Dalton Transactions

Supporting Information

Single Crystal Growth of the Novel Mn$_2$(OH)$_2$SO$_3$, Mn$_2$F(OH)SO$_3$, and Mn$_5$(OH)$_4$(H$_2$O)$_2$[SO$_3$]$_2$[SO$_4$] Compounds through the Hydrothermal Method

Hamdi Ben Yahia,* Masahiro Shikano,* and Hironori Kobayashi

Electronic Supplementary Information (ESI)

10 Table S1

B.V.S. before introducing the H atoms		B.V.S. after introducing the H atoms		
Atom	B.V.S.	Atom	B.V.S.	Charge
Mn1	1.920(5)	Mn1	1.911(5)	+2
Mn2	1.983(4)	Mn2	1.985(4)	+2
Mn3	2.042(4)	Mn3	2.044(4)	+2
S1	4.126(12)	S1	4.128(12)	+4
S2	4.090(12)	S2	4.086(12)	+4
S3	6.36(2)	S3	6.38(2)	+6
O1	1.763(8)	O1	2.178(16)	-2
O2	2.005(7)	O2	2.004(6)	-2
O3	2.017(6)	O3	2.015(6)	-2
O4	1.929(9)	O4	1.931(9)	-2
O5	1.682(16)	O5	2.35(2)	-2
O6	2.029(10)	O6	2.029(10)	-2
O7	1.938(10)	O7	1.939(10)	-2
O8	**0.344(2)**	**O8**	**1.91(5)**	**-2**
		H8a	0.77(4)	+1
		H8b	1.02(3)	+1
O9	**1.127(3)**	**O9**	**1.83(3)**	**-2**
		H9	0.91(3)	+1
O10	**1.184(3)**	**O10**	**1.93(2)**	**-2**
		H10	0.95(2)	+1
O11	**1.099(4)**	**O11**	**1.85(3)**	**-2**
		H11	0.75(3)	+1

B.V. = e$^{(r0-r)/b}$ with the following parameters: $b = 0.37$, r_0 (S^{IV}–O) = 1.644, and r_0 (Mn^{II}–O) = 1.790 Å. [15, 16]

Table S2. Anisotropic displacement parameters (Å^2) for for Mn$_2$(OH)$_2$SO$_3$, Mn$_2$F(OH)SO$_3$, and Mn$_5$(OH)$_4$(H$_2$O)$_2$[SO$_3$]$_2$[SO$_4$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+...+2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn$_2$(OH)$_2$SO$_3$						
Mn	0.0110(4)	0.0201(4)	0.0121(4)	-0.0002(3)	0.0007(3)	-0.0015(3)
S	0.0119(8)	0.0135(8)	0.0120(7)	0	-0.0008(6)	0
O1	0.015(3)	0.021(2)	0.017(2)	0	0.0063(18)	0
O2	0.0125(17)	0.0191(17)	0.0134(14)	-0.0033(15)	-0.0008(12)	-0.0022(12)
O3h	0.0118(17)	0.0167(19)	0.0162(15)	0.0014(16)	-0.0012(12)	-0.0006(14)
Mn$_2$F(OH)SO$_3$						
Mn	0.0093(7)	0.0158(7)	0.0094(8)	-0.0005(6)	0.0018(6)	-0.0006(7)
S	0.0081(14)	0.0066(14)	0.0117(19)	0	-0.0015(14)	0
O1	0.013(5)	0.011(4)	0.016(5)	0	0.014(4)	0
O2	0.009(3)	0.014(3)	0.007(4)	-0.004(2)	-0.001(3)	0.002(3)
O3h/F	0.009(3)	0.028(3)	0.012(3)	0.001(3)	-0.001(2)	-0.002(3)
Mn$_5$(OH)$_4$(H$_2$O)$_2$[SO$_3$]$_2$[SO$_4$]						
Mn1	0.0148(2)	0.0195(2)	0.0115(3)	0	-0.00018(19)	0
Mn2	0.01267(19)	0.0177(2)	0.0170(2)	-0.00077(10)	-0.00246(16)	-0.00040(11)
Mn3	0.0194(2)	0.0186(2)	0.0125(2)	-0.00111(11)	-0.00063(17)	0.00100(11)
S1	0.0109(3)	0.0185(3)	0.0116(3)	0	-0.0015(3)	0
S2	0.0157(3)	0.0168(3)	0.0098(3)	0	-0.0026(3)	0
S3	0.0117(3)	0.0196(3)	0.0162(4)	0	-0.0020(3)	0
O1	0.0100(8)	0.0270(10)	0.0161(11)	0	-0.0010(8)	0
O2	0.0136(6)	0.0203(7)	0.0283(9)	-0.0020(5)	-0.0011(6)	0.0057(6)
O3	0.0314(8)	0.0202(7)	0.0140(8)	-0.0054(6)	-0.0015(7)	0.0002(6)
O4	0.0286(10)	0.0181(8)	0.0105(11)	0	-0.0027(9)	0
O5	0.0236(11)	0.0444(13)	0.0329(15)	0	0.0058(11)	0
O6	0.0139(9)	0.0200(9)	0.0319(14)	0	-0.0012(10)	0
O7	0.0222(7)	0.0511(11)	0.0478(13)	0.0071(8)	0.0021(9)	0.0320(11)
O8	0.0402(13)	0.0465(12)	0.0388(14)	0.0199(9)	0.0020(11)	0.0078(9)
O9	0.0137(6)	0.0185(6)	0.0162(8)	-0.0004(6)	-0.0016(6)	-0.0013(6)
O10	0.0108(8)	0.0222(9)	0.0132(10)	0	0.0001(8)	0
O11	0.0118(8)	0.0214(9)	0.0155(10)	0	0.0009(8)	0

