Supporting Information

A new compound $Na_5Mn_4(PO_4)_4F_4·2H_2O$ with a rarely mixed valence spin chain showing multiple magnetic transitions

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Experimental details:

1. Synthesis

$Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$ was obtained by a hydrothermal method using the mixture of Mn_2O_3 (AR, 0.1816g), $MnCl_2$ (AR, 0.01g), NaF (AR, 0.6g), and 0.5 ml H_3PO_4 (AR, ≥85%) as the starting materials. The mixture was stirred completely in 1 mL of deionized water and sealed in autoclaves equipped with 28 mL Teflon liners. The autoclaves were heated to 210 °C and held for 3 days, and then slowly cooled for 3 days to room temperature. Following that, some black crystals were produced by washing with anhydrous ethanol and drying at 60 °C. Lastly, they were chosen manually under a microscope. The powder samples were generated by grinding such tiny single crystals, and the purity was determined using powder X-ray diffraction (XRD) data obtained on a Rigaku Mini-Flex 600 diffractometer (Fig. S1), and the results are good agreement with that simulated from single crystal data. The EDS studies (Fig. S2) yielded an average molar ratio of 5.1/3.9/3.8 for Na/Mn/P, which is consistent with the stoichiometric ratio of $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$.

2. X-ray crystallographic studies

A small-size single crystal was selected and mounted on a glassy fiber for single-crystal X-ray diffraction measurements. Single-crystal data of the compound were collected on an XtaLAB Synergy diffractometer using Cu-Kα radiation (λ = 1.54184 Å) at 293 K. The structure was solved by direct methods and refined by Olex-2 software[1]. The structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimization. Crystallographic data and structure refinement parameters are summarized in Table S1. The detailed crystal parameters including the final refined atomic positions, displacement parameters, the selected bond lengths [Å], and selected bond angles [deg] are listed in Tables S2–S6 in the supporting information. Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex-600 diffractometer using Cu Kα radiation (λ = 0.154 nm) at room temperature. Temperature dependent PXRD measurements were performed in the range of 2θ = 5 – 65 º with a scan speed of 1º/min.

3. Magnetic measurements

Magnetic measurements were performed using a Quantum Design Physical Property Measurement System (PPMS, QD). The powder sample was placed in a gel capsule sample holder suspended in a plastic drinking straw. Magnetic susceptibilities were measured between 2 K and 300 K under different magnetic fields. Magnetization was measured at different temperatures under applied field from -8 T to 8 T. Heat capacity data were determined by a relaxation method using the same PPMS system under zero field.

4. Thermal analysis and FT–IR spectroscopy

Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10 °C·min^{-1} by using a NETZSCH STA449F3 thermogravimetric analyzer. The samples were placed in Al_2O_3 crucibles and heated from room temperature to 800 °C. Fourier transform infrared (IR) spectroscopy was performed using KBr pellets on a Bruker VERTEX 70 spectrometer in the 400–4000 cm^{-1}.

