Supporting information

for

Cascade of Magnetic Phase Transitions and 1/3-Magnetization Plateau in Selenite-Selenate Co$_3$(SeO$_3$)(SeO$_4$)(OH)$_2$ with Layers of a Kagomé-like Co^{2+} Ion Arrangement: Importance of Identifying a Correct Spin Lattice

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S1. Supplementary figures
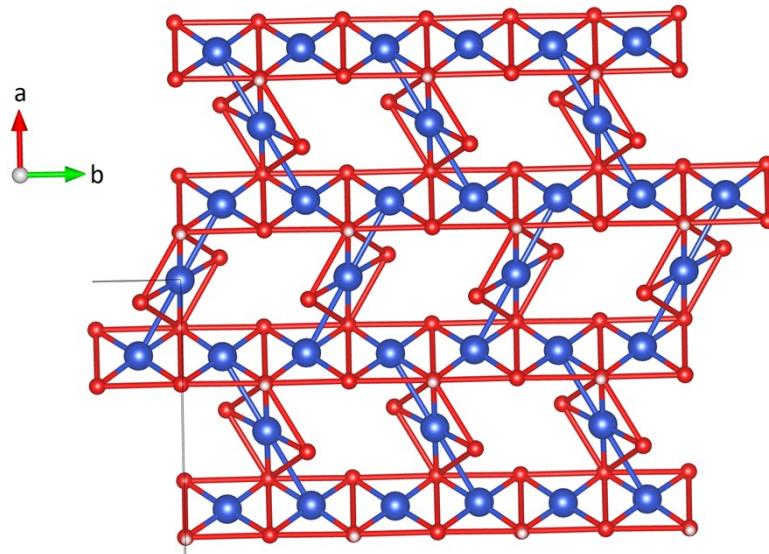
Fig. S1. The kagomé-like arrangement of the Cu^{2+} ions in volborthite Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O. The three different orientations of the CuO$_4$ square planes possessing the x^2-y^2 magnetic