$Mn_2F(OH)SO_3$

Elem	Wt %	At %
C K	5.17	10.68
O K	32.83	50.92
F K	6.51	8.50
S K	15.00	11.61
MnK	40.49	18.29
Total	100.00	100.00

$Mn_2(OH)_2SO_3$

Elem	Wt %	At%
C K	7.28	14.42
O K	39.33	58.48
S K	12.88	9.56
MnK	40.50	17.54
Total	100.00	100.00

$Mn_5(OH)_4(H_2O)_2[SO_3]_2[SO_4]$

Elem	Wt %	At %
C K	3.13	6.62
O K	38.93	61.91
S K	14.03	11.13
MnK	43.92	20.34
Total	100.00	100.00
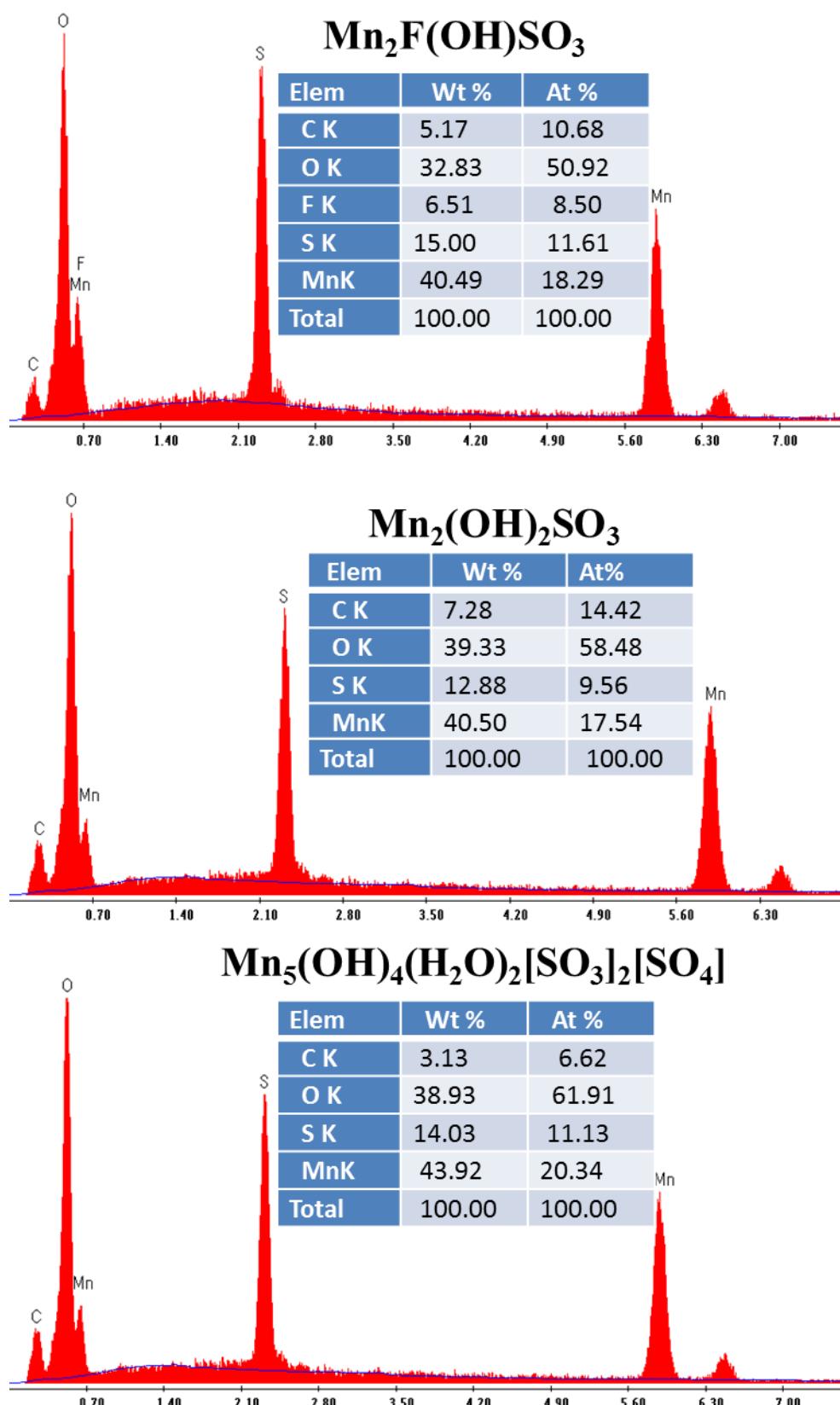
Fig. S1. EDX analysis of the single crystals investigated on the diffractometer.
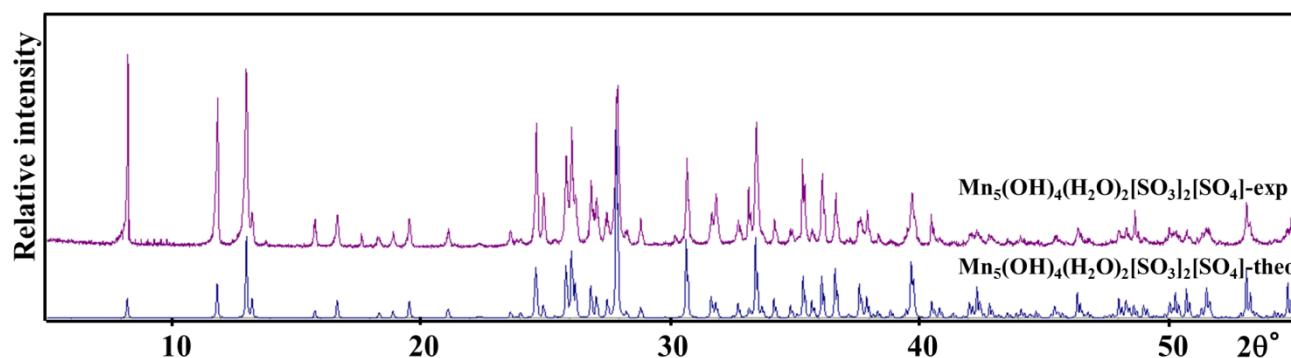
Fig. S2. The XRPD pattern of $Mn_5(OH)_4(H_2O)_2[SO_3]_2[SO_4]$ sample obtained from hydrothermal synthesis.
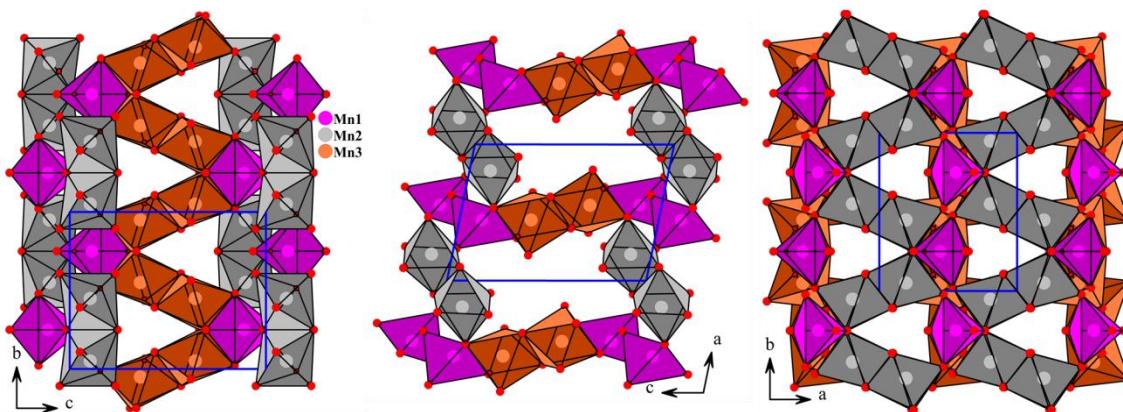

