Supporting Information for:

Synthesis and characterization of robust three-dimensional chiral metal sulfates

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COMPUTATION DETAILS

To ascertain structural stability of the crystals and understand distribution of charges we calculate electronic structure from first principles using a planewave implementation of density functional theory (DFT)[1] available in PWSCF.[2] We use ultra-soft pseudo potentials[3] with many-body exchange-correlation energy approximated through gradient corrected PBE[4] and PW91[5] functional for $Mn_8(SO_4)_{12}$ and $Mg_8(SO_4)_{12}$ respectively. Pseudo-potentials for Mn and Mg include semi-core states. For the experimentally observed cubic unit-cells of lattice constants around 10 Å, total energies and density of states have been converged up to plane-wave cutoff up to 800 eV and 7 x 7 x 7 Monkhorst-Pack grid of k-points. Structural relaxation is done using the BFGS scheme,[6] wherein forces on atoms are calculated from ground-state electronic structure using the Hellmann-Feynmann theorem.[7] For a series of lattice constants around the observed value, crystals structure is relaxed till magnitude of forces are less than 10^{-4} Ry/Au. Total energies thus obtained as a function of lattice constant are then fitted to the Murnaghan's equation of state[8] of the generic form $E(V) = A + BV^{-C} + DV$, where $E(V)$ is the total energy corresponding to unit cell-volume V. Values of total energy, unit-cell volume, bulk-modulus and its pressure derivative at equilibrium can be calculated from the constants A, B, C and D. Cohesive energy per atom is also an important measure of stability of any assembly of atoms. It is calculated as $(E_{cohesive} = E_{unitcell} - \Sigma_i^N E_i^{isolated})/N$ for an N atom unit-cell. Evidently, stability of an atomic configuration increases as the cohesive energy becomes more negative. To ascertain charge associated with each atom we estimate Lowdin charges[9] which are obtained by projecting wave functions on to an orthogonal basis made of atomic orbitals. Lowdin charges do not exactly add up to the total number of electrons and the deviation is associated to the covalent nature of bonds.

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4. Perdew, J.; Burke, P. K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996,** *77*, 3865.

5. Perdew, J. P.; Wang, Y. *Phys. Rev.* B **1992**, *45* 13244.

6. (a) Broyden, C.G.; *Notices Amer. Math. Soc.* **1969**, 16; (b) Fletcher, R. *Comput. J.* , **1970**, *13*; (c) Goldfarb, D. *Math. Comp.* **1970**, 2; (d) Shanno, D.F. *Math. Comp.* **1970**, 24.