orbitals are emphasized to show that the correct spin lattice is not a kagomé spin lattice, but superposed three-leg spin ladders. Volborthite is perfectly described by a spin-half antiferromagnetic uniform Heisenberg chain model.
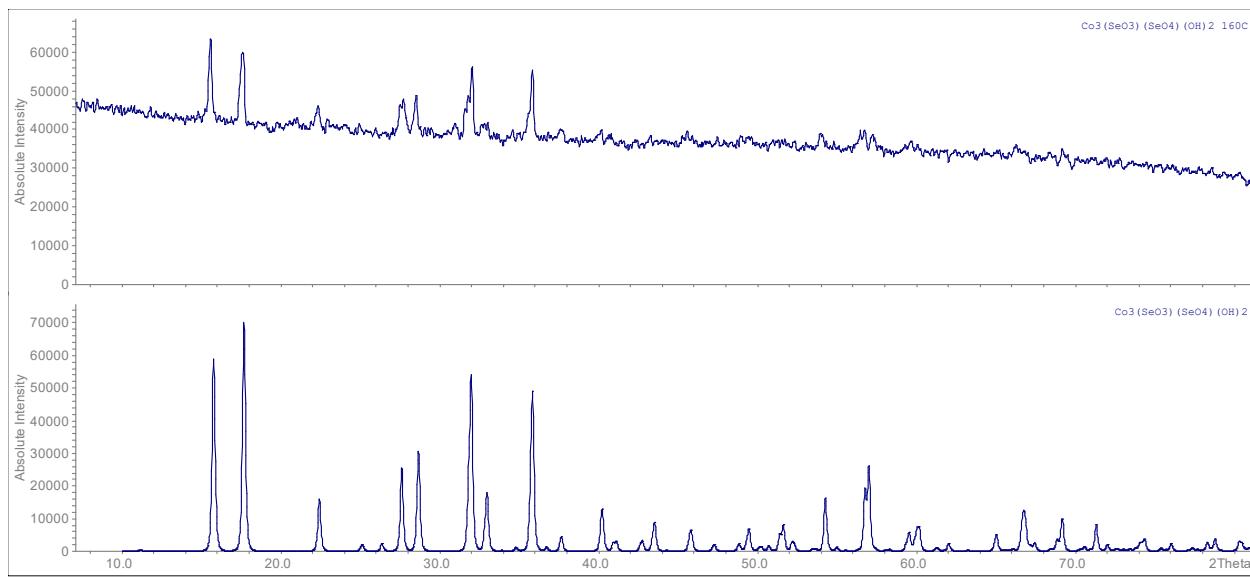
Fig. S2. Comparison of Powder XRD for hydrothermally prepared sample of $Co_3(SeO_3)(SeO_4)(OH)_2$ (upper panel) and simulated from single crystal data experiment at Cu $K_{\alpha 1}$ radiation (lower panel).
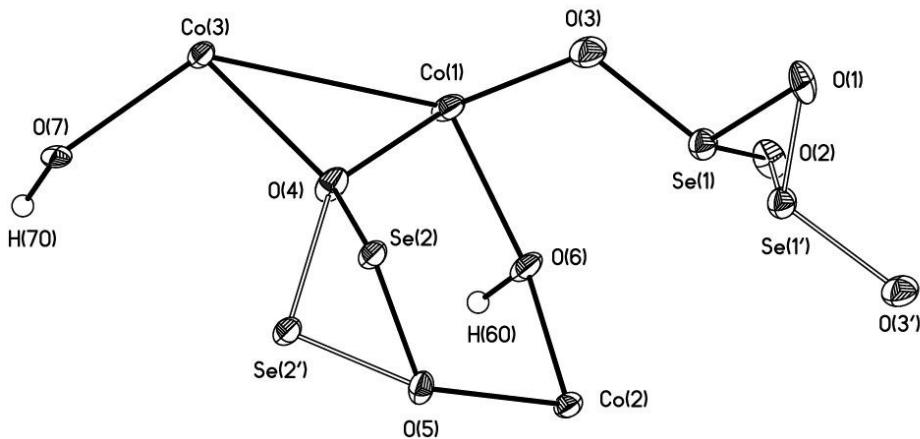
**Fig. S3.** Asymmetric unit for $Co_3(SeO_3)(SeO_4)(OH)_2$.
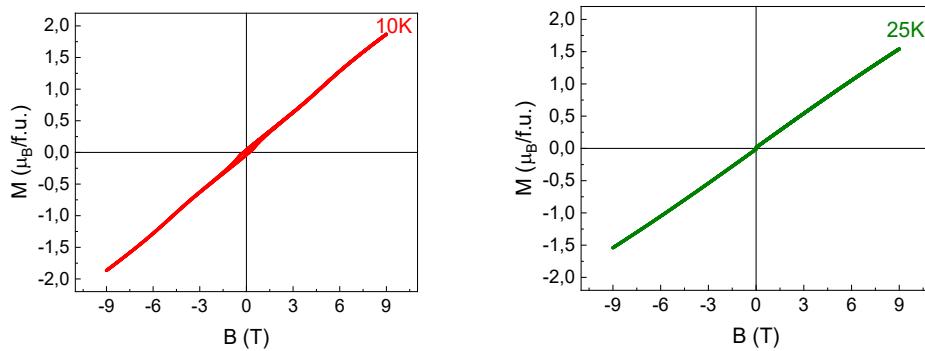
