)***
O(18)^{viii}	95.7(3)	89.2(3)	175.6(3)	96.4(3)	***2.126(7)***	
F(1)	89.7(3)	89.4(3)	87.7(2)	***2.114(6)***		
F(3)	82.6(3)	92.5(3)	***2.103(6)***			
O(14)^{vii}	175.1(3)	***2.084(7)***				
O(15)	***2.060(7)***					

[M(4)$O_2(H_2O)_2F_2$] octahedron

Fe(4)	F(4)	O(18)	O(16W)	O(13)^{vi}	F(2)	O(17W)
O(17W)	83.2(3)	85.5(3)	171.7(3)	88.2(3)	86.7(3)	***2.274(8)***
F(2)	86.1(3)	91.2(3)	94.1(3)	171.8(3)	***2.148(6)***	
O(13)^{vi}	99.6(3)	82.1(3)	91.9(3)	***2.112(7)***		
O(16W)	88.5(3)	102.8(3)	***2.105(7)***			
O(18)	168.5(3)	***2.062(7)***				
F(4)	***1.996(6)***					

Table S1. Continuation.

[HP(1)O$_3$] pseudotetrahedron

P(1)	**O(1´)**	**O(1)**	**O(3)^{v1}**	**O(18)**	**H(1)**
H(1)	4(2)	107.9(7)	107.2(7)	106.7(7)	***1.31(5)***
O(18)	108(2)	111.7(4)	111.8(4)	***1.539(7)***	
O(3)^{v1}	109(2)	111.2(4)	***1.529(7)***		
O(1)	104(2)	***1.517(7)***			
O(1´)	***1.55(4)***				

[HP(2)O$_3$] pseudotetrahedron

P(2)	**O(2´)**	**O(7)**	**O(13)**	**O(9)**	**H(2)**
H(2)	7(5)	108.2(7)	107.5(7)	106.5(7)	***1.31(5)***
O(9)	106(5)	109.0(4)	112.9(4)	***1.533(7)***	
O(13)	113(5)	112.4(4)	***1.517(7)***		
O(7)	102(5)	***1.503(7)***			
O(2´)	***1.50(5)***				

[HP(3)O$_4$] pseudotetrahedron

P(3)	**O(3´)**	**O(14)**	**O(10)**	**O(6)**	**H(3)**
H(3)	16(3)	108.2(7)	107.1(7)	106.7(7)	***1.31(5)***
O(6)	117(2)	111.6(4)	108.1(5)	***1.544(8)***	
O(10)	92(3)	114.8(4)	***1.535(8)***		
O(14)	112(2)	***1.517(7)***			
O(3´)	***1.49(4)***				

O(1´), O(2´) and O(3´) are the oxygen atoms of the tetrahedral groups

[HP(4)O$_3$] pseudotetrahedron

P(4)	**O(8)**	**O(15)**	**O(5)**	**H(4)**
H(4)	109(7)	103(7)	108(7)	***1.32(5)***
O(5)	108.2(5)	114.4(4)	***1.533(8)***	
O(15)	113.6(5)	***1.515(8)***		
O(8)	***1.482(9)***			

N,N'-Bis(2-aminoethyl)-1,3-propanediamine (baepn = $C_7N_4H_{20}$)

C(1)-N(1)	1.508(16)	**N(1)-C(1)-C(2)**	108.8(13)
C(1)-C(2)	1.524(15)	**N(2)-C(2)-C(1)**	110.2(12)
C(2)-N(2)	1.481(15)	**N(2)-C(3)-C(4)^{i}**	113.8(15)
C(3)-N(2)	1.499(15)	**N(2)-C(3)-C(4)**	106.2(10)
C(3)-C(4)^{i}	1.50(2)	**C(4)-C(3)-C(4)**	72.4(18)
C(3)-C(4)	1.53(2)	**C(3)-C(4)-C(3)**	107.6(18)
C(4)-C(3)	1.50(2)	**C(3)-N(2)-C(2)**	118.8(14)

Torsion angles	
N(1)-C(1)-C(2)-N(2)	-176.48(11)
C(1)-C(2)-N(2)-C(3)	-174.53(10)
C(2)-N(2)-C(3)-C(4)	**Conformer A** 87.70(14)
	Conformer B 10.23(17)
N(2)-C(3)-C(4)^{i}-C(3)^{i}	**Conformer A** -110.40(13)
	Conformer B -100.35(13)

Symmetry codes: *i* = -x-1, -y+1, -z; *ii* = -x+1, -y, -z; *iii* = -x+1, y-1/2, -z+1/2; *iv* = -x+1, y+1/2, -z+1/2; *v* = x-1, -y+1/2, z-1/2; *vi* = x, -y+1/2, z+1/2; *vii* = -x, -y, -z; *viii* = x, -y+1/2, z-1/2; *ix* = x+1, -y+1/2, z+1/2.