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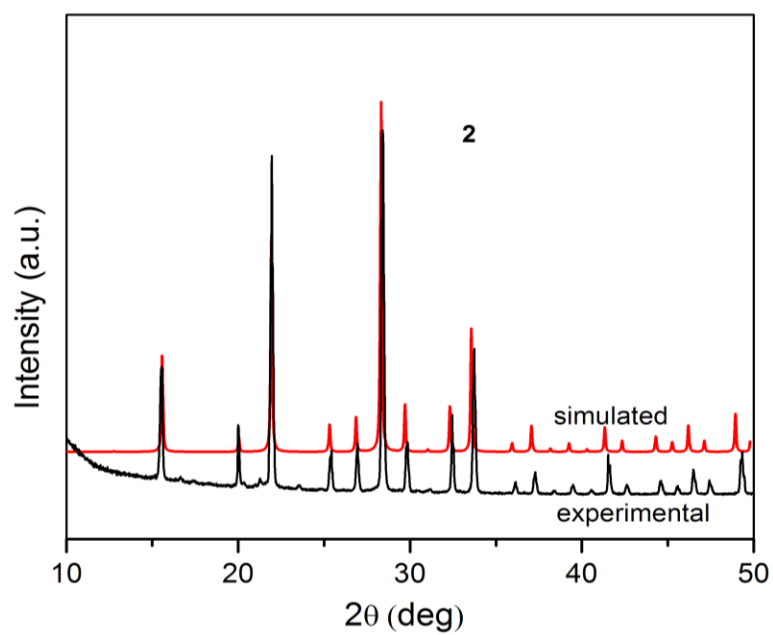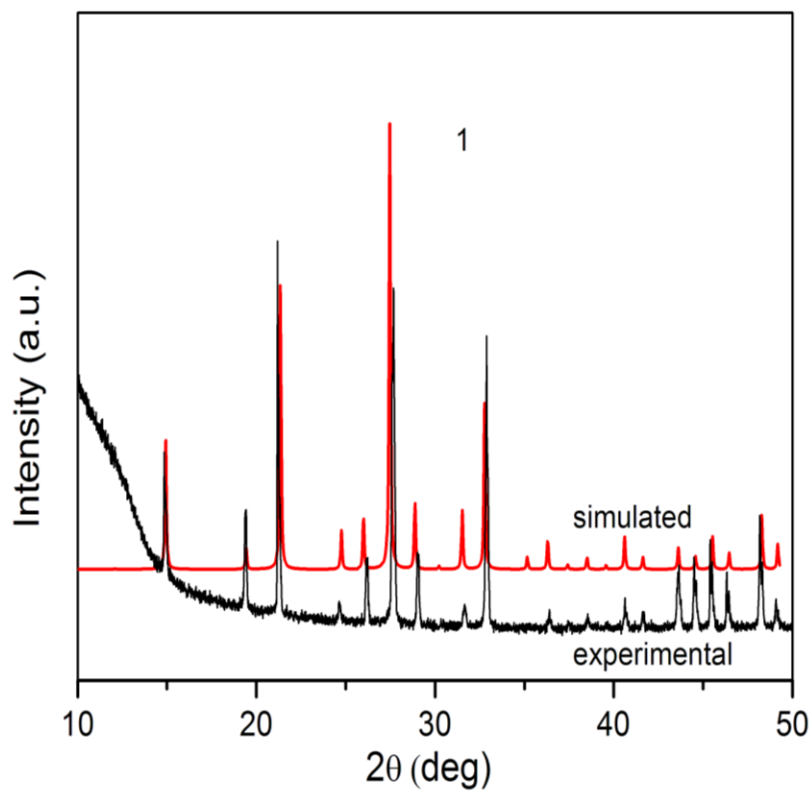9. Löwdin, P. O. *Adv Quantum Chem*, 1970 **5**, 185.

