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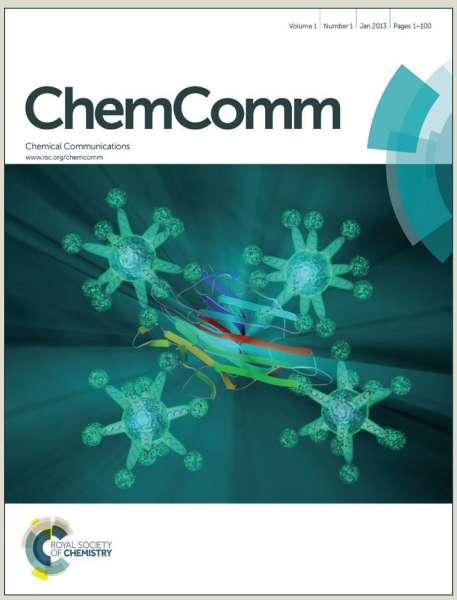

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ARTICLE

The First Organically Templated Open-Framework Metal-Sulfites with Layered and Three-Dimensional Diamondoid Structures

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Dedicated to Professor C. N. R. Rao

The crystallographic signatures and characterization data of two novel organically templated open-framework zinc-sulfite $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** and $(CN_3H_6)_2[Zn(SO_3)_2]$, **2** are reported for the first time, synthesized under hydrothermal conditions using different amines namely ethylenediamine and guanidine to generate 2D (for **1**) and 3D (for **2**) assemblies with 4, 6, 8 and 12-membered rings.

Open framework materials based on oxyanions like phosphate,[1] phosphite,[2, 3] selenate,[4] selenite,[5, 6] and sulfate[7, 8] are known to exhibit great structural diversity.[9] The structural variant can be achieved by modulating the synthetic condition and by prejudice selection of organic templates.[10-14] Amine templated open framework materials offer greater structural diversity and facilitate the access of materials which are not possible otherwise. Similar strategy has been exploited for the synthesis of many zeolite materials which find significant industrial applications.[15] Additionally, the amine groups also provide charge neutralization *via* protonation to the anionic inorganic framework. While there have been few organically-templated open-framework metal sulfates,[7, 8, 16-21] selenates[4, 22, 23] and selenites[5, 6, 22-25] with different dimensionalities synthesized and characterized recently,[26] it has not been possible to synthesize the corresponding sulfites, possibly because of the instability of S in its +4 oxidation state. While the stable oxidation state of Se is +4 in SeO_3^{2-} and $Se_2O_5^{2-}$ that of S is +6 as in SO_4^{2-}.[27] Sulfates are therefore obtained as products in most of the time even though one uses SO_3^{2-} as the source of S. Probably due to this difficulty, it has not been possible to prepare amine-templated open-framework metal sulfites, though there are few amine co-ordinated metal sulfites are known.[28-30] Harrison et al has reported the first organically-templated selenite[31] followed by the reports of three-dimensional metal selenite by Rao *et al*.[6] The structural similarity of sulfite with selenite, tellurite and phosphite anions prompted research in the area to realise similar structure. However, most of the synthetic conditions used for other oxyanions are incompatible with sulfite anions; as a result this domain remains relatively less explored.[28-30, 32-34] Consequently, many structures which have been realized with other oxyanions remained elusive for sulfite anions.

We have been exploring sulfur based anionic complexes like sulfide, sulfite, sulfate, thiosulfate etc., as secondary building units for generating open-framework materials.[20, 35] In an effort to synthesize open-framework metal sulfites, we have been able to synthesize for the first time organically-templated open-framework metal sulfites with layered structure of the formula $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** and three-dimensional structures of the formula $(CN_3H_6)_2[Zn(SO_3)_2]$, **2** possessing the diamondoid network under hydrothermal conditions.