Table S2. Bond distances (Å) and angles (°) for **2**.

[Fe(1)O$_4$F$_2$] octahedron

Fe(1)	**F(1)**	**O(3)**	**O(6)**	**O(5)**	**F(2)**	**O(1)**
O(1)	86.7(2)	178.4(2)	89.1(2)	89.5(2)	89.7(2)	***2.000(5)***
F(2)	176.0(2)	88.9(2)	87.4(2)	92.7(2)	***1.992(5)***	
O(5)	89.1(2)	89.8(3)	178.6(3)	***1.989(6)***		
O(6)	90.8(2)	91.6(2)	***1.983(6)***			
O(3)	94.8(2)	***1.981(6)***				
F(1)	***1.949(5)***					

[Fe(2)O$_4$F$_2$] octahedron

Fe(2)	**F(3)^{iv}**	**O(8)**	**F(4)^{iii}**	**O(9)^{iv}**	**O(7)^{ii}**	**O(10)^{ix}**
O(10)^{ix}	89.3(3)	177.9(3)	85.5(3)	89.6(3)	87.2(3)	***2.000(6)***
O(7)^{ii}	87.0(2)	92.5(3)	94.1(2)	176.7(3)	***1.982(6)***	
O(9)^{iv}	92.2(2)	90.7(3)	86.4(2)	***1.974(6)***		
F(4)^{iii}	174.7(2)	92.4(3)	***1.950(5)***			
O(8)	92.8(3)	***1.936(6)***				
F(3)^{iv}	***1.929(5)***					

[M(3)O$_4$F$_2$] octahedron

Fe(3)/Co(3)	**O(15)**	**O(14)^{vii}**	**F(3)**	**F(1)**	**O(18)^{viii}**	**O(13)**
O(13)	93.6(2)	87.8(2)	96.4(2)	175.0(2)	80.3(2)	***2.125(5)***
O(18)^{viii}	95.6(2)	89.3(2)	176.3(2)	95.5(2)	***2.116(5)***	
F(1)	89.6(2)	89.4(2)	88.0(2)	***2.089(5)***		
F(3)	83.0(2)	92.2(2)	***2.078(5)***			
O(14)^{vii}	175.1(2)	***2.072(5)***				
O(15)	***2.059(6)***					

[M(4)O$_2$(H$_2$O)$_2$F$_2$] octahedron

Co(4)	**F(4)**	**O(18)**	**O(16W)**	**O(13)^{vi}**	**F(2)**	**O(17W)**
O(17W)	84.4(2)	86.6(2)	172.8(2)	88.3(2)	87.6(2)	***2.215(6)***
F(2)	86.5(2)	91.6(2)	93.3(2)	172.8(2)	***2.125(5)***	
O(13)^{vi}	98.9(2)	82.4(2)	91.5(2)	***2.095(5)***		
O(16W)	88.5(2)	100.6(2)	***2.086(6)***			
O(18)	170.8(2)	***2.056(5)***				
F(4)	***1.995(5)***					

Table S2. Continuation.

[HP(1)O$_4$] pseudotetrahedron

P(1)	O(1´)	O(3)^{v1}	O(1)	O(18)	H(1)
H(1)	2(2)	107.1(7)	107.0(7)	106.9(7)	***1.32(5)***
O(18)	109(2)	112.8(3)	111.6(3)	***1.526(6)***	
O(1)	105(2)	111.2(3)	***1.524(6)***		
O(3)^{v1}	107(2)	***1.522(6)***			
O(1´)	***1.59(3)***				

[HP(2)O$_4$] pseudotetrahedron

P(2)	O(2´)	O(7)	O(13)	O(9)	H(2)
H(2)	5(3)	108.0(7)	107.6(7)	107.2(7)	***1.32(5)***
O(9)	109(3)	108.1(4)	113.1(3)	***1.526(6)***	
O(13)	110(3)	112.6(3)	***1.521(5)***		
O(7)	103(3)	***1.512(6)***			
O(2´)	***1.50(4)***				

[HP(3)O$_4$] pseudotetrahedron

P(3)	O(3´)	O(14)	O(10)	O(6)	H(3)
H(3)	15(2)	107.9(7)	107.4(7)	107.0(7)	***1.32(5)***
O(6)	116(2)	111.6(3)	108.3(4)	***1.540(6)***	
O(10)	93(2)	114.4(3)	***1.532(6)***		
O(14)	113(2)	***1.524(6)***			
O(3´)	***1.52(4)***				

