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ARTICLE TYPE

Synthesis and characterization of robust three-dimensional chiral metal sulfates

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Two chiral three-dimensional metal sulfates of the compositions, $[NH_4]_8[Mn_8(SO_4)_{12}]$, (**1**) and $[NH_4]_8[Mg_8(SO_4)_{12}]$, (**2**), of the Langbeinites family have been synthesized under hydro/solvothermal conditions and studied from first principles. Both the two compounds **1** and **2** are isostructural and crystallize in the cubic chiral space group *P2(1)3*. In the presence of NH_4^+cations, the frameworks of **1** and **2** have three-dimensional structures formed by corner sharing of metal octahedra and sulphate tetrahedra through M-O-S linkages, which leads to a pinwheel arrangement of metal octahedra surrounded by six sulfate tetrahedra. Both **1** and **2** are observed to retain their structures upon thermal decomposition of ammonium ion resulting into compositions $[H]_8[Mn_8(SO_4)_{12}]$ and $[H]_8[Mg_8(SO_4)_{12}]$ respectively. Magnetic measurement of **1** shows paramagnetic behaviour and hydrogen adsorption of **1** and **2** shows 0.45 and 0.7 wt% respectively at 77 K. The proton conductivity of **1** under various relative humidity (RH) shows 2.6 x 10^{-7} Scm^{-1} at RH = 80% and reaches to 3.1 x 10^{-4} S cm^{-1} at RH = 90%. First Principles calculations suggest structural evolution yet retention of framework structures of similar stabilities by both the compounds after de-ammoniation.

Introduction

The synthesis of complex inorganic materials with open architecture is one of the major activities in contemporary solid state chemistry for their applications in catalysis, ion-exchange, sorption and separation process. In particular, solid materials with chiral three-dimensional structures are of great interest in both material as well as coordination chemistry owing to their great structural diversity supporting a host of useful physical and chemical properties such as magnetism, ferroelectricity, fluorescence, catalysis, and solid state proton conductors to list a few.[1-3]Although synthesis of new crystalline solids with unusual structures is a growing trend, synthesis of higher-dimensional framework solids with chiral structures still remains a challenge.[4,5] Notwithstanding the modest progress in designing chiral structure of zeolite[6] and metal phosphate,[7] complete control of framework chirality has not been achieved due to the complexity and poor understanding of the reaction mechanisms involved in the process.

During the last two decades or so large number of new materials with novel architectures have been synthesized and characterized. Accordingly, inorganic open-framework structures involving silicates,[8] phosphates[9] and carboxylates[10] have been investigated widely in the past few years. It has been demonstrated recently that oxyanions such as selenite,[11] selenate[12] and sulfate[13] can also be used to build up open architectures. Nevertheless, most of the organically-templated transition metal sulfates reported in the literature have one- or two-dimensional structures in accordance with the observation that formation of three-dimensionally extended robust sulfate networks is generally difficult.[14] Three-dimensional sulfate networks are most likely obtained by using the element which support higher coordination number such as the lanthanides and actinides.[15] However, inorganic open-framework metal sulfates based on main group metals (light main group metal in particular) have not been synthesized hitherto. Compared to f- and d-block cations, s-block cations are far less popular as building blocks owing to their unpredictable coordination numbers and geometries in the absence of ligand field stabilization affects.[16] The main problem for framework assembly with s-block ions is their high affinity for oxygen donors. Magnesium (II) ion has a number of similarities with transition metal ions as it prefers octahedral coordination, and has a comparable ionic radius (72 pm for Mg^{2+} compared to 80 pm for Mn^{2+}, 74 pm for Zn^{2+} and 73 pm for Cu^{2+}) despite having a much smaller molar mass. Use of such light metals in porous materials is appealing as they predictably have strong binding affinities for small molecules such as dihydrogen, methane, thus presenting new possibilities for light weight sorption materials.[17] The chemistry of manganese

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†Electronic Supplementary Information (ESI) available: X-ray crystallographic data in CIF format; IR spectra, PXRD patterns and computational details of **1** and **2.** CCDC 1017343 (**1**) and 1017344 (**2**).

system represents an important subfamily of the inorganic open-framework materials and attract significant attention owing to their feasibility of achieving different oxidation states that lead to interesting magnetic properties.[18]

Chemistry of noncentrosymmetric sulfate materials is still in its infancy with very few compounds reported in the literature. Broadly, two synthetic strategies have been used so far to prepare chiral solids, one being the stereo selective synthesis[19,20] employing chiral organic ligands, while the other involves spontaneous resolution upon crystallization without chiral species.[21,22] Chiral porous frameworks represent a novel class of recyclable and reusable solid asymmetric catalysts as a result of their truly single-site nature, and straightforward structural characterization by X-ray crystallography. Since the chirality of the compounds should be controlled in the molecular level, as well as in the entire crystal structure, there has been countably few chiral metal sulfates are reported till date.[23] To add to the scant repository of 3D-chiral metal sulfates with transition as well as main group metals built without using any chiral auxillary, in this article we report synthesis, structure, proton conductivity and electronic properties of $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1,** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2** compounds.