Fig. S1 Experimental and simulated powder X-ray diffraction patterns of $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2**, indicating the phase purity of the as-synthesized product.
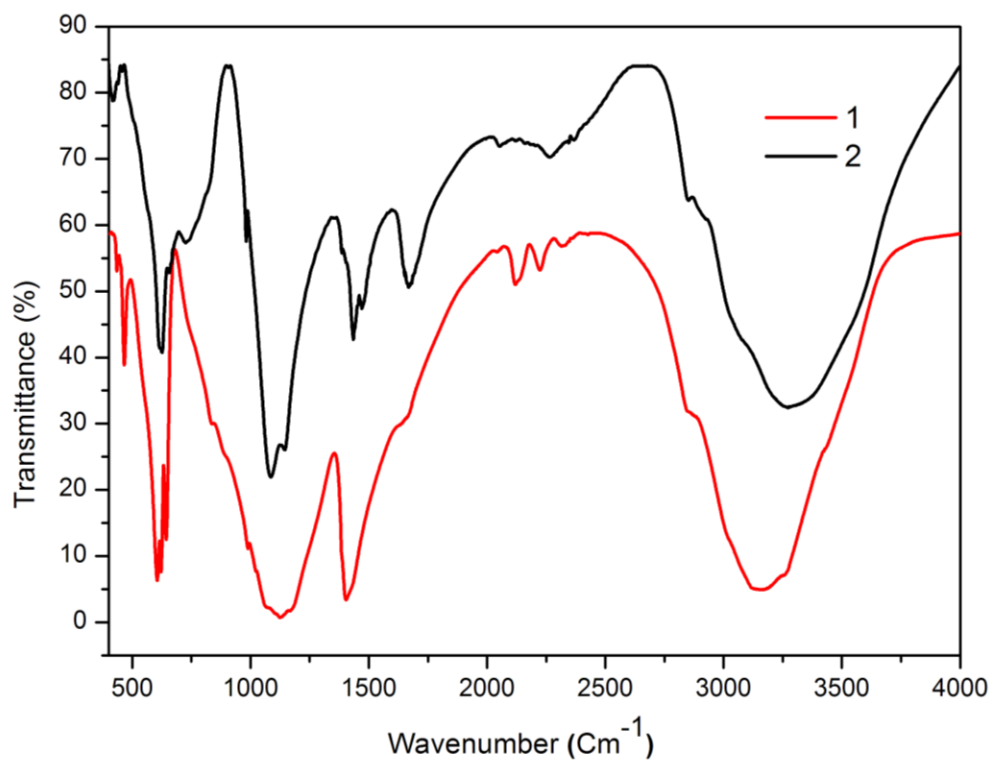
Fig. S2 Infrared spectra of $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2.**
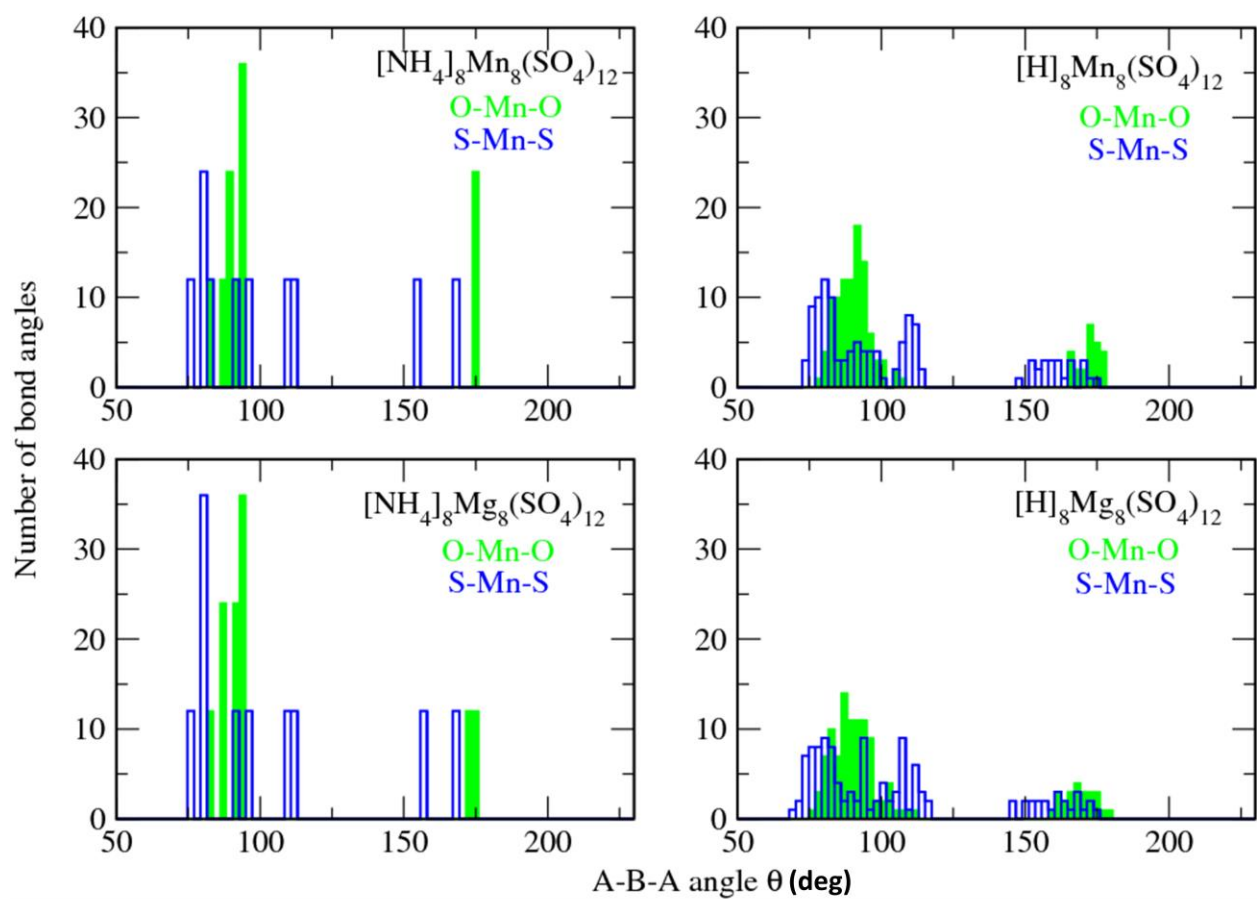
Fig. S3 Histogram showing the O-M-O and S-M-S bond angles of $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1;** $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2** and their de-ammoniated products $[H]_8[Mn_8(SO_4)_{12}]$, $[H]_8[Mg_8(SO_4)_{12}]$.