References

1 V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*, 2009, **42**, 339-341.

2 G. M. Sheldrick, *Acta Crystallogr A Found Adv*, 2015, **71**, 3-8.

3 G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3-8.

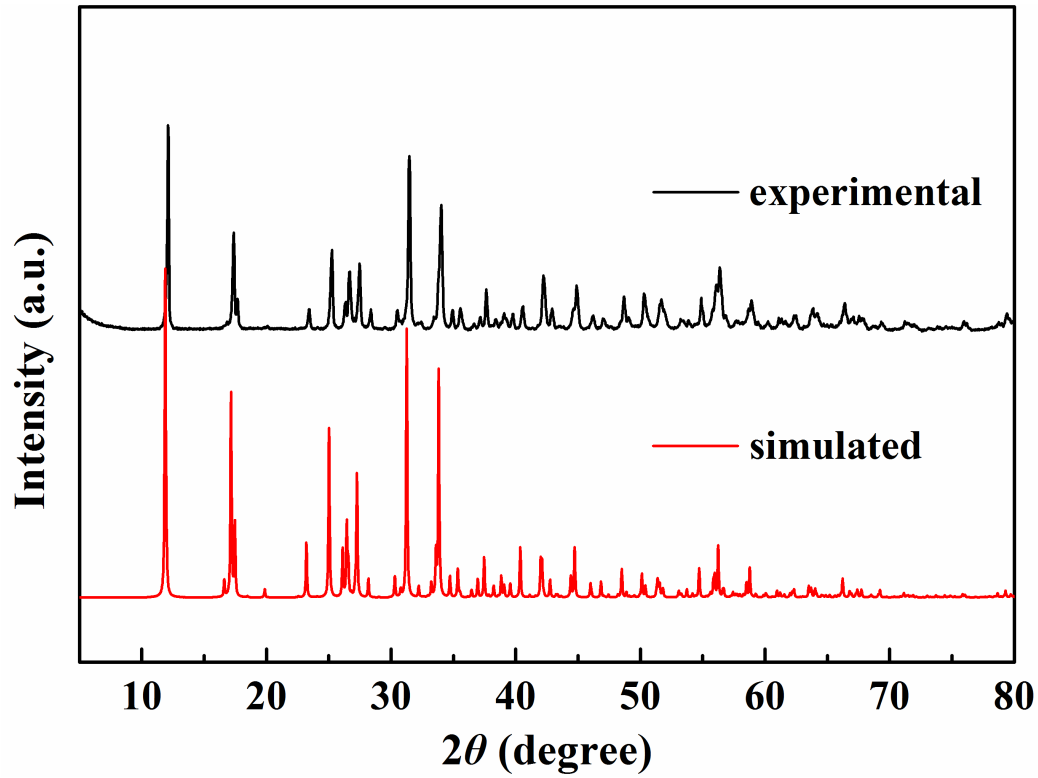

Fig. S1 The powder XRD patterns of $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$.

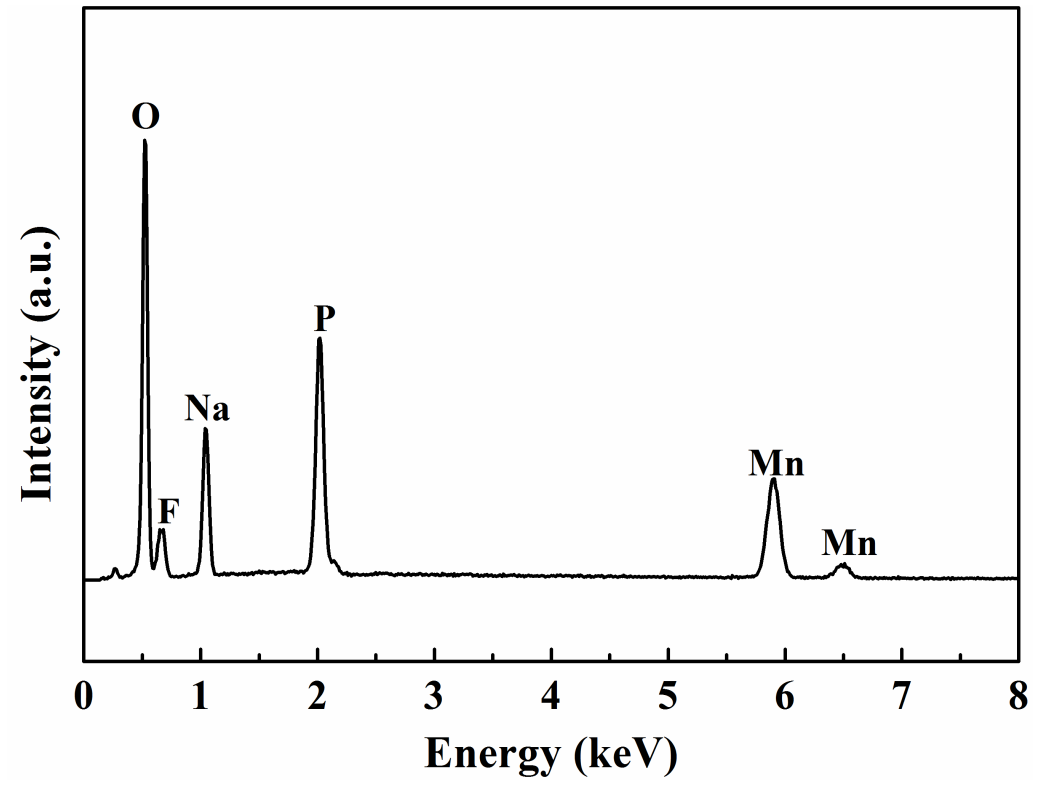

Fig. S2 The energy-dispersive spectrometry (EDS) of $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$