Experimental section

Synthesis of Compounds. Compounds **1** and **2** were synthesized by employing hydro/solvothermal methods. In an effort to synthesize three-dimensional metal sulfates, we have used ammonium sulfite as the source of sulfate that gets oxidized to sulfate easily during the synthetic conditions. Efforts of getting the same phase using H_2SO_4 as the source of sulfate was unsuccessful. It seems the pH of the reaction mixture is playing an important role for the synthesis of both **1** and **2.** In a typical synthesis of **1**, 0.251 g of $Mn(NO_3)_2.4H_2O$ was dispersed in an EG/water mixture (2.8 and 0.9 mL, respectively) under constant stirring. To this mixture, 0.268 g of $(NH_4)_2SO_3$ was added and the mixture was stirred for 20 minutes to obtain the clear solution. The final mixture with the molar composition of $Mn(NO_3)_2.4H_2O/(NH_4)_2SO_3/H_2O/EG$ (1:2:50:50) was transferred into a 15-mL Teflon-lined acid digestion bomb and heated at 180 °C for 48 h. The reaction mixture after above heat treatment did not show any appreciable change in pH and remains at pH 6. After cooling white block-shaped crystals were obtained with 75% yield. Compound **2** was prepared in the same way and the final mixture with the molar composition of $Mg(OAc)_2.4H_2O/(NH_4)_2SO_3/EG/H_2O$ (1:2:70:80) was transferred into a 15-mL Teflon-lined acid digestion bomb which was subjected to heat treatment similar as above. The product containing white block-shaped crystals were obtained with 80% yield.

Physical measurements. Infrared spectra were recorded on a PerkinElmer FTIR spectrometer equipped with an attenuated total reflectance accessory. EDAX was performed by field emission scanning electron microscopy (FE-SEM, Zeiss, Oxford). Thermogravimetric analyses were carried out at a ramp rate of 1°C/min under a flow of nitrogen using a PerkinElmer STA 8000. Powder X-ray diffraction data were collected on a Bruker D8 Advance with DIVINCI design fitted with HTK 16 temperature chamber X-ray powder diffractometer using Cu K_α radiation (λ = 1.5418 Å). DC magnetic susceptibility measurements were performed on powdered samples of **1** at temperatures between 5 and 300 K, using a Quantum Design SQUID magnetometer. Gas adsorption measurements of **1** and **2** were collected using a Micromeritics ASAP 2020 gas sorption analyzer. 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. Carbon, hydrogen and nitrogen analyses were obtained from the Sophisticated Analytical Instrument at Central Drug Research Institute, Lucknow. Structure and stability of the crystal structures, particularly after de-ammoniation, is studied through calculations of cohesive energies, bulk-modulus and charge balancing obtained from first principles within the framework of density functional theory (DFT**).**

Initial characterization of **1** and **2** was carried out by powder X-ray diffraction (PXRD), energy dispersive analysis of X-rays (EDAX), chemical analysis, thermogravimetric analysis (TGA) and IR spectroscopy. The PXRD pattern exclusively exhibited signatures of a hitherto unknown material consistent with the structure determined by single crystal XRD, which gave the compositions of **1** and **2** as $[NH_4]_8[Mn_8(SO_4)_{12}]$ and $[NH_4]_8[Mg_8(SO_4)_{12}]$ respectively. X-ray diffraction patterns of **1** and **2** were almost in good agreement with the simulated patterns based on their respective single-crystal data, (Fig. S1 in the supporting information). Both **1** and **2** gave satisfactory elemental analysis. The experimental and calculated (in wt %) values of H, N and S were as follows. **1,** H = 3.7; N = 7.2 and S = 17.2 (calc. H = 3.3, N = 7.0 and S = 17.15); **2,** H = 5; N = 7.4 and S = 21.6 (calc.: H = 4.6 N = 7.2 and S = 22). EDAX indicated the ratios of M and S to be 2**:**3 in both **1** and **2**, in agreement with the molecular formulae. TGA showed weight loss corresponding to the loss of ammonia for both the compounds. These analytical data confirm the molecular formulae of **1** and **2** as obtained from crystallography. The IR spectra of **1** and **2** **(**Fig. S2**)** showed characteristic bands for the sulfate as well as the ammonium moieties. The stretching mode of –N–H bond (of the amine) is observed around 3004 cm^{-1}. The N–H bending modes of the amine and NH_4^+ are observed in the range 1440–1586 cm^{-1}. The characteristic stretching bands, ν_3(N–H) and $2\nu_4$(N–H) of the NH_4^+ ion are observed at 3243 and 2830 cm^{-1} respectively. Strong bands in the region 850–1015 cm^{-1} correspond to ν_1 and ν_3 while bands in the region 583–644 cm^{-1} can be assigned to ν_2 and ν_4 fundamental modes of sulfate ion.[24]

