Supplementary Information

Pb_2Cu_{10} Observation of a 1/3 magnetization plateau in $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$ arising from $(Cu^{2+})_7$ clusters of corner-sharing $(Cu^{2+})_4$ tetrahedra

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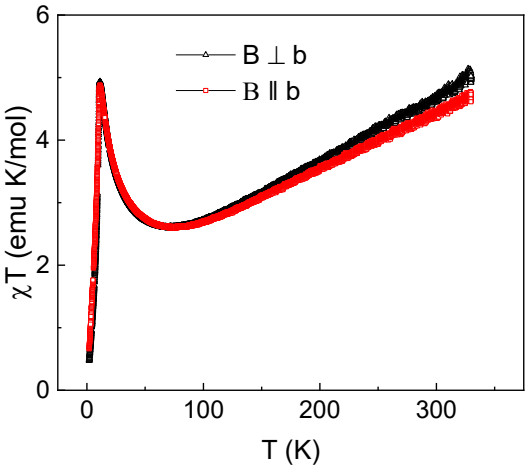
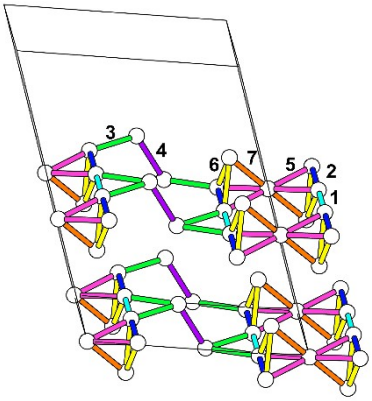
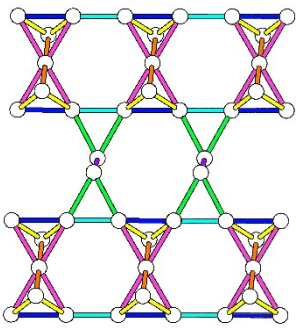


Fig. S1. χT vs. T plot for Pb2Cu10O4(SeO3)4Cl7.

[1]. Spin exchange paths $J_1 - J_7$



(a)



(b)

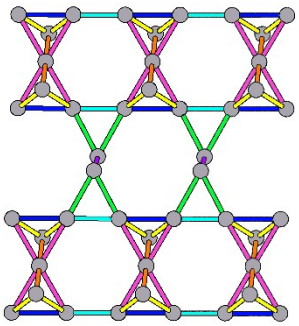
Paths	Cu …Cu
J_1	3.0209
J_2	3.1831
J_3	3.2195
J_4	3.1877
J_5	3.1451
J_6	3.0376
J_7	2.9781

Fig. S2. (a) Seven intralayer spin exchange paths and (b) Projection view along the a-axis of the one-magnetic layer in $Pb_2Cu_{10}O_4(SeO_3)4Cl_7$. The cyan, blue, green, purple, pink, yellow and orange cylinders indicate the J_1 to J_7 paths.

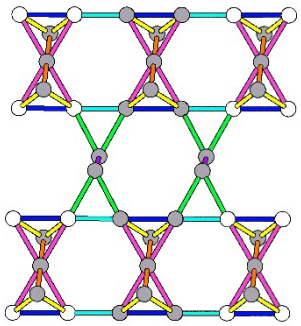
Table S1. Geometrical parameters of spin exchange paths, J_1 to J_7

Paths	Cu …Cu	∠Cu-O-Cu	O…O	∠Cu-O…O, O…O-Cu
J_1	3.0209	103.4		
J_2	3.1831	114.5		
J_3	3.2195	114.6	2.5717	101.9, 141.8
J_4	3.1877	106.8, 106.8		
J_5	3.1451	112.9	2.6287	96.9, 98.1
J_6	3.0376	105.9, 95.9		
J_7	2.9781	103.5		

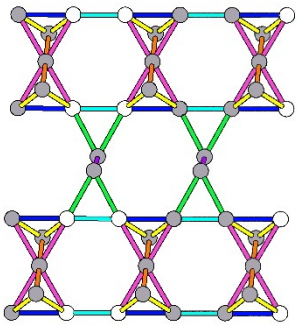
[2] Ordered spin states used to extract the spin exchanges $J_1 - J_7$