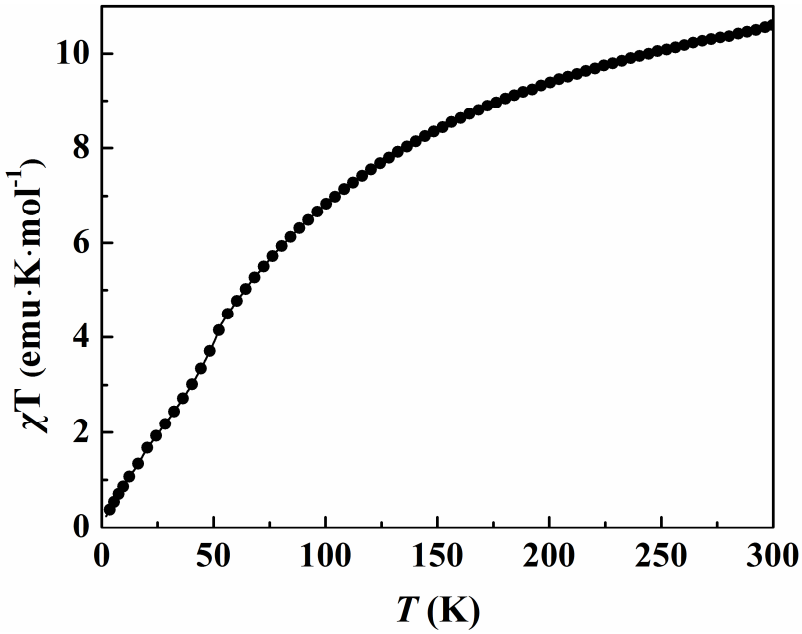

Fig. S3 The χT -T curve (effective magnetic moment) of $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$.

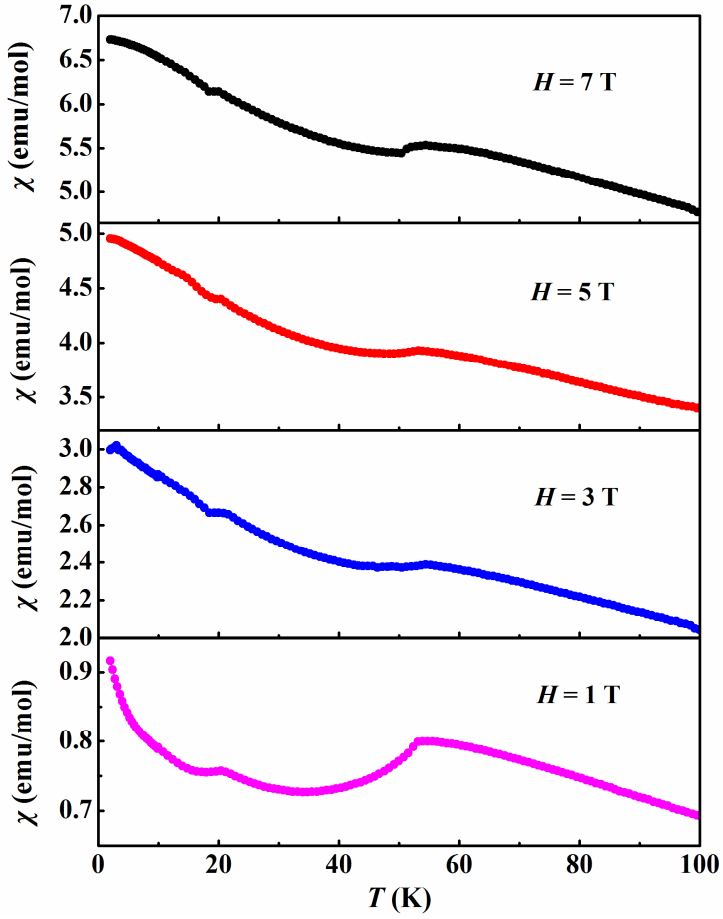

Fig. S4 Magnetic susceptibilities of $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$ measured at different magnetic fields.