Single-crystal structure determination. Single crystal structure determination by X-ray diffraction was performed on a Bruker Smart Apex II diffractometer equipped with an Oxford Cryostream low-temperature device and a fine-focus sealed-tube X-ray source (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromated) operating at 50 kV and 30 mA. The structure was solved by direct methods using SHELXS-97,[25]which readily revealed all the heavy atom positions (Mn, S) and enabled us to locate the other non-hydrogen (Mg, N and O) positions from the difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS.[26]All the hydrogen positions were found in the difference Fourier maps. For the final refinement, ammonium ion in **1** and **2** were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full -matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[27] package of programs. Details of the structure determination and final refinements for **1** and **2** are listed in Table 1.

Results and discussion.

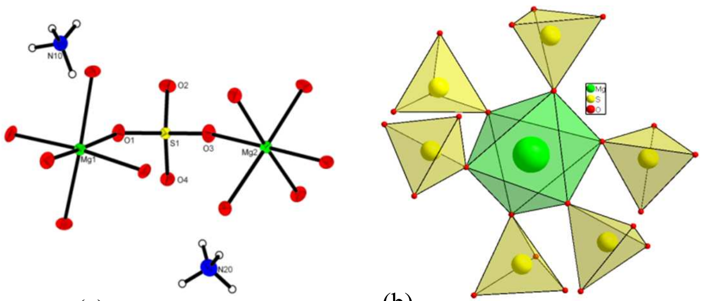
Three-dimensional $[NH_4]_8[M_2(SO_4)_{12}]$, (M = Mn; 1, Mg; 2): The two compounds **1** and **2** are isostructural, and have a three dimensional network structure made up of MO_6 octahedra and SO_4 tetrahedra with interstitial NH_4^+ ions. The asymmetric unit consists of 9 non-hydrogen atoms out of which 7 belong to the inorganic framework and 2 to the guest NH_4^+ ions as shown in the Fig. 1a. Both metal and nitrogen atoms are present in one-third occupancy. There are two crystallographically distinct M atoms and one S atom with both the metal atoms in octahedral coordination with the O neighbors from the six sulfate groups.

Table 1. Crystal data and structure refinement parameters for $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1,** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2**

Parameters	**1**	**2**
Empirical formula	H2.67 Mn0.67 N0.67 O4 S	H2.67 Mg0.67 N0.67 O4 S
Crystal system	Cubic	Cubic
Crystal size (mm)	0.20x0.17x0.15	0.18x0.16x0.15
$a = b = c$ (Å)	10.1846(2)	10.0022(8)
$\alpha = \beta = \gamma$ (^{0})	90	90
V (Å^3)	1056.41(4)	1000.66(14)
Z	12	12
Formula weight	144.71	124.29
Space group	*P2(1)3(198)*	*P2(1)3(198)*
T (^{o}C)	23	23
λ(MoKα) Å	0.71073	0.71073
ρ_{calc}(gcm^{-3})	2.730	2.475
μ (mm^{-1})	3.056	0.943
R[I.>2σ(I)]	R1 = 0.0150 wR2 = 0.0378	R1 = 0.0162 wR2 = 0.0440
R (all data)	R1 = 0.0153, wR2 = 0.0379	R1 = 0.0163, wR2 = 0.0441

$R_1=\sum|F_0| - |F_c|$; $wR_2=\{[w(F_0^2-F_c^2)^2] / [w(F_0^2)^2]\}^{1/2}$, $w=1/[\sigma^2(F_0)^2+(aP)^2+bP]$ $P=[F_0^2+2Fc^2]/3$;
where a=0.0247; b=0.1707for **1** anda=0.0301; b =0.2038 for **2.**