Fig. S3. Details of the connectivity between $Mn1O_5$, $Mn2O_6$, and $Mn3O_6$ polyhedra.
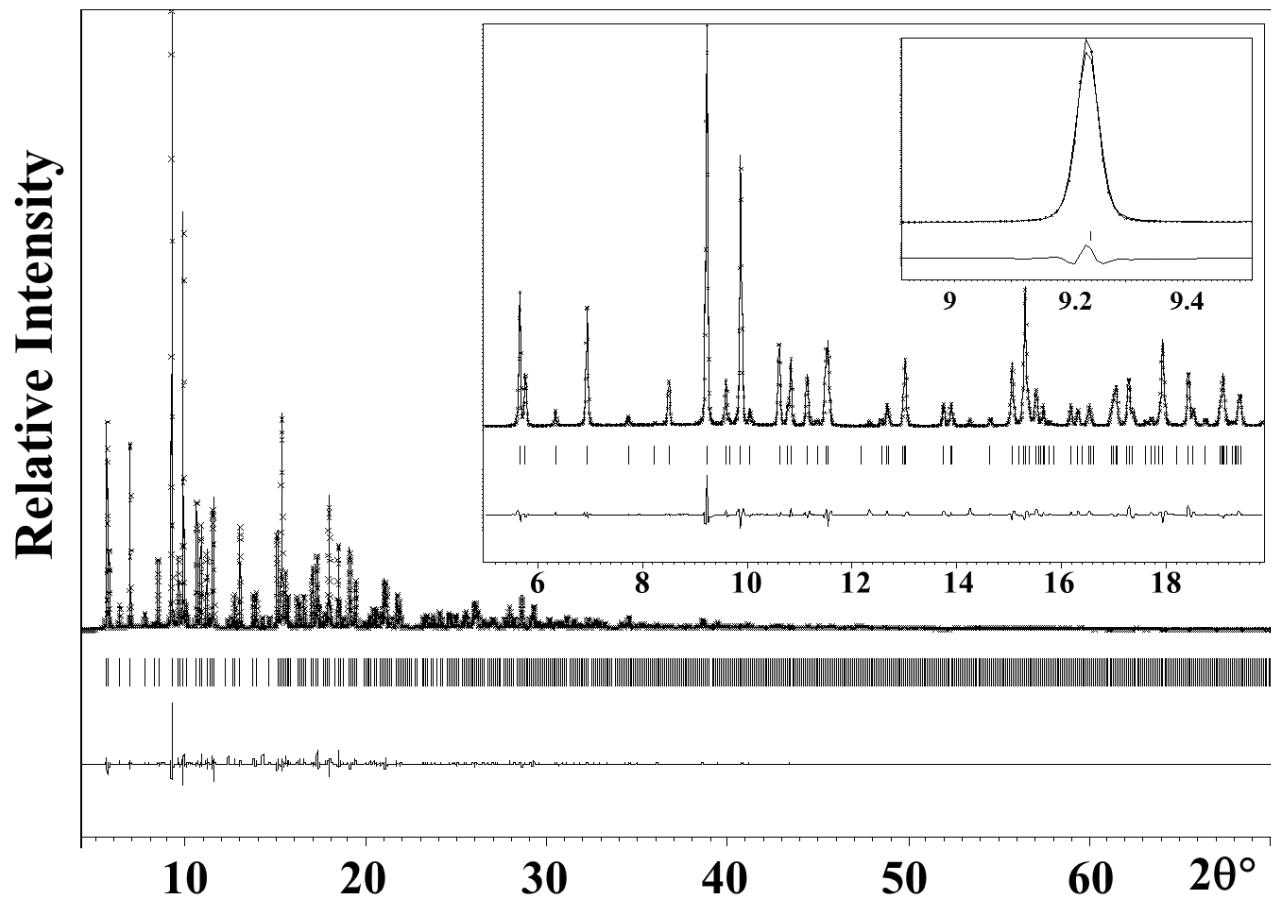
Fig. S4. Final observed, calculated and difference plots for synchrotron X-ray powder diffraction refinement ($\lambda = 0.5001$ Å) of $Mn_2(OH)FSO_3$.

[5] "High resolution X-ray powder diffraction measurements were performed for $Mn_2(OH)FSO_3$. The data were collected on BL19B2 at SPring-8 (with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2011A1795)) at room temperature over the 2θ angle range $0° \leq 2\theta \leq 78°$ with a step size of $0.01°$ ($\lambda = 0.5001$ Å). Full pattern matching refinements were performed with the Jana2006 program package. The backgrounds were estimated by a Legendre function, and the peak [10] shapes were described by a pseudo-Voigt function. Asymmetry and preferential orientation parameters have been also refined using Simpson and March-Dallase functions, respectively. Then the single crystal structure of $Mn_2(OH)_2SO_3$ was used as starting model for the Rietveld refinement (Figure S4). After introducing OH/F statistical disorder, the reliability factors dropped to $Rp = 0.0401$, $R_{wp} = 0.0595$, and $R_B = 0.0459$, confirming the accuracy of the model. Furthermore, the careful comparison [15] of the obtained atomic positions to those from $Mn_2(OH)FSO_3$ single crystal refinement did not show any significant difference except for the proton atom which showed a slight shift of the x coordinate (Table 2)."