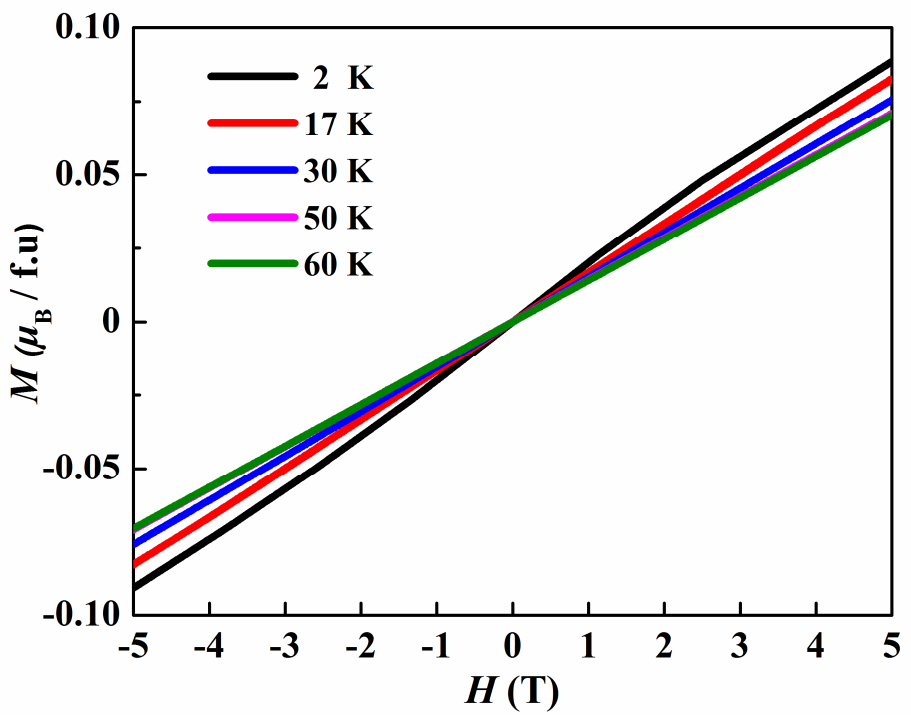

Fig. S5 Magnetization curves of $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$ measured under applied field of -8T to 8T at different temperatures.

Table S1 Crystal data and structure refinements for $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$.

Formula	$Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$
Fw	826.62
Space group	*C*2/*m*
a (Å)	13.1778(8)
b (Å)	8.9315(5)
c (Å)	7.4586(5)
α (°)	90
β (°)	93.243(6)
γ (°)	90
V (Å^3)	876.45(9)
Z	2
ρ_{calc} (g/cm^3)	3.132
μ (mm^{-1})	29.000
GOF on F^2	1.085
R_1, wR_2 [$I > 2\sigma(I)$] [a]	0.0411, 0.1095
R_1, wR_2 [all data]	0.0422, 0.1103

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Mn1	5000	0	5000	14.6(3)
Mn2	5000	5000	10000	13.7(3)
Mn3	7217.0(5)	0	10712.8(9)	13.0(3)
P1	6209.9(6)	2531.5(9)	7904.1(10)	13.6(3)
Na1	5000	0	10000	21.8(6)
Na2	3690.4(11)	2778.9(19)	6866(2)	28.2(4)
F1	8439(2)	0	9114(4)	20.1(6)
F2	5934(2)	0	2696(4)	20.0(6)
O1	5269.9(16)	3494(3)	8239(3)	17.5(5)
O2	7174.5(17)	3502(3)	7758(3)	18.0(5)
O3	6015.8(17)	1693(3)	6156(3)	21.2(5)
O4	6380.2(16)	1485(3)	9533(3)	21.2(6)
O5	2981(3)	5000	5623(5)	29.7(8)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	17.2(5)	9.9(5)	17.0(5)	0	3.7(4)	0
Mn2	16.4(5)	8.0(5)	17.0(5)	0	4.4(4)	0
Mn3	15.2(4)	7.1(4)	16.7(4)	0	1.9(3)	0
P1	16.2(5)	7.6(5)	17.4(5)	-0.2(2)	3.3(3)	-0.5(3)
Na1	18.0(13)	20.2(14)	27.6(14)	0	3.5(10)	0
Na2	26.0(7)	24.5(8)	34.1(8)	1.6(6)	2.2(6)	-2.9(6)
F1	16.4(12)	23.7(15)	20.8(14)	0	5.0(10)	0
F2	21.2(13)	18.7(15)	20.6(14)	0	5.1(10)	0
O1	19.0(11)	12.3(11)	21.4(11)	-2.3(8)	2.2(8)	1.1(9)
O2	20.6(11)	12.3(11)	21.5(11)	-3.2(8)	4.9(8)	-3.5(9)
O3	24.1(12)	15.4(12)	24.5(12)	-6.5(9)	4.6(9)	-2.4(10)
O4	20.8(11)	15.4(12)	27.6(13)	6.9(9)	1.7(10)	-0.3(8)
O5	37(2)	31(2)	21.8(18)	0	3.2(15)	0