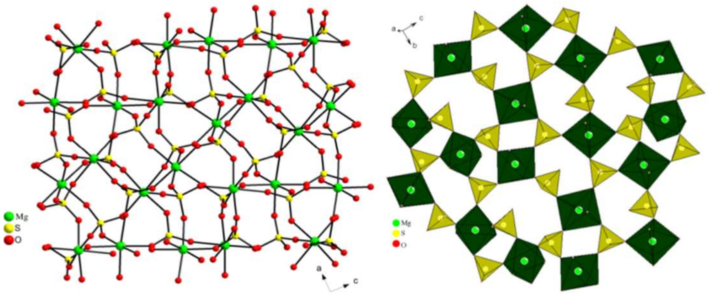
The Mg-O bond distances are in the range 2.070(4)-2.072(4) Å [Mg(1)-O_{av}= 2.071, Mg(2)- O_{av}=2.072 Å]. The *trans* O-Mg-O bond angles are in the range 175.9(2)-168.7(2)º and the *cis* O-Mg-O are in the range 78.89(14)-101.1(2)º with an average of 172.4 and 85.06º respectively. The Mn-O bond distances are significantly larger than the the Mg-O bond distances and are in the range 2.1585 (13)- 2.1728 (14) Å [Mn(1)-O_{av}= 2.165, Mn(2)-O_{av}=2.164 Å]. The *trans* O-Mn-O bond angles are in the range 173.7(6)-174.2(5)º and the *cis* O-Mn-O are in the range 81.79(6)-94.93 (5)º with an average of 173.9 and 70.14º respectively. Selected bond distances for both **1** and **2** are listed in Table 2. Both M(1) and M(2) make six M-O-S linkage by sharing corner with six sulfate groups resulting into a pinwheel arrangement of MO_6 octahedra and SO_4 tetrahedra (Fig. 1b). From the M-O bond lengths, it can be seen that MnO_6 octahedra are little distorted than the MgO_6 octahedra. The unique S atom is tetrahedrally coordinated by the oxygen neighbors with the S-O bond distance ranged between 1.489(4)-1.459(4) with an average bond distance of 1.474 Å. The S-atom makes four S-O-M linkages through four of its oxygen atoms. Bond-valence sum (BVS) calculations[28] (Mn (1) = 2.17, Mn(2) = 2.17, Mg(1) = 2.11, Mg(2) = 2.16,) and the average M-O bond lengths indicate that the oxidation state of both manganese the magnesium to be +2 and S to be +6 although we expect deviations from these estimates due to the fully and partially covalent nature of the S-O and M-O bond respectively. Thus the framework structure $[M(SO_4)_{12}]^{8-}$ is negatively charged and it gets neutralized by the presence of eight ammonium ions in the unit cell.



(a) (b)

Fig. 1 (a) ORTEP plot of $[NH_4]_8[Mg_8(SO_4)_{12}]$ in **2**. The asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability. (b) Pinwheel arrangement of MO_6 octahedra and SO_4teterahedra in **1** and **2**.

The prominent feature of **1** and **2** is the three-dimensional chiral structure with cubic symmetry that crystallizes in the space group *P2(1)3*. The structures are built from strictly alternating MO_6 octahedra and SO_4tetrahedra units that linked through their vertexes throughout the structure. Both MO_6 octahedra and SO_4 tetrahedra share corner alternatively to form four- and six-membered rings that form infinite chains. These chains are alternately stacked one over the other along the [100] direction and are interlinked by sharing corners with the tetrahedral corners of the SO_4 groups to form a layer as shown in Fig. 2a. Within each layer, each sulfate tetrahedra shares three of its corners with the octahedra of three adjacent chains, one due to M(1) and two due to M (2) (Fig. 2b). The layers thus formed are cross-linked by SO_4 tetrahedra along the *b*-axis through corner sharing S-O-Mg linkages to form the three-dimensional structure (Fig. 3). The interstitial ammonium ions interact with the framework oxygen through strong N-H···O hydrogen bonds. The details of the N-H···O hydrogen bonding interactions in **1** and **2** are given in Table S5.



(a) (b)

Fig. 2 (a) Top view of the layer parallel to the *ac*-plane of the unit cell in **2** (b) Polyhedral representation of the inorganic layer **2** in the *bc*-plane forming 4-, 6- and 8-membered aperture.