Hydrothermal reaction of $Zn(OAc)_2$ with sodium disulfite in presence of ethylenediamine[§] afforded $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** as block shape single crystals. Crystallographic analysis suggested monoclinic system with *C2/c* space group. The asymmetric unit of **1** is built up of 12 non-hydrogen atoms out of which 10 belong to the inorganic framework and 2 belong to the extra framework amine molecule. Two crystallographically independent Zn(II) ions are encountered in the asymmetric unit with one atom having half occupancy (Fig. S1a). The Zn-O bond lengths are in the ranges of 1.949-2.003 Å and S-O bond lengths are in the ranges of 1.523-1.5363 Å and are comparable to the literature reports.[28, 29, 35, 36] The crystal structure refinement parameters and complete list of bond lengths and angles are given in Table S1 and S2 respectively. The Zn center is tetrahedrally coordinated with four oxygen atoms, of which two form Zn-O-S1 linkages and the remaining two form Zn-O-S2 linkage. Both the unique sulfite anions offer all three oxygen atoms towards Zn(II) coordination in $\eta^1\mu^3$-manner however with significant differences. Two $S(2)O_3^{2-}$ anions coordinates three zinc ions in a way to form a sulfite capped triangular node $[Zn_3(SO_3)_2]$ (Fig. 1, grey polyhedra) where three adjacent ZnO_4 tetrahedra are interconnected. These nodes are interconnected by $S(1)O_3^{2-}$ anion to generate

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† Electronic Supplementary Information (ESI) available: Detail of synthesis and characterization, crystal structure refinement parameters, H-bond, bond lengths and bond angles as Tables, crystal lattice pictures, PXRD data as picture and X-ray crystallographic data in CIF format has been given as supporting information. See DOI: 10.1039/x0xx00000x

a 2D layer in *bc*-plane with embedded 4, 6 and 8-membered rings (excluding the intervening O atoms, Fig. S2); where distorted ZnO_4 tetrahedra and SO_3 pyramids are joined by their vertices. Similar kind of triangular node was observed with guanidinium templated Zn-selenite system however the crystal lattice is different in case of **1** with embedded 4, 6 and 8 membered rings whereas the Zn-selenite system has only 12 membered ring.[31] The inorganic framework is further stabilized by the strong hydrogen bonding interactions with the protonated ethylenediamine molecule occupying the interlamellar space. Interestingly, the amine hydrogens are only involved in hydrogen bonding with sulfite groups which are making the triangular node (Fig. S3). Thus, each triangular node acts as acceptor to engender six H-bond with $d_{N1\text{-}H1A\cdots O6}$ = 2.120 Å; $d_{N1\text{-}H1B\cdots O5}$ = 2.049 Å and $d_{N1\text{-}H1C\cdots O4}$ = 2.149 Å and extends the lattice in three dimension. Different hydrogen bonding interactions for **1** and **2** are given in Table S3.

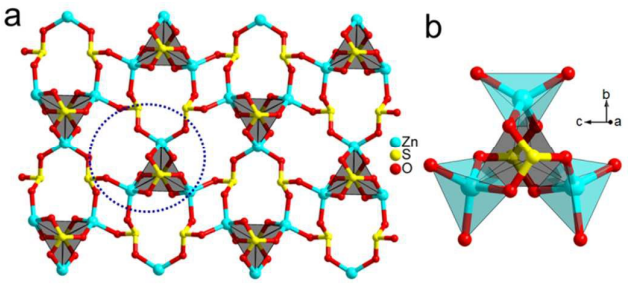

Fig. 1 (a) Crystal lattice of $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** showing infinite anionic 2D layer as viewed close to *a*-axis, (b) The arrangement of Zn(II) ions in a triangular node having $[Zn_3S_2O_{12}]^{10-}$ fragment capped by two sulfite groups as highlighted in (a).

