SUPPORTING INFORMATION

Sawtooth chains self-assembled by clusters of MnO_6 octahedra within the silicate framework of $K_3Mn_4Si_{10}O_{24.33}(H_2O,OH)_3$

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1. Geometric parameters

Table S1. Selected geometric parameters (Å)

Mn2—O3^{i}	2.138 (6)	K1—O1^{iv}	2.881 (7)
Mn2—O11	2.141 (6)	K1—O1^{ix}	2.881 (7)
Mn2—O2	2.184 (6)	K1—O11	3.183 (8)
Mn2—O4^{ii}	2.190 (6)	K1—O11^{vii}	3.183 (8)
Mn2—O2^{iii}	2.241 (7)	K1'—O5	2.71 (3)
Mn2—O4^{i}	2.244 (7)	K1'—O1^{ix}	2.90 (2)
Mn1—O12^{iv}	2.079 (9)	K1'—O1^{iv}	2.90 (2)
Mn1—O11	2.092 (7)	K1'—O11	3.14 (2)
Mn1—O3^{iv}	2.111 (7)	K1'—O11^{vii}	3.14 (2)
Mn1—O9	2.255 (10)	K1'—O12^{ix}	3.16 (2)
Mn1—O2	2.390 (6)	K1'—O12^{iv}	3.16 (2)
Mn1—O4^{i}	2.449 (6)	K1'—O8^{i}	3.17 (3)
V1—O9	1.61 (2)	K1'—O6^{x}	3.29 (2)
V1—O12^{iv}	1.817 (19)	K1'—O6^{i}	3.29 (2)
V1—O11	2.325 (18)	K2—O8^{iv}	2.902 (11)
V1—O3^{iv}	2.475 (19)	K2—O9^{xi}	2.903 (9)
Si1—O11	1.574 (7)	K2—O9	2.903 (9)
Si1—O10	1.616 (8)	K2—O6	2.983 (8)
Si1—O1	1.630 (7)	K2—O6^{xi}	2.983 (8)
Si1—O5	1.633 (4)	K2—O3^{iv}	3.007 (7)
Si2—O2	1.601 (7)	K2—O3^{xii}	3.007 (7)
Si2—O4	1.607 (7)	K2—O5^{ii}	3.062 (10)
Si2—O6	1.642 (6)	K2—O1^{xiii}	3.125 (7)
Si2—O1^{ii}	1.648 (6)	K2—O1^{ii}	3.125 (7)
Si3—O3	1.596 (7)	K2'—O9^{xi}	2.61 (2)
Si3—O8	1.617 (3)	K2'—O9	2.61 (2)
Si3—O6	1.626 (7)	K2'—O6	2.85 (3)
Si3—O7	1.629 (7)	K2'—O6^{xi}	2.85 (3)
Si4—O12	1.593 (10)	K2'—O8^{iv}	3.09 (4)
Si4—O10	1.593 (9)	K2'—O3^{iv}	3.15 (2)
Si4—O13	1.603 (8)	K2'—O3^{xii}	3.15 (2)

Si4—O7	1.652 (7)	K2'—O1^{xiii}	3.33 (3)
V2—O7	1.42 (2)	K2'—O1^{ii}	3.33 (3)
V2—O9	1.87 (2)	K3—O16	2.84 (3)
V2—O10	1.99 (2)	K3—O12^{iv}	2.958 (13)
V2—O13	2.26 (2)	K3—O12^{ix}	2.958 (13)
Mn3—O14	1.85 (4)	K3—O15^{v}	3.05 (2)
Mn3—O16^{v}	1.87 (2)	K3—O10^{vii}	3.371 (14)
Mn3—O16	1.87 (2)	K3—O10	3.371 (14)
Mn3—O16^{vi}	1.87 (2)	K3'—O16	2.63 (5)
Si6—O14	1.27 (4)	K3'—O12^{ix}	2.78 (4)
Si6—O15^{v}	1.590 (13)	K3'—V3^{vii}	2.88 (5)
Si6—O15^{vi}	1.590 (13)	K3'—O9^{vii}	2.99 (3)
Si6—O15	1.590 (12)	K3'—O17^{v}	2.99 (4)
Si7—O13	1.570 (8)	K3'—O15^{v}	3.03 (4)
Si7—O13^{vii}	1.570 (8)	K3'—O10^{vii}	3.16 (4)
Si7—O15^{viii}	1.60 (2)	Mn4—O16	2.188 (17)
Si7—O16	1.66 (3)	Mn4—O16^{v}	2.188 (17)
K1—O5	2.802 (12)	V3—O17^{v}	1.82 (4)
K1—O12^{ix}	2.806 (9)	V3—O9^{vii}	2.42 (3)
K1—O12^{iv}	2.806 (9)		

Symmetry code(s): (i) -*x*+*y*+1/3, -*x*+5/3, *z*+2/3; (ii) -*y*+5/3, *x*-*y*+4/3, *z*+1/3; (iii) -*x*+*y*+1/3, -*x*+5/3, *z*-1/3; (iv) *x*, *y*, *z*+1; (v) -*y*+1, *x*-*y*+1, *z*; (vi) -*x*+*y*, -*x*+1, *z*; (vii) -*x*+*y*, *y*, *z*; (viii) -*y*+1, *x*-*y*+1, *z*-1; (ix) -*x*+*y*, *y*, *z*+1; (x) -*y*+4/3, -*x*+5/3, *z*+2/3; (xi) *x*, *x*-*y*+1, *z*; (xii) *x*, *x*-*y*+1, *z*+1; (xiii) -*y*+5/3, -*x*+4/3, *z*+1/3.