Table 1. Important M-O bond distances in $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1,** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2**

$[NH_4]_8[Mn_8(SO_4)_{12}]$ **(1)**		$[NH_4]_8[Mg_8(SO_4)_{12}]$ **(2)**	
Moiety	Distance (Å)	Moiety	Distance (Å)
Mn(1)-O(1) #1#2	2.1585(13)	Mg(1)-O(1) #1#2	2.0711(10)
Mn(1)-O(2)#3#4#5	2.1728(14)	Mg(1)-O(2)#3#4#5	2.0863(11)
Mn(2)-O(3) #6#7	2.1622(13)	Mg(2)-O(3) #6#7	2.0697(11)
Mn(2)-O(4)#2#8#9	2.1673(13)	Mg(2)-O(4)#2#8#9	2.0707(11)

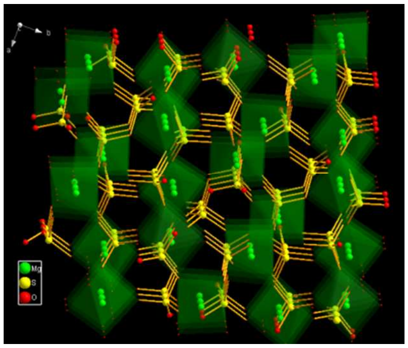
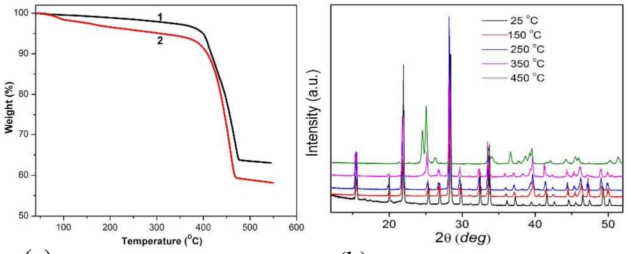


Fig. 3 View down the crystallographic *c*-axis showing the inorganic framework structure of **2**, showing channels in the structure. Ammonium ions are removed for clarity.

Thermogravimetric studies. Thermogravimetric analysis of **1** and **2** was carried out under constant flow of N_2 at a heating rate of 2 ^{o}C min^{-1} in the temperature range 35–750 ^{o}C (Fig. 4a) **1** showed a two-step weight loss corresponding to the loss of ammonia in the range 70–380 ^{o}C (obs = 7.0%, calcd = 6.8%), followed by removal of of SO_2 around 400^{o}C. The total observed weight loss of 60.5 % corresponds to the loss of the amine along with sulfates is in good agreement with the calculated value of 59.5 %. The PXRD pattern of the sample heated to 550˚C diffracted very weakly and could not be recognized. TGA curve of **2,** shows a mass loss of 7.5% in the range 70–380 °C which could be accounted for the removal of ammonia (theo. = 8.0%, obs = 7.5%). A major weight loss in the region 380–475 °C was observed corresponding to the decomposition of the sulfate [theo. = 31.2%, obs. = 31.6%]. To ascertain the stability of the compounds, high temperature X-ray studies of **2** were carried out at different temperatures on a Bruker D8 Advance with DIVINCI design fitted with HTK 16 temperature chamber. It was observed that the structure remains intact even after the thermal treatment of 350 ^{o}C as can be seen from the powder pattern shown in Fig. 4b. The framework collapses when it is heated at 450 ^{o}C which is also supported by the TGA data.