O(1´), O(2´) and O(3´) are the oxygen atoms of the tetrahedral groups

[HP(4)O$_3$] pseudotetrahedron

P(4)	O(8)	O(15)	O(5)	H(4)
H(4)	109(4)	103(5)	110(4)	***1.32(5)***
O(5)	107.9(4)	114.3(3)	***1.532(6)***	
O(15)	112.8(4)	***1.506(6)***		
O(8)	***1.493(7)***			

N,N'-Bis(2-aminoethyl)-1,3-propanediamine (baepn = $C_7N_4H_{20}$)

C(1)-N(1)	1.496(13)	**N(1)-C(1)-C(2)**	109.5(10)
C(1)-C(2)	1.500(13)	**N(2)-C(2)-C(1)**	111.7(9)
C(2)-N(2)	1.481(11)	**N(2)-C(3)-C(4)^{i}**	113.8(11)
C(3)-N(2)	1.473(13)	**N(2)-C(3)-C(4)**	106.0(8)
C(3)-C(4)^{i}	1.508(16)	**C(4)-C(3)-C(4)**	70.1(13)
C(3)-C(4)	1.567(16)	**C(3)-C(4)-C(3)**	109.9(13)
C(4)-C(3)	1.508(16)	**C(3)-N(2)-C(2)**	119.9(9)

Torsion angles	
N(1)-C(1)-C(2)-N(2)	-178.15(9)
C(1)-C(2)-N(2)-C(3)	-175.10(9)
C(2)-N(2)-C(3)-C(4)	**Conformer A** 88.28(12)
	Conformer B 13.41(15)
N(2)-C(3)-C(4)^{i}-C(3)^{i}	**Conformer A** -110.07(12)
	Conformer B -99.27(12)

Symmetry codes: *i* = -x-1, -y+1, -z; *ii* = -x+1, -y, -z; *iii* = -x+1, y-1/2, -z+1/2; *iv* = -x+1, y+1/2, -z+1/2; *v* = x-1, -y+1/2, z-1/2; *vi* = x, -y+1/2, z+1/2; *vii* = -x, -y, -z; *viii* = x, -y+1/2, z-1/2; *ix* = x+1, -y+1/2, z+1/2.

Table S3. Crystallographic data and structure Rietveld refinement parameters for **3** from the structural model of **2**.

Phase	***3***
Formula	$(H_4baepn)_{0.5}[Fe^{III}_{2.0}Fe^{II}_{0.62}Co^{II}_{1.38}(H_2O)_2(HPO_3)_{4-x}(HPO_4)_xF_4]$ (x≃0.38)
Molecular weight ($gmol^{-1}$)	747.81
Space group	$P2_1/c$
a, b, c (Å)	13.6883(8), 12.6278(6), 12.7429(7)
β(º)	116.925(5)
V ($Å^3$), Z	1963.9(2)
Independent Reflections	1203
Structural Parameters	81
Profile Parameters	37
Soft Distance Constraints	33
R_{Bragg}	6.63
R_f	5.18
R_p	14.8
R_{wp}	14.7
R_{exp}	24.48
χ^2	0.360

Table S4. Atomic coordinates and equivalent isotropic displacement parameters, B_{iso} ($Å^2$), for inorganic skeleton of **3**.