Gas sorption measurements. Sample tubes of a known weight of **1** and **2** were loaded with 250mg of sample and sealed using a transeal. Samples were degassed at 120 °C for 48 h on a Micromeritics ASAP 2020 analyzer until the outgas rate was no more than 1 mTorr/s. The degassed sample and sample tube were weighed precisely and then transferred back to the analyzer (with the transeal preventing exposure of the sample to air after degassing). The outgas rate was again confirmed to be no more than 1 mTorr/s. Measurements were performed at 77 K in a liquid nitrogen bath.
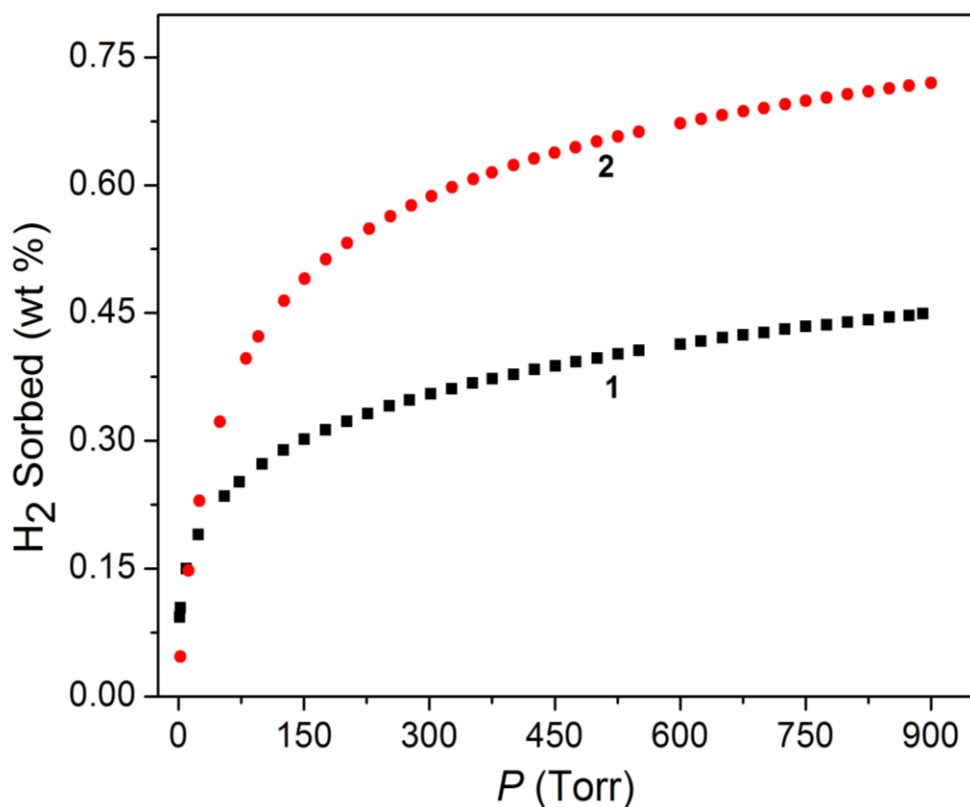

Fig. S4 Hydrogen adsorption isotherms for $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1;** $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2,** at 77 K.

Proton conductivity studies.

Controls of temperature and relative humidity (RH) for preparation and conductivity measurement of samples.