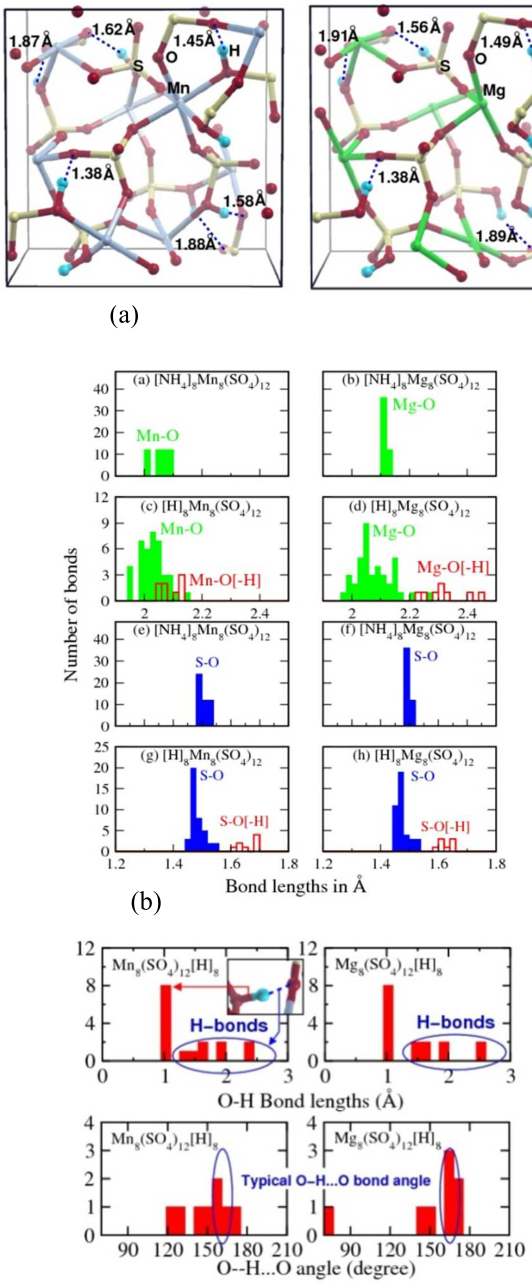


(a) (b)

Fig. 4 (a) Thermogravimetric data for $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2** (b) PXRD patterns of compound 2 at different temperatures. The structure remains intact when it is heated to 350 ºC.

First principles studies

We study the observed crystal structures from first principles within the framework of density functional theory (DFT) which approximates the many-body exchange and correlation interactions by local functionals of single particle density and its derivatives. In this section we attempt to address whether the two experimentally observed ammoniated crystals $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1** and $[NH_4]_8[Mg_8(SO_4)_{12}]$, **2**, would retain their open framework structure upon de-ammoniation or not. We use a gradient corrected exchange-correlation functional which inherently describe the lower-bound of crystal binding. Oxidation states of atoms are estimated in terms of Lowdin charges[29](LC) which are obtained by projecting the occupied manifold of wave functions on to a set of orthonormalized atomic orbitals. While LCs are not logically expected to exactly add up to the total charge, they constitute more than 90% of total charge for all the systems studied in this work.



(a)

(b)

(c)

Fig.5 (a) Structures showing hydrogen bonding between adjacent –S-O-M-O-S- bridges in de-ammoniated compounds $[H]_8[Mn_8(SO_4)_{12}]$, and $[H]_8[Mg_8(SO_4)_{12}]$. (b) Histogram showing the bond distances of M-O, and S-O for the ammoniated compounds $[NH_4]_8[Mn_8(SO_4)_{12}]$, **1** and$[NH_4]_8[Mg_8(SO_4)_{12}]$, **2** and bond distances of Mn-O-[-H] and S-O[-H] in the de-ammoniated compounds $[H]_8[Mn_8(SO_4)_{12}]$, and $[H]_8[Mg_8(SO_4)_{12}]$. (c) Histogram showing O-H bond length and O-H···O bond angles in the de-ammoniated compounds $[H]_8[Mn_8(SO_4)_{12}]$, and $[H]_8[Mg_8(SO_4)_{12}]$.

The de-ammoniated crystal structure is obtained by minimizing total energy as function of unit-cell volume and atomic positions starting from the respective ammoniated crystal structures with the NH_4^+ ions replaced by H atoms. We choose cubic unit-cells in order to allow lowering of symmetry through asymmetric chemisorption of the H atoms to the framework. With 48 O atoms and 8 H atoms per cubic unit-cell there exist a large number of such configurations without much variation of total energies and structural generalities. The H atoms, besides forming O-H bonds with the framework O atoms, also lead to intra-framework O-H···O hydrogen bonding as evident from the distribution of O-H···O angle and O-H bond lengths shown in Fig. 5. De-ammoniation is thus expected to increase the level of crystal binding which is evident in the resultant reduction of cohesive energies (Fig. 6) of the Mn(Mg)-compound from -5.65 (-5.6) eV/atom to -5.85(-5.8) eV/atom. Relatedly, bulk-modulus values obtained by fitting the Murnaghan equation of state[30] to total energies calculated as functions of unit cell volume for both the ammoniated compounds is about 40 GPa, which increases marginally upon de-ammonication accompanied by shrinkage ofequilibrium unit-cell volume by about 6% and 3% for the Mn and Mg compounds respectively, implying that both the compounds may be expected to remain structurally as stable as the common oxide perovskites (ABO_3) even after of de-ammoniation.