$(CN_3H_6)_2[Zn(SO_3)_2]$, **2** was isolated under similar conditions when the organic template was changed to guanidine resulting a 3D network.[§] Plate like crystals were obtained showing orthorhombic crystal system with a non-centrosymmetric space group F*dd*2. The asymmetric unit has 9 non hydrogen atoms where 5 atoms form inorganic framework and the remaining four are due to guanidine template (Fig. S1b). In the asymmetric unit, a Zn(II) ion with half occupancy lies on a two-fold rotational axis. The crystal lattice is composed of ZnO_4 tetrahedra connecting four SO_3^{2-} pyramidal units through Zn-O-S links. The SO_3^{2-} with average S-O bond length of 1.518 Å offers two oxygens for Zn(II) ion coordination in a bidentate fashion giving rise to a 3D network. The non-coordinated oxygen atom has relatively shorter S-O bond length of 1.478 Å. The Zn-O1 and Zn-O3 bond lengths are 1.950 and 1.952 Å respectively, matches well with the similar compounds. Other geometrical parameters are listed in Table S2. **2** is isostructural to the phosphate $(CN_3H_6)_2[Zn(HPO_4)_2]$, phosphite $(CN_3H_6)_2[Zn(HPO_3)_2]$ and sulfate $(CN_3H_6)_2[Zn(SO_4)_2]$ analogue thus, the present study further extends the series of guanidinium templated oxyanions.[37-39]

The 3D network is composed of 12-membered ring system having six ZnO_4 and six SO_3 units arranged alternately (Fig. 2a). Each ring is occupied by the guanidinium cation which is held *via* strong N-H···O hydrogen bonding interactions as shown in Fig. 2a. The H-bond lengths range between 2.07-2.28 Å. Similar observation has been reported for guanidine templated metal-selenite[31] and phosphite[37] structures. The Zn···Zn separation within the 12-membered ring ranges from 10.39-11.77 Å. These 12 membered rings are arranged within the lattice in a distorted adamantane like topology, as shown in Fig. 2b and Fig. S4. As can be seen from Fig. 2b that the four 12-membered rings which are involved in the formation of adamantane unit; each accommodates guanidinium cation, thus the position and orientation of guanidinium cation forms a distorted tetrahedral arrangement within the adamantane cavity.

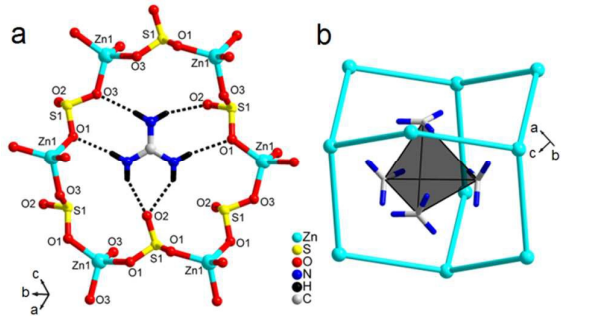

Fig. 2 (a) 12-membered ring with alternating ZnO_4 tetrahedra and SO_3 pyramids templated by guanidinium cation in case of $(CN_3H_6)_2[Zn(SO_3)_2]$, **2**; H-bonds are shown with fragmented bonds. (b) Adamantane topology adopted by four 12-membered rings in the crystal lattice of **2**, the position of guanidinium cation in a tetrahedral arrangement is also highlighted with grey color; Part of the lattice has been omitted for clarity).

The crystal lattice of **2** is composed of strictly alternating ZnO_4 tetrahedra SO_3 pyramids *via* vertex sharing. The guanidinium cations occupy almost central position of each 12-membered ring which runs back and forth in a form of distorted adamantane like topology to give rise to an infinite, anionic 3D-diamondoid network (Fig. 3a).[6] Interestingly, part of the crystal lattice can also be visualized as a helix running along *b*-axis with a pitch length of 12.12 Å where the grooves are occupied by the guanidinium cation and the plane is pointing toward the helical axis as shown in Fig. 3b.