2. Powder diffraction data

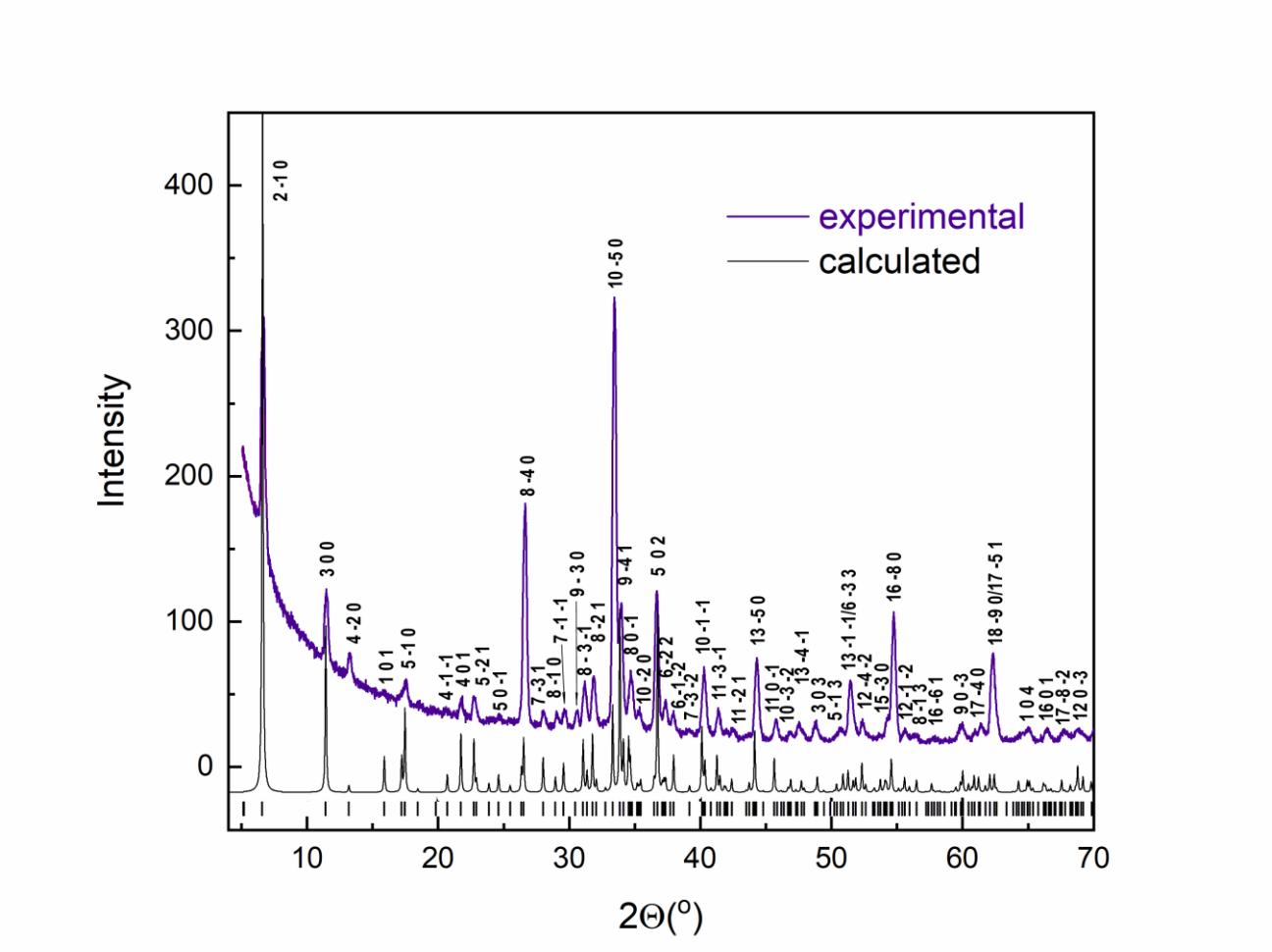

Figure S1. Experimental and calculated powder XRD patterns of $K_3Mn_4Si_{10}O_{24.33}(H_2O,OH)_3$ (the vertical ticks indicate the Bragg positions).