**Fig. S4**. Hysteresis loops in $Co_3(SeO_3)(SeO_4)(OH)_2$ at various temperatures.
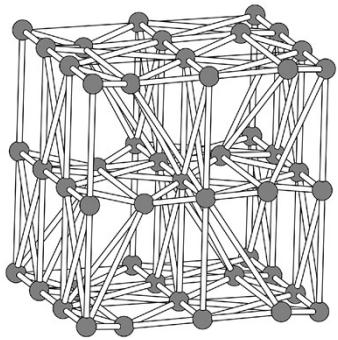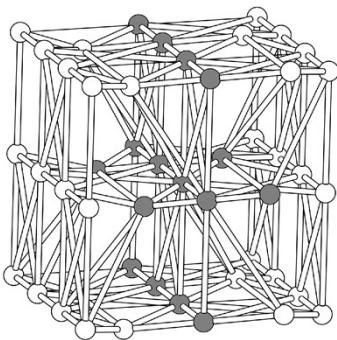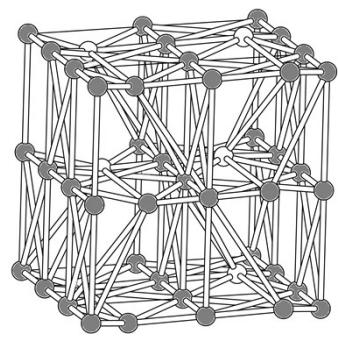
FM   AF1   AF2
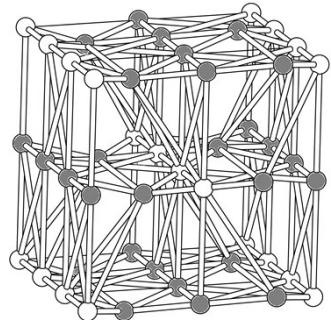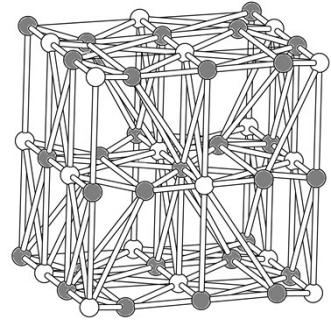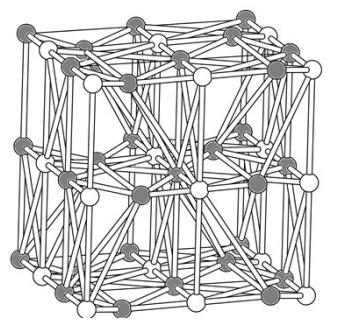
AF3 (E$_3$)   AF4   AF5 (E$_1$)
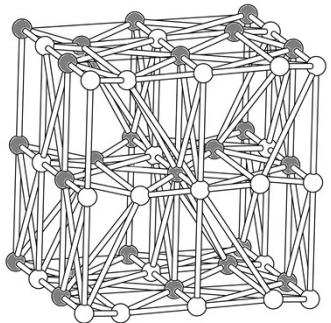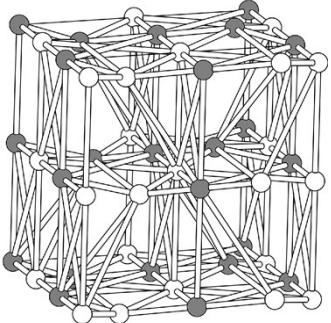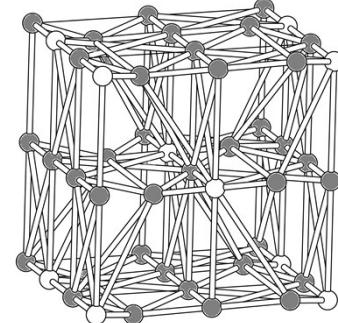
AF6 (GS)   AF7   AF8
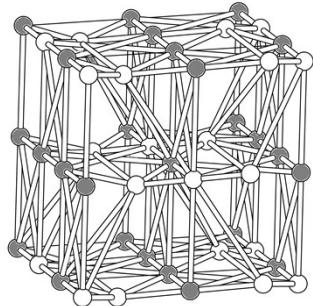
AF9 (E2)