Atoms	*X*	*Y*	*Z*	B_{iso} ($Å^2$)	*Occ. Factor*
Fe1	0.1836(9)	0.2453(8)	0.1335(9)	2.8(2)	1.0
Fe2	0.6892(9)	0.2455(10)	0.3067(7)	2.8(2)	1.0
Co3	0.2589(7)	-0.0023(10)	0.0371(8)	2.8(2)	0.32
Fe3	0.2589(7)	-0.0023(10)	0.0371(8)	2.8(2)	0.68
Co4	0.2508(10)	0.5032(12)	0.2871(10)	2.8(2)	1.0
P1	0.162(2)	0.2931(11)	0.3640(17)	3.7(5)	1.0
O1'	0.036(2)	0.3037(11)	0.2726(17)	1.7	0.15
H1	0.057(2)	0.3057(11)	0.2906(17)	1.7	0.85
P2	0.339(2)	-0.2162(11)	-0.0396(13)	3.7(5)	1.0
O2'	0.461(2)	-0.2327(11)	0.0232(13)	1.6	0.08
H2	0.446(2)	-0.2260(11)	0.0232(13)	1.6	0.92
P3	-0.0669(15)	0.1655(14)	-0.0203(15)	3.7(5)	1.0
O3'	-0.0275(15)	0.1063(14)	-0.0973(15)	2.4	0.15
H3	-0.0125(15)	0.1053(14)	-0.0603(15)	2.4	0.85
P4	0.4188(12)	0.2022(13)	0.1528(17)	3.7(5)	1.0
H4	0.4043(12)	0.2369(13)	0.0500(17)	1.7	1.0
O1	0.207(4)	0.222(3)	0.301(2)	3.8(5)	1.0
O3	0.173(5)	0.264(3)	-0.028(2)	3.8(5)	1.0
O5	0.3477(15)	0.245(4)	0.207(3)	3.8(5)	1.0
O6	0.0195(16)	0.234(3)	0.073(4)	3.8(5)	1.0
O7	0.313(5)	-0.266(4)	-0.156(3)	3.8(5)	1.0
O8	0.5350(14)	0.215(4)	0.244(3)	3.8(5)	1.0
O9	0.304(5)	-0.285(3)	0.035(3)	3.8(5)	1.0
O10	-0.1497(16)	0.233(4)	-0.118(3)	3.8(5)	1.0
O13	0.311(4)	-0.0991(18)	-0.064(2)	3.8(5)	1.0
O14	-0.107(3)	0.085(3)	0.040(3)	3.8(5)	1.0
O15	0.401(2)	0.0850(18)	0.127(5)	3.8(5)	1.0
O16W	0.403(2)	0.454(4)	0.309(4)	3.8(5)	1.0
H16A	0.457(2)	0.487(4)	0.315(4)	3.9	1.0
H16B	0.374(2)	0.421(4)	0.248(4)	7.1	1.0
O17W	0.098(2)	0.593(3)	0.235(4)	3.8(5)	1.0
H17B	0.100(2)	0.601(3)	0.300(4)	1.6	1.0
H17A	0.092(2)	0.650(3)	0.202(4)	1.6	1.0
O18	0.204(5)	0.408(2)	0.384(3)	3.8(5)	1.0
F1	0.197(4)	0.0922(15)	0.132(4)	3.1(7)	1.0
F2	0.181(4)	0.4044(15)	0.146(4)	3.1(7)	1.0
F3	0.309(4)	-0.097(3)	0.191(3)	3.1(7)	1.0
F4	0.281(4)	0.5925(16)	0.175(3)	3.1(7)	1.0

Table S5. Bond distances (Å) and angles (°) for **3**.

[Fe(1)O_4F_2] octahedron

Fe(1)	**F(1)**	**O(3)**	**O(6)**	**F(2)**	**O(5)**	**O(1)**
O(1)	84(2)	175(3)	91(2)	94(2)	84(3)	***2.03(3)***
O(5)	85(2)	91(2)	174(2)	91(2)	***2.00(2)***	
F(2)	176(2)	88(3)	93(2)	***2.02(2)***		
O(6)	91(2)	94(4)	***2.02(2)***			
O(3)	94(3)	***2.01(4)***				
F(1)	***1.94(2)***					

[Fe(2)O_4F_2] octahedron

Fe(2)	**F(3)^{iv}**	**O(8)**	**O(9)^{iv}**	**F(4)^{iii}**	**O(10)^{ix}**	**O(7)^{ii}**
O(7)^{ii}	83(3)	95(4)	176(4)	99(3)	89(2)	***1.92(5)***
O(10)^{ix}	82(3)	175(2)	90(4)	87(2)	***1.99(2)***	
F(4)^{iii}	169(3)	89(2)	77(3)	***1.97(2)***		
O(9)^{iv}	100(3)	86(2)	***2.01(5)***			
O(8)	102(3)	***1.93(2)***				
F(3)^{iv}	***1.99(4)***					

[M(3)O_4F_2] octahedron

Fe(3)/Co(3)	**O(15)**	**O(14)^{vii}**	**F(3)**	**F(1)**	**O(18)^{viii}**	**O(13)**
O(13)	99(2)	88(3)	100(3)	177(4)	81(2)	***2.12(4)***
O(18)^{viii}	94(3)	89(3)	178(3)	98(4)	***2.11(3)***	
F(1)	84(3)	89(3)	81(2)	***2.13(5)***		
F(3)	88(3)	89(2)	***2.13(4)***			
O(14)^{vii}	173(3)	***2.13(4)***				
O(15)	***2.07(3)***					

[M(4)$O_2(H_2O)_2F_2$] octahedron

Co(4)	**F(4)**	**O(18)**	**O(16W)**	**O(13)^{vi}**	**F(2)**	**O(17W)**
O(17W)	88(3)	88(3)	163(3)	84.6(20)	93(3)	***2.20(3)***
F(2)	83(2)	91(3)	89(2)	175(3)	***2.04(4)***	
O(13)^{vi}	101(3)	84(2)	95(3)	***2.08(3)***		
O(16W)	75(2)	108(4)	***2.07(4)***			
O(18)	173(4)	***2.02(5)***				
F(4)	***2.00(5)***					

Table S5. Continuation.