3. Bond valence data

Table S2. Bond valence data for $K_3Mn_4[Si_{10}O_{24.33}](H_2O,OH)_{2.81}$/V,B*

Atom	Mn1	Mn2	Si1	Si2	Si3	Si4	Si5/Mn3	Si6/B1	Si7/B2	K1	K2	K3	K3’	Σ
O1			0.989	0.937						$0.130_{\downarrow 2}$	$0.068_{\downarrow 2}$			2.12
O2	0.199	0.346;0.290		1.073										1.91
O3	0.417	0.395			1.079						$0.093_{\downarrow 2}$			1.98
O4	0.168	0.340;0.297		1.039										1.89
O5			$0.979_{\rightarrow 2}$							0.165	0.079			2.20
O6				0.945	0.997						$0.102_{\downarrow 2}$			2.04
O7					0.987	0.937								1.92
O8					$1.016_{\rightarrow 2}$						0.125			2.16
O9	0.285										$0.123_{\downarrow 2}$		0.07	0.48
O10			1.025			1.079						$0.02_{\downarrow 2}$		2.12
O11	0.443	0.382	1.154							$0.059_{\downarrow 2}$				2.04
O12	0.460					1.064				$0.165_{\downarrow 2}$		$0.04_{\downarrow 2}$	0.04	1.77
O13						1.053			$1.089_{\downarrow 2}$				0.02	2.16
O14							1.134	0.971						2.10
O15								$0.937_{\downarrow 3}$	0.987			0.03	$0.02_{\rightarrow 2}$	1.99
O16							$0.626_{\downarrow 3}$		1.031			0.06	$0.01_{\rightarrow 2}$	1.74
O17														0.00
Σ	1.97	2.05	4.15	3.99	4.08	4.13	3.01	3.78	4.20	0.87	0.98	0.21	0.16	

* The calculation is made without considering K and V sites with the low occupancy. Symbols → and ↓ denote an increase in the corresponding contributions in rows and columns due to symmetry.

4. Magnetic data interpretation

The magnetic subsystem in the title compound represents a rare case of quasi-one dimensional arrangement of MnO_6 octahedra forming sawtooth-like chain. In the absence of first principles calculations rough estimate of magnetic exchange interactions within saw – tooth chains can be done basing on *J* dependence versus distances and angles between Mn^{2+} ions Ref. 1. The Mn1 – Mn2 distances are equal to 3.03 and 3.05 Å which corresponds to antiferromagnetic exchange interactions J_{AF1} = 14.5 K and J_{AF2} = 10.15 K, while Mn2-Mn2 distance equals to 3.28 Å corresponding to ferromagnetic exchange interaction J_F = -4.4 K. The magnetic topology of saw – tooth chain is shown in the inset to Fig. S2. In the first approximation we may assume $J_{AF1} = J_{AF2} = J$ and neglect much weaker J_F which makes studied saw – tooth chain close to the model of antiferromagnetic S = 5/2 chain. The magnetic susceptibility of $K_3Mn_4Si_{10}O_{24.33}(H_2O,OH)_3/V,B$ can be fitted in the range 100 – 300 K by the sum of temperature independent term χ_0, Curie – Weiss term χ_{para} from paramagnetic Mn3 ions weakly coupled to the saw-tooth chains and χ_{chain} described by the formula:[2]

$$\chi_{chain} = \frac{N_A g^2 S(S+1)\mu_B^2}{3k_B T}\frac{1+u}{1-u}, u = \coth\left(\frac{2JS(S+1)}{k_B T}\right) - \frac{k_B T}{2JS(S+1)},$$

$$\chi_{sum} = \chi_0 + \chi_{para} + \alpha\chi_{chain}$$

Obtained from the fit values of parameters are χ_0 = - 3.9 × 10^{-4} emu/mol, α = 0.7, *J* = 6.6 K. The temperature independent term is close to that obtained from the fit with Curie – Weiss law. The coefficient α is different from unity signaling the presence of some defects in the structure. Obtained value of *J* is close to J_{AF1} and J_{AF2}.

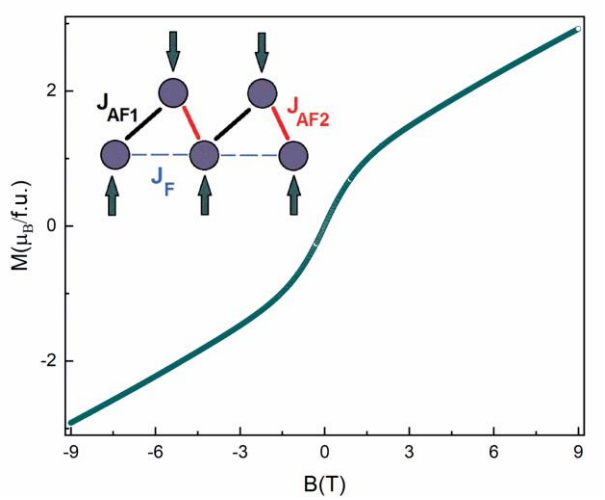

Figure S2. The field dependence of magnetization at *T* = 2 K and topology of magnetic chains in the structure. The Mn^{2+} (S = 5/2) ions are shown by spheres, antiferromagnetic and ferromagnetic exchange interactions are shown by lines.

5. References

1 R. Li, R.I. Smith and S. Greaves, *Chem. Commun.*, 2021, **57**, 7027.
2 R. Dingle, M. E. Lines, S. L. Holt, *Phys. Rev.*, 1969, **187**, 643.