Table S4 Bond lengths for $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Mn1-F2[4]	2.169(3)	P1-O1	1.540(2)
Mn1-F2	2.169(3)	P1-O2	1.548(2)
Mn1-O3[2]	2.166(2)	P1-O3	1.513(2)
Mn1-O3	2.166(2)	P1-O4	1.539(2)
Mn1-O3[3]	2.166(2)	Na1-F2[4]	2.297(3)
Mn1-O3[4]	2.166(2)	Na1-F2[11]	2.297(3)
Mn2-F1[8]	2.124(3)	Na1-O4[7]	2.294(2)
Mn2-F1[9]	2.124(3)	Na1-O4[10]	2.294(2)
Mn2-O1[6]	1.927(2)	Na1-O4[2]	2.294(2)
Mn2-O1[7]	1.927(2)	Na1-O4	2.294(2)
Mn2-O1	1.927(2)	Na2-F1[9]	2.630(2)
Mn2-O1[5]	1.927(2)	Na2-F2[4]	2.5483(18)
Mn3-F1	2.058(3)	Na2-O1	2.355(3)
Mn3-F2[11]	2.309(3)	Na2-O2[14]	2.427(3)
Mn3-O2[8]	1.905(2)	Na2-O3[3]	2.504(3)
Mn3-O2[12]	1.905(2)	Na2-O4[7]	2.930(3)
Mn3-O4	1.908(2)	Na2-O5	2.360(3)
Mn3-O4[2]	1.908(2)	-	

[1]+X,+Y,-1+Z; [2]1-X,+Y,1-Z; [3]1-X,-Y,1-Z; [4]+X,-Y,+Z; [5]+X,1-Y,+Z; [6]1-X,+Y,2-Z; [7]1-X,1-Y,2-Z; [8]3/2-X,1/2-Y,2-Z; [9]-1/2+X,1/2+Y,+Z; [10]1-X,-Y,2-Z; [11]+X,+Y,1+Z; [12]3/2-X,-1/2+Y,2-Z; [13]1/2+X,1/2-Y,+Z; [14]-1/2+X,1/2-Y,+Z