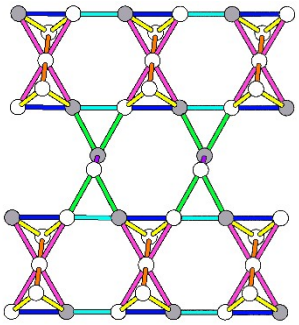
(a) FM



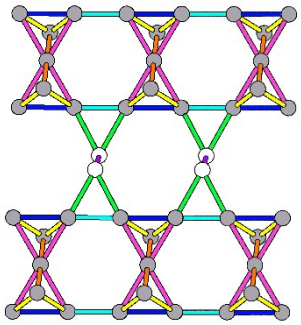
(b) AF1



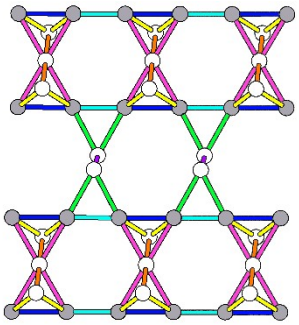
(c) AF2



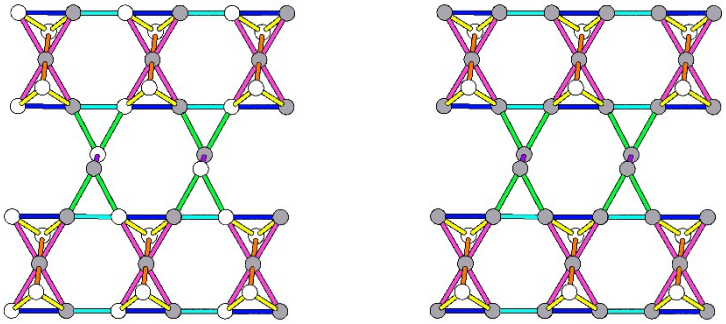
(d) AF3



(e) AF4



(f) AF5



(g) AF6 (h) AF7

Fig. S3. Ordered spin states, FM and AF(i) (i = 1 to 7), in $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$, where the grey and white circles indicate the up spin and down spin sites of Cu^{2+} ions. In these arrangements, we show the one-magnetic layer in $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$.

[3] Energy-mapping analysis

To determine the seven spin exchanges J_1 to J_7 $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$, we considered eight ordered spin states FM, AF(i) (i = 1 to 7) shown in Figure S2. Then, the total spin exchange energies of these states in (a, 2b, c) supercell can be written as

$$E = \left(\sum_{i=1}^{7} n_i J_i S^2 \right)$$

where S refers to the spin of the Cu^{2+} ions (i.e., S = 1/2). The values of n_i (i = 1 to 7) found for the seven spin states are listed in Table S2. The relative energies (meV/FU) obtained for the FM, AF(i) (i = 1 to 7) states by DFT+U calculations are listed in Table S3. By mapping the relative energies of the ordered magnetic states determined by DFT+U calculations to those determined by the spin exchange energies, we obtain the values of the spin exchanges, J_1 to J_7 by using the equation S1.

Table S2. Energy expression of the ordered spin arrangements of $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$

	J_1	J_2	J_3	J_4	J_5	J_6	J_7
E_{FM}	-8	-8	-16	-4	-16	-16	-8
E_{AF1}	8	-8	0	-4	0	0	-8
E_{AF2}	-8	8	0	-4	0	0	-8
E_{AF3}	8	8	0	4	0	0	-8
E_{AF4}	-8	-8	16	-4	-16	-16	-8
E_{AF5}	-8	-8	16	-4	16	16	-8
E_{AF6}	8	8	0	4	0	0	8
E_{AF7}	-8	-8	-16	-4	-16	16	8

Table S3. Relative energies (meV/FU) of $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$ obtained from DFT+U calculations

	U = 4 eV	U = 5 eV

E_{FM}	163.73	131.02
E_{AF1}	133.12	108.71
E_{AF2}	124.07	103.61
E_{AF3}	60.14	48.77
E_{AF4}	163.85	131.57
E_{AF5}	77.69	66.12
E_{AF6}	32.47	27.02
E_{AF7}	0	0

$J_3 = (1/32)(E_{AF4} – E_{FM})(4/N^2)$
$J_7 = (1/16)(4/N^2)(E_{AF6} – E_{AF3})$
$J_6 = (1/32)\{(E_{AF7} – E_{FM)}(4/N^2) – 16J_7\}$
$J_5 = (1/32)\{(E_{AF5} – E_{AF7})(4/N^2) – 32J_3 – 16J_7\}$
$J_2 = (1/16)\{(E_{AF2} – E_{FM})(4/N^2) – 16J_3 – 16J_5 – 16J_6\}$
$J_1 = (1/16)\{(E_{AF1} – E_{AF2})(4/N^2) + 16J_2\}$
$J_4 = (1/8)\{(E_{AF3} – E_{AF2})(4/N^2) – 16J_1\}$

[4] Computational details

To determine the spin exchanges of $Pb_2Cu_{10}O_4(SeO_3)_4Cl_7$, we carried out spin polarized DFT+U calculations by using the frozen core projector augmented plane wave (PAW)[1,2] encoded in the Vienna ab Initio Simulation Packages (VASP)[3] and the PBE[4] exchange correlation functional. The electron correlation associated with the 3d states of Cu was taken into consideration by DFT+U calculations[5] with an effective on-site repulsion Ueff = U – J = 4 and 5 eV. All our DFT calculations used the plane wave cutoff energy of 450 eV, a set of (2×4×4) k-points and the threshold of 10-6 eV for self-consistent-field energy convergence.

References

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