To assess the nature of structural changes and the degree of retention of their framework structures we note that the distribution of O-Mn(Mg)-O and O-S-O angles in the ammoniated and de-ammoniated phases suggests modest distortions to the $Mn(Mg)O_6$ octahedra and the SO_4 tetrahedra primarily due to in-equivalence among the O atoms at their vertices owing to bonding to H by one or more of them. Specifically the Mg-O[-H] bonds are observed to increase by 25% compared to the other Mg-O bonds, while the S-O[-H] bonds are about 17% longer than other S-O bonds. To assess whether these structural changes modify the open-framework nature of crystals we note that the distribution of the S-[O]-Mn(Mg)-[O]-S angles imply gross retention of the framework except for admissible buckling of the S-O-Mn(Mg)-O-S bridges primarily on account of the inter-bridge O-H···O hydrogen bonding, which nevertheless leaves 35%(30%)d of the unit-cell effectively empty as interstitial voids accounting for only 0.01% of total charge. Details of the M-O and S-O bond lengths of **1** and **2** and their de-ammoniated compounds are given in the form of histogram in Fig. 5. The O-M-O and S-M-S bond angles for **1** and **2** and their de-ammoniated products are given as histogram in Fig. S3. Oxidation states implied by the Lowdin charges (Table S6), which are different from that implied by the semi-empirical BVS analysis, suggests major depletion of electrons from 3s(4s) states of Mn(Mg) and from 3s and 3p states of S, leading to oxidation states about +2 and +2.5 for Mn(Mg) and S atoms respectively. The remaining valence electrons of S undergo sp^3 typehybridization leading to the SO_4 tetrahedra with S-O covalent bonds. Thus the eight O atoms with O-H bonds achieve complete sub shell filling without the electrons released by the Mn(Mg) atoms, thus leading to longer Mn(Mg)-O[-H] bonds owing majorly to their covalent interactions with the Mn(Mg) atoms. Also the total number of electrons released by the Mn(Mg) and S atoms are sufficiently enough for complete sub-shell filling of the rest of the O atoms. Thus the hydrogenated framework can indeed sustain charge neutrality throughout the structure due to complete sub shell of all constituent atoms without any of them requiring any additional coordination which otherwise would have resulted into major structural modification.

Magnetic properties.

We show the variable temperature magnetic susceptibility (χ) data of **1** recorded at 1000 Oe in Fig. 6. The compound is predominantly paramagnetic and the inverse susceptibility data show a linear behavior in the temperature range 50-300 K, yielding a negative Weiss temperature of –30 K, indicating weak antiferromagnetic interaction. The effective magnetic moment per manganese atom calculated from the fit of the χ_M^{-1} versus T curve is 5.6 μ_B, almost equal to the spin only S = 5/2 value of 5.92 μ_B since there is negligible orbital contribution to the moment and is comparable to that of manganese (II) compounds reported in the literature.[31] Furthermore, no magnetic hysteresis was observed at 5 K (inset of Fig. 7).

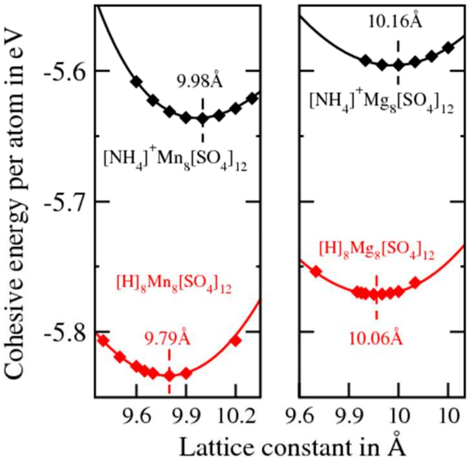


Fig. 6 Fit of Murnagan equation of state to cohesive energy per atom calculated from first principles using PBE exchange-correlation to obtain equilibrium lattice constant.

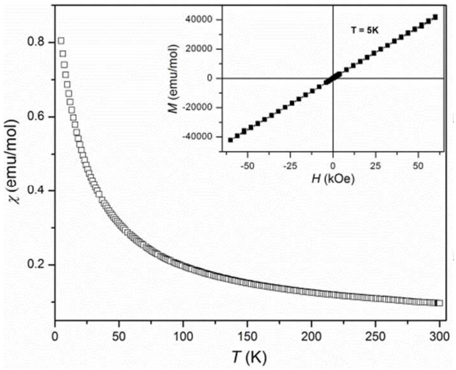


Fig. 7 Temperature dependence of the magnetic susceptibility of **1** measured at 1000 Oe. Inset shows the isothermal M–H cycles of **1** at 5 K.