Impedance analyses were performed on powders of samples. The powders were pressed at 400 kg N for 1 minute by a standard 5 mm diameter and sandwiched between two gold electrodes. Measurements were performed using an impedance and gain-phase analyzer (Solartron SI 1260 Impedance/Gain-Phase analyzer) over frequency range 1 Hz – 1 MHz with an input voltage amplitude of 30 mV. Each conductivity measurement was conducted after waiting for 8 hours at the target condition (temperature and RH). ZView software was used to fit impedance data sets by means of an equivalent circuit simulation to obtain the resistance values. Temperature and RH above 40% at 25 °C were controlled by Espec Corp. SH-221 incubator.
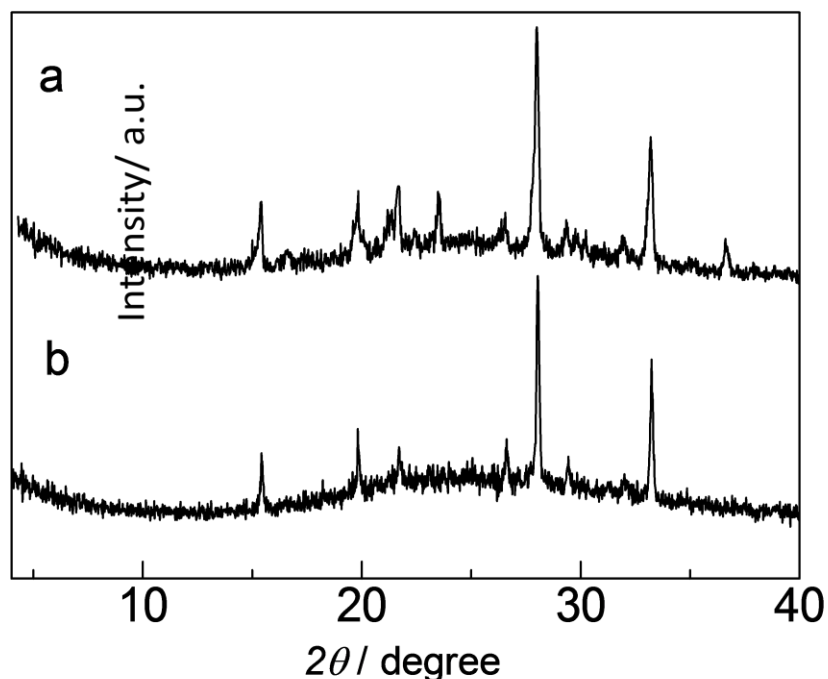

Fig. S5. Powder X-ray diffraction patterns of $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1** (a) after and (b) before impedance spectroscopy measurements under various RH at 298 K.

Table S1. Selected bond distances and angles for [NH$_4$]$_8$[Mn$_8$(SO$_4$)$_{12}$], **1.**

Moiety	Distance (Å)	Moiety	Angle (deg)
Mn(1)-O(1)	2.1585(13)	O(1)-Mn(1)-O(1)#1	94.67(5)
Mn(1)-O(1)#1	2.1585(13)	O(1)-Mn(1)-O(2)#3	
		O(1)#2-Mn(1)-	
Mn(1)-O(1)#2	2.1585(13)	O(2)#3#4#5	81.79(6)
Mn(1)-O(2)#3	2.1728(14)	O(1)#2-Mn(1)-O(2)#3#5	90.81(5)
Mn(1)-O(2)#4	2.1728(14)	O(2)#3-Mn(1)-O(2)#4	93.03(5)
Mn(1)-O(2)#5	2.1728(14)	O(3)#6#7-Mn(2)-O(3)	94.93(5)
Mn(2)-O(3)#6	2.1622(13)	O(3)-Mn(2)-O(4)#2#9	88.97(5)
Mn(2)-O(3)#7	2.1622(13)	O(4)#2-Mn(2)-O(4)#8	86.81(6)
Mn(2)-O(3)	2.1622(13)	O(3)#7-Mn(2)-O(4)#9	174.20(5)
Mn(2)-O(4)#2	2.1673(13)	O(4)-S(1)-O(2)	108.43(8)
Mn(2)-O(4)#8	2.1673(13)	O(4)-S(1)-O(1)	110.91(9)
Mn(2)-O(4)#9	2.1673(13)	O(2)-S(1)-O(1)	108.08(8)
S(1)-O(4)	1.4608(13)	O(4)-S(1)-O(3)	108.80(8)
S(1)-O(2)	1.4674(13)	O(2)-S(1)-O(3)	110.38(8)
S(1)-O(1)	1.4702(13)	O(1)-S(1)-O(3)	110.21(8)
S(1)-O(3)	1.4716(12)	S(1)-O(1)-Mn(1)	146.93(9)
N(10)-H(1)	0.917(18)	S(1)-O(2)-Mn(1)#10	151.48(9)
N(10)-H(2)	0.91(2)	S(1)-O(3)-Mn(2)	129.96(8)
N(20)-H(3)	0.93(3)	S(1)-O(4)-Mn(2)#11	168.27(9)
N(20)-H(4)	0.82(5)	H(1)-N(10)-H(2)	108(3)
		H(3)-N(20)-H(4)	106(2)