Table S5 Angles for $Na_5Mn_4(PO_4)_4F_4 \cdot 2H_2O$.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
F2-Mn1-F2^3	180.00(15)	O4^4-Mn3-O4	88.11(15)
O3^2-Mn1-F2^3	87.13(8)	O1-P1-O2	111.72(14)
O3^2-Mn1-F2	92.87(8)	O3-P1-O1	108.52(13)
O3^4-Mn1-F2	87.13(8)	O3-P1-O2	108.42(13)
O3^4-Mn1-F2^3	92.87(8)	O3-P1-O4	112.95(16)
O3-Mn1-F2	87.13(8)	O4-P1-O1	107.09(13)
O3^3-Mn1-F2^3	87.13(8)	O4-P1-O2	108.19(13)
O3-Mn1-F2^3	92.87(8)	F2^3-Na1-F2^{11}	180
O3^3-Mn1-F2	92.87(8)	O4^{10}-Na1-F2^3	75.11(8)
O3^3-Mn1-O3^2	88.56(13)	O4-Na1-F2^{11}	75.11(8)
O3^3-Mn1-O3^4	91.44(13)	O4^{10}-Na1-F2^{11}	104.89(8)
O3^4-Mn1-O3^2	180	O4^4-Na1-F2^{11}	75.11(8)
O3^2-Mn1-O3	91.44(13)	O4^5-Na1-F2^3	75.11(8)
O3^3-Mn1-O3	180	O4-Na1-F2^3	104.89(8)
O3^4-Mn1-O3	88.56(13)	O4^4-Na1-F2^3	104.89(8)
F1^9-Mn2-F1^8	180	O4^5-Na1-F2^{11}	104.89(8)
O1^6-Mn2-F1^8	89.96(8)	O4^{10}-Na1-O4^4	109.32(13)
O1^7-Mn2-F1^9	89.96(8)	O4-Na1-O4^{10}	180
O1^6-Mn2-F1^9	90.04(8)	O4^{10}-Na1-O4^5	70.68(13)
O1-Mn2-F1^9	89.96(8)	O4-Na1-O4^4	70.68(13)
O1^7-Mn2-F1^8	90.04(8)	O4^4-Na1-O4^5	180
O1^5-Mn2-F1^9	90.04(8)	O4-Na1-O4^5	109.32(13)
O1-Mn2-F1^8	90.04(8)	F1^8-Na2-O4^5	72.63(8)
O1^5-Mn2-F1^8	89.96(8)	F2^3-Na2-F1^8	133.12(10)
O1-Mn2-O1^5	91.50(14)	F2^3-Na2-O4^5	60.97(8)
O1^6-Mn2-O1^5	88.50(14)	O1-Na2-F1^8	70.02(9)
O1^6-Mn2-O1	180	O1-Na2-F2^3	92.75(10)
O1^6-Mn2-O1^7	91.50(14)	O1-Na2-O2^{14}	136.85(11)
O1^7-Mn2-O1^5	180	O1-Na2-O3^2	108.57(10)
O1-Mn2-O1^7	88.50(14)	O1-Na2-O4^5	77.39(8)
F1-Mn3-F2^{11}	175.58(10)	O1-Na2-O5	105.27(12)
O2^{12}-Mn3-F1	91.73(9)	O2^{14}-Na2-F1^8	92.62(9)

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O2^{9}-Mn3-F1	91.73(9)	O2^{14}-Na2-F2^{3}	70.30(9)
O2^{12}-Mn3-F2^{11}	85.12(9)	O2^{14}-Na2-O3^{2}	103.63(10)
O2^{9}-Mn3-F2^{11}	85.12(9)	O2^{14}-Na2-O4^{5}	59.59(8)
O2^{9}-Mn3-O2^{12}	89.19(14)	O3^{2}-Na2-F1^{8}	153.81(10)
O2^{12}-Mn3-O4^{4}	90.03(11)	O3^{2}-Na2-F2^{3}	72.49(9)
O2^{9}-Mn3-O4	90.03(11)	O3^{2}-Na2-O4^{5}	133.39(10)
O2^{9}-Mn3-O4^{4}	167.67(11)	O5-Na2-F1^{8}	63.59(11)
O2^{12}-Mn3-O4	167.67(11)	O5-Na2-F2^{3}	159.84(12)
O4-Mn3-F1	100.59(9)	O5-Na2-O2^{14}	100.95(12)
O4^{4}-Mn3-F1	100.59(9)	O5-Na2-O3^{2}	92.86(12)
O4-Mn3-F2^{11}	82.55(9)	O5-Na2-O4^{5}	131.23(12)
O4^{4}-Mn3-F2^{11}	82.55(9)		

^{1}+X,+Y,-1+Z; ^{2}+X,-Y,+Z; ^{3}1-X,+Y,1-Z; ^{4}1-X,-Y,1-Z; ^{5}1-X,+Y,2-Z; ^{6}+X,1-Y,+Z; ^{7}1-X,1-Y,2-Z; ^{8}-1/2+X,1/2+Y,+Z; ^{9}3/2-X,1/2-Y,2-Z; ^{10}1-X,-Y,2-Z; ^{11}+X,+Y,1+Z; ^{12}3/2-X,-1/2+Y,2-Z; ^{13}1/2+X,1/2-Y,+Z; ^{14}-1/2+X,1/2-Y,+Z; ^{15}1/2+X,-1/2+Y,+Z

Table S6 Hydrogen Atom Coordinates (Å×10^{4}) and Isotropic Displacement Parameters (Å^{2}×10^{3}) for $Na_5Mn_4(PO_4)_4F_4·2H_2O$.

Atom	*x*	*y*	*z*	U(eq)
H5A	3069.94	5000	4341.04	36
H5B	2256.5	5000.01	5791.59	36