[HP(1)O$_3$] pseudotetrahedron

P(1)	**O(1´)**	**O(3)^{v1}**	**O(1)**	**O(18)**	**H(1)**
H(1)	3(2)	109(3)	106(4)	102(4)	***1.32(3)***
O(18)	104(3)	115(4)	116(4)	***1.54(3)***	
O(1)	103(4)	108(5)	***1.51(5)***		
O(3)^{v1}	110(3)	***1.50(4)***			
O(1´)	***1.59(3)***				

[HP(2)O$_3$] pseudotetrahedron

P(2)	**O(2´)**	**O(7)**	**O(13)**	**O(9)**	**H(2)**
H(2)	5(2)	105(3)	109(3)	98(5)	***1.32(3)***
O(9)	100(5)	112(5)	124(4)	***1.52(6)***	
O(13)	111(3)	106(4)	***1.52(3)***		
O(7)	100(3)	***1.50(5)***			
O(2´)	***1.50(3)***				

[HP(3)O$_3$] pseudotetrahedron

P(3)	**O(3´)**	**O(14)**	**O(10)**	**O(6)**	**H(3)**
H(3)	15(2)	102(4)	111(3)	105(4)	***1.32(3)***
O(6)	114(4)	109(4)	111(3)	***1.51(4)***	
O(10)	96(3)	119(4)	***1.51(4)***		
O(14)	108(4)	***1.52(5)***			
O(3´)	***1.51(3)***				

[HP(4)O$_3$] pseudotetrahedron

P(4)	**O(8)**	**O(15)**	**O(5)**	**H(4)**
H(4)	112(3)	100(3)	120(4)	***1.31(3)***
O(5)	106(3)	112(4)	***1.52(4)***	
O(15)	107(3)	***1.51(3)***		
O(8)	***1.49(2)***			

Table S6. Hydrogen bonds systems in compounds **1** and **2**.

Compound 1

Donor-H-Acceptor	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (º)*
N(1)-H(1C)-F(2)^{b}	0.89	2.23	2.916(18)	133
N(1)-H(1C)-F(4)^{b}	0.89	2.15	2.928(19)	146
N(1)-H(1D)-O(6)^{a}	0.89	2.17	3.03(2)	162
N(1)-H(1E)-O(17W)^{a}	0.89	2.39	3.16(2)	146
N(2)-H(2A)-F(1)^{c}	0.90	2.18	2.867(16)	133
N(2)-H(2A)-O(1)^{c}	0.90	2.13	2.939(18)	149
N(2)-H(2B)-F(3)^{c}	0.90	1.93	2.757(17)	151
C(2)-H(C2A)-O(3)^{b}	0.97	2.54	3.369(17)	144
C(2)-H(C2B)-O(9)^{d}	0.97	2.45	3.247(17)	139
C(4)-H(4A)-F(3)^{c}	0.97	2.52	3.13(2)	121
C(4)-H(4A)-O(7)^{d}	0.97	2.41	3.356(19)	164

Compound 2

Donor-H-Acceptor	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (º)*
N(1)-H(1C)-F(2)^{b}	0.89	2.23	2.904(10)	132
N(1)-H(1C)-F(4)^{b}	0.89	2.14	2.928(10)	147
N(1)-H(1D)-O(6)^{a}	0.89	2.18	3.039(13)	163
N(1)-H(1E)-O(17W)^{a}	0.89	2.42	3.184(11)	145
N(2)-H(2A)-F(1)^{c}	0.90	2.14	2.863(10)	136
N(2)-H(2A)-O(1)^{c}	0.90	2.16	2.938(12)	145
N(2)-H(2B)-F(3)^{c}	0.90	1.94	2.746(11)	148
N(2)-H(2B)-O(7)^{d}	0.90	2.55	3.278(12)	138
C(2)-H(C2A)-O(3)^{b}	0.97	2.48	3.329(14)	146
C(2)-H(C2B)-O(9)^{d}	0.97	2.46	3.232(14)	136
C(4)-H(4A)-O(7)^{d}	0.97	2.39	3.337(15)	164

Symmetry codes*: a* = x, y, z; *b* = -x, 1-y, -z; *c* = -x, 1/2+y, 1/2-z; *d* = -x, -y, -z.