Symmetry transformations used to generate equivalent atoms:
#1 -z+1/2,-x+1,y-1/2   #2 -y+1,z+1/2,-x+1/2   #3 y,z+1,x
#4 -x+1/2,-y+1,z+1/2   #5 -z,x+1/2,-y+1/2   #6 z+1/2,-x+1/2,-y
#7 -y+1/2,-z,x-1/2   #8 -z,x-1/2,-y+1/2   #9 -x+1,y-1/2,-z-1/2
#10 -x+1/2,-y+1,z-1/2   #11 -x+1,y+1/2,-z-1/2

Table S2: Selected bond distances and angles for [NH$_4$]$_8$[Mg$_8$(SO$_4$)$_{12}$], **2.**

Moiety	Distance (Å)	Moiety	Angle (deg)
Mg(1)-O(1)	2.0711(10)	O(1)#1-Mg(1)-O(2)#3#4	92.36(4)
Mg(1)-O(1)#1	2.0711(10)	O(1)#2-Mg(1)-O(2)#3#4#5	83.00(4)
Mg(1)-O(1)#2	2.0711(10)	O(2)#3-Mg(1)-O(2)#4#5	92.09(5)
Mg(1)-O(2)#3	2.0863(11)	O(1)#1-Mg(1)-O(2)#5	173.48(4)
Mg(1)-O(2)#4	2.0863(11)	O(1)#2-Mg(1)-O(2)#5	92.36(4)
Mg(1)-O(2)#5	2.0863(11)	O(3)-Mg(2)-O(3)#6#7	87.80(5)
Mg(2)-O(3)	2.0697(11)	O(3)#6#7-Mg(2)-O(4)#8	175.83(5)

Mg(2)-O(3)#6	2.0697(11)	O(3)#7-Mg(2)-O(4)#8#9	88.34(4)
Mg(2)-O(3)#7	2.0697(11)	O(3)#7-Mg(2)-O(4) #8#9	90.49(4)
Mg(2)-O(4)#8	2.0707(11)	O(3)-Mg(2)-O(4)#2	88.34(4)
Mg(2)-O(4)#9	2.0707(11)	O(4)#8#9-Mg(2)-O(4)#2	93.26(5)
Mg(2)-O(4)#2	2.0707(11)	O(3)-S(1)-O(2)	108.37(7)
S(1)-O(3)	1.4679(10)	O(3)-S(1)-O(4)	109.00(6)
S(1)-O(2)	1.4752(10)	O(2)-S(1)-O(4)	110.08(6)
S(1)-O(4)	1.4764(10)	O(3)-S(1)-O(1)	110.37(6)
S(1)-O(1)	1.4779(10)	O(2)-S(1)-O(1)	108.74(7)
N(10)-H(1)	0.86(3)	O(4)-S(1)-O(1)	110.25(6)
N(10)-H(2)	0.86(4)	S(1)-O(1)-Mg(1)	149.99(7)
N(20)-H(3)	0.85(3)	S(1)-O(2)-Mg(1)#10	152.36(7)
N(20)-H(4)	0.91(2)	S(1)-O(3)-Mg(2)	169.67(8)
Moiety	Angle (deg)	S(1)-O(4)-Mg(2)#11	132.16(6)
O(1)-Mg(1)-O(1)#1#2	92.89(5)	H(1)-N(10)-H(2)	103.9(18)
O(1) #2-Mg(1)-O(2)#3#4	173.48(4)	H(3)-N(20)-H(4)	110(2)

Symmetry transformations used to generate equivalent atoms:
 #1 y+1,z,x-1   #2 z+1,x-1,y   #3 -y+1,z-1/2,-x+1/2   #4 -x+3/2,-y,z-1/2   #5 z+1/2,-x+1/2,-y
 #6 -z+3/2,-x+1,y+1/2   #7 -y+1,z-1/2,-x+3/2   #8 -x+2,y-1/2,-z+1/2 #9 -y+3/2,-z,x-1/2
#10 -x+3/2,-y,z+1/2   #11 -x+2,y+1/2,-z+1/2

Table S3. Atomic Coordinates [x10^4] and Equivalent Isotropic Displacement Parameters [$Å^2$ x 10^3] for [NH$_4$]$_8$[Mn$_8$(SO$_4$)$_{12}$], **1** U(eq) is defined as one third of the trace of the orthogonal zed U$_{ij}$ tensor.