Gas adsorption properties.

The rigidity and the porosity of the structures **1** of **2** were proven by gas-sorption analysis. Hydrogen adsorption measurements of **2** showed a fully reversible uptake of 0.7 wt % at 77 K and 890 Torr (see Fig. S4, ESI). In contrast compound **1** showed only 0.45 wt % of hydrogen likely arises from the heavier atomic weight of manganese. However, they are nonporous to nitrogen as its channels size is very small and is almost equal to the kinetic diameter of nitrogen. Although the hydrogen sorption is somewhat less, the magnesium compound, **2** compares well with the value of 0.7 wt % obtained for the highest capacity zeolite (ZSM-5) and some of Mg-MOFs reported in the literature.[32]

Proton conductivity studies.

We measured H_2O adsorption for **1** at 298 K as shown in Fig. 8a. Because of the nonporosity of **1**, it does not adsorb H_2O until P = 2.7 kPa (P/P_0 = 0.85). This adsorption profile also suggests that the surface of **1** does not have H_2O condensation on the surface of crystals, because of the negligible uptake. We measured the hydrous proton (H^+) conductivity for **1** under various relative humidity (RH) at 298 K (Fig. 8b). It does not show any H^+ conductivity below RH = 80%, and it comes to show 2.6×10^{-7} S cm^{-1} at RH = 80%. The observed H^+ conductivity reaches to 3.1×10^{-4} S cm^{-1} at RH = 90%. The proton conductivity of a NH_4^+ ion containing MOF $(NH4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$[33] was found to show 8×10^{-3} S cm^{-1} at 25 C under 98% relative humidity (RH) conditions. The significant enhancement of H^+ conductivity in the range of RH of 80 to 90% is not accountable from the H_2O adsorption uptake, because we do not observe an increase of uptake at this RH region. We assume that the H_2O molecules on the crystal surface of **1** above RH = 80% would form an effective H^+ hopping pathway with the aid of ordered SO_4^{2-} groups, which contributes the H^+ conductivity. We measured PXRD after the impedance spectroscopy measurements as shown in Fig. S5, and the observed diffraction pattern was identical to that of the original state of **1**. This indicates the crystal structure is intact even under the high RH conditions, and this supports that H_2O molecules would locate on the crystal surface to promote the H^+ hopping.

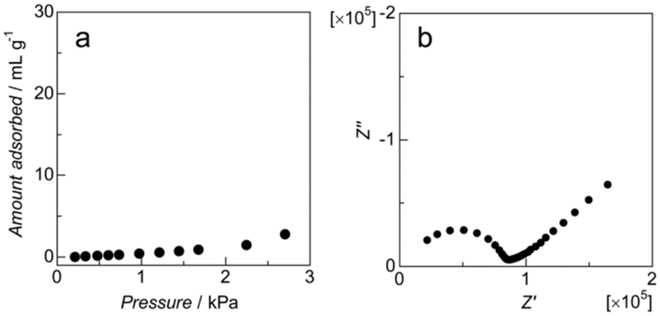


Fig. 8 (a) H_2O vapor adsorption isotherm for **1** at 298 K**.** (b) Nyquist plot of the proton conductivity of **1** under relative humidity of 85% at 298 K.

Conclusions

Two isostructural chiral three-dimensionalmetal sulfates $[NH_4]_8[Mn_8(SO_4)_{12}]$, (**1**) and $[NH_4]_8[Mg_8(SO_4)_{12}]$, (**2**), have been synthesized and well characterized, establishing thereby the versatility of the sulfate group in building open-architectures with the main group as well as transition metal atoms. High temperature X-ray diffraction, thermogravimetric analysis and DFT calculations suggest gross retention of framework structure of both **1** and **2** even after thermal decomposition of the ammonium ion resulting into the formation of $[H]_8[Mn_8(SO_4)_{12}]$ and $[H]_8[Mg_8(SO_4)_{12}]$ respectively. The magnetic behavior of **1** is predominantly paramagnetic in nature. Both **1** and **2** shows reversible hydrogen adsorption of 0.45 and 0.7 wt% respectively at 77 K. The proton conductivity of **1** under various relative humidity (RH) increases from 2.6×10^{-7} Scm^{-1} at RH = 80% to 3.1×10^{-4} S cm^{-1} at RH = 90%.

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