Fig. S5. 10 ordered spin states of $Co_3(SeO_3)(SeO_4)(OH)_2$ employed for the energy-mapping analysis. In the text, the AF6, AF5, AF9 and AF3 arrangements are referred to as the GS, E_1, E_2 and E_3 states, respectively.

S2. Supplementary tables

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Co_3(SeO_3)(SeO_4)(OH)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	4507(2)	2500	2867(2)	12(1)
Co(2)	5000	5000	0	11(1)
Co(3)	5000	5000	5000	10(1)
Se(1)	2603(1)	2500	813(1)	12(1)
Se(2)	4145(1)	7500	2438(1)	11(1)
Se(2')	5601(8)	7500	2516(6)	11(1)
O(1)	1156(7)	2500	534(9)	15(2)
O(2)	3164(6)	381(9)	223(6)	14(2)
O(3)	2766(9)	2500	2261(8)	16(2)
O(4)	4805(6)	5511(10)	3189(6)	15(2)
O(5)	4943(6)	7500	1181(7)	11(2)
O(6)	5289(9)	2500	1223(8)	14(2)
O(7)	6021(8)	7500	5347(8)	10(2)
Se(1')	2448(7)	2500	-146(11)	12(1)
O(3')	2223(19)	2500	-1587(10)	16(2)

$$E_{spin} = -\sum_{i=1}^{9} n_i J_i S^2$$

Table S2. Values of n_i in the energy expressions, , for the ordered spin states FM and AF_i (i = 1 − 9) of $Co_3(SeO_3)(SeO_4)(OH)_2$

	J_1	J_2	J_3	J_4	J_5	J_6	J_7	J_8	J_9
FM	-8	-8	-16	-16	-8	-16	-16	-16	-16
AF1	-8	-8	-16	16	-8	16	16	-16	-16
AF2	-8	-8	0	0	8	-16	0	-16	-16
AF3	-8	-8	-16	16	-8	16	-16	16	16
AF4	8	8	0	0	-8	-16	0	16	-16
AF5	8	8	0	0	-8	16	0	-16	16
AF6	8	8	0	0	8	16	0	-16	16
AF7	8	8	0	0	8	-16	0	-16	16
AF8	-8	8	0	-16	-8	0	0	0	0
AF9	-8	8	0	16	-8	0	0	0	0

Table S3. Relative energies (in meV/FU) of the 10 ordered spin states obtained from DFT+U calculations

	$U_{\text{eff}} = 3$ eV	$U_{\text{eff}} = 4$ eV
FM	34.76	26.14
AF1	9.50	7.17
AF2	23.85	18.33
AF3 (E3)	4.25	3.07
AF4	18.20	13.99
AF5 (E1)	2.84	2.14
AF6 (GS)	0	0
AF7	8.16	6.24
AF8	18.74	14.00
AF9 (E2)	3.40	2.61

In the text, the AF6, AF5, AF9 and AF3 arrangements are referred to as the GS, E_1, E_2 and E_3 states, respectively.

S3. Computational details

We carried out DFT calculations for the (a, 2b, c) supercell of $Co_3(SeO_3)(SeO_4)(OH)_2$ using the frozen core projector augmented plane wave (PAW) [28, 29] encoded in the Vienna ab Initio Simulation Packages (VASP) [30] and the PBE potential [31] for the exchange-correlation functional. The electron correlation associated with the $3d$ states of Co was taken into consideration by DFT+U calculations with an effective on-site repulsion $U_{\text{eff}} = U - J = 3$ and 4 eV [32] All our DFT+U calculations used the plane wave cutoff energy of 450 eV, a set of (4x4x4) k-points, and the threshold of 10^{-6} eV for self-consistent-field energy convergence.

In terms of the spin Hamiltonian defined in Equation 1 of the text, the total spin exchange energies E per (a, 2b, c) supercell for each of the 10 ordered spin states can be written as

$$E_{spin} = \frac{-\sum_i n_i J_i S^2}{}$$

where $S = 3/2$, and $i = 1 - 9$. The values of n_i found for the 10 ordered spin states are listed in **Table S2**. We then carry out spin-polarized DFT+U calculations for the 10 ordered spin states to obtain their relative energies listed in **Table S3**. By mapping these relative energies on to the corresponding energies expressed in terms of the total spin exchange energies, we obtain the values of $J_1 - J_9$ summarized in **Table 3**.