Atom	x	y	z	U(eq)
Mn(1)	4168(1)	5832(1)	832(1)	12(1)
Mn(2)	3438(1)	1562(1)	-1562(1)	13(1)
S(1)	3749(1)	4691(1)	-2366(1)	11(1)
O(1)	3461(1)	5004(1)	-986(1)	23(1)
O(2)	2547(1)	4901(1)	-3132(1)	25(1)
O(3)	4188(1)	3320(1)	-2486(1)	22(1)
O(4)	4773(1)	5552(1)	-2883(1)	24(1)
N(10)	7018(2)	2982(2)	-2018(2)	26(1)
N(20)	5665(2)	-665(2)	665(2)	20(1)

Table S4: Atomic Coordinates [x10^4] and Equivalent Isotropic Displacement Parameters [Å^2 x 10^3] for [NH$_4$]$_8$[Mg$_8$(SO$_4$)$_{12}$], **2**. U(eq) is defined as one third of the trace of the orthogonal zed U$_{ij}$ tensor.

Atom	x	y	z	U(eq)
Mg(1)	9153(1)	-847(1)	-847(1)	11(1)
Mg(2)	11512(1)	-1512(1)	3488(1)	11(1)
S(1)	8754(1)	356(1)	2341(1)	9(1)
O(1)	8502(1)	-13(1)	932(1)	16(1)
O(2)	7516(1)	149(1)	3114(1)	17(1)
O(3)	9804(1)	-497(1)	2911(1)	18(1)
O(4)	9179(1)	1766(1)	2432(1)	15(1)
N(10)	5677(1)	-677(1)	677(1)	16(1)
N(20)	12056(2)	2056(2)	2056(2)	21(1)

Table S5. The Hydrogen Bonding Interactions of the compounds [NH$_4$]$_8$[Mn$_8$(SO$_4$)$_{12}$], **1** and [NH$_4$]$_8$[Mg$_8$(SO$_4$)$_{12}$], **2**.

D-H…A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(º)
1				
N(10)-H(1)···O(3)	0.91(3)	2.07(2)	2.941(2)	159(5)
N(20)-H(3)···O(1)	0.92(3)	2.06(3)	2.944(2)	159(3)
N(20)-H(4)···O(4)	0.82(3)	2.48(3)	3.125(2)	136(3)
N(20)-H(4)···O(4)	0.82(3)	2.48(3)	3.125(2)	136(3)
2				
N(10)-H(1)···O(1)	0.87(3)	2.09(3)	2.9139(17)	158(3)
N(10)-H(2)···O(3)	0.86(2)	2.37(2)	3.0432(17)	135.6(17)
N(10)-H(2)···O(3)	0.86(2)	2.37(2)	3.0432(17)	135.6(17)
N(10)-H(2)···O(3)	0.86(2)	2.37(2)	3.0432(17)	135.6(17)
N(20)-H(3)···O(4)	0.85(2)	2.10(3)	2.9164 (18)	161 (4)

Table S6: Lowdin charges of semicore and valence orbitals of atoms.

Element	Orbital charge					
	1s	2s	2p	3s	3p	3d
[NH$_4$]$_8$[Mg$_8$(SO$_4$)$_{12}$], 2						
Mg			6.0	0.3	0.9	0.7
S				1.0	2.5	
O		1.7	5.0			
N		1.3	4.2			
H	0.6					
[H]$_8$Mg$_8$(SO$_4$)$_{12}$]						
Mg			6.0	0.3	0.9	0.6
S				1.0	2.5	
O		1.6	5.0			
H	0.6					

[NH$_4$]$_8$[Mn$_8$(SO$_4$)$_{12}$], 1

Element	1s	2s	2p	3s	3p	3d	4s	4p
Mn				2.0	6.0	5.6	0.4	0.9
S				1.0	2.5			
O		1.7	4.9					
N		1.3	4.2					

H	0.7							
[H]$_8$ [Mn$_8$(SO$_4$)$_{12}$]								
Mn				2.0	6.0	5.6	0.4	0.9
S				1.0	2.5			
O		1.6	5.0					
H	0.6							