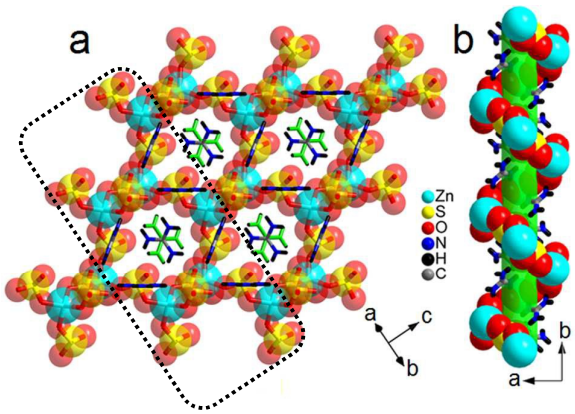

Fig. 3 (a) 3D-Crystal lattice of **2** with guanidinium cations at the centre of 12-MR window; (b) helical assembly observed in case of **2** which is highlighted in (a); (guanidinium cations in (a) are represented with different colour for better visualization)

TGA analyses were performed to probe thermal stability of **1** and **2** (Fig. S5). **1** showed multistep decomposition in the range of 165-670 °C leading to 60.4 % weight loss which can be accounted for the combined loss of ethylenediamine, sulfite anions and SO_2 (calc. 60.5%). Similarly, TGA curve of **2** showed two-step decomposition where the first step is the decomposition of guanidinium moiety in the temperature range of 185-300 °C which accounts for 34.5 % weight loss (calc. 34.76%). The second step is the decomposition of SO_3 anions in the range of 400-630 °C resulting 23.39 % weight loss (calc. 23.14%). The PXRD analysis of as synthesized material showed the phase purity of the complexes which is in good agreement with simulated patterns (Fig. S6). The temperature dependent PXRD analysis of **2** also corroborates with the TGA result and shows the decomposition of the framework above ≈ 280 °C (Fig. S7). In both the cases, the PXRD analysis of calcined samples showed characteristic peaks for ZnO (PDF-01-075-0576) as given in Fig. S8. We have also investigated the propensity of **2** for gas adsorption (Fig. S9). The BET surface area was found to be ≈ 21 m^2/g which is relatively low as expected because of the presence of guanidinium template in the channels present in **2**.

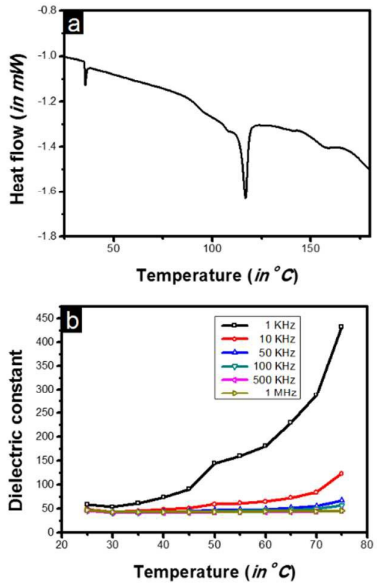

Fig. 4 (a) DSC and (b) dielectric constant profile of $(CN_3H_6)_2[Zn(SO_3)_2]$, **2**.

DSC profile of **2** (Fig. 4a) showed a phase transition at 36.90 °C although there was no heat change observed from -80 °C to 30 °C. Further, two glass transitions which occur at 89.9 °C and 106.78 °C, respectively were observed followed by two melting curves at 118.66 °C and 164.51 °C, respectively. Since, **2** belongs to a polar point group, dielectric behaviour was studied with temperature at different frequencies (Fig 4b and S10). The data shows that the dielectric constants rapidly drops at higher frequencies and increases with increase in temperature. Similarly, the real part of the impedance increases at low frequency (Fig. S10). These observations suggest the presence of dipole relaxation at lower frequencies.

In conclusion, the successful synthesis of amine-templated metal sulphites with layered and three-dimensional diamondoid structures has been accomplished. The ethylenediamine templated 2D structure is composed of $Zn_3(SO_3)_2$ triangular nodes connected by sulfite anion to give a layer structure with 4, 6 and 8-membered rings. The guanidinium templated structure gives a 3D structure with embedded 12-membered rings which adopts a distorted adamantane topology. These result shows that the sulphite ion can be usefully employed in designing new open-framework inorganic materials.

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Notes and references

‡CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC **1424543** (**1**) & **1424544** (**2**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Crystal data for **1**: $(NH_3CH_2CH_2NH_3)$ $[Zn_3(SO_3)_4]$, *Mr* = 578.47, monoclinic, space group *C* 2/*c* , *a* = 13.7379(4), *b* = 8.3487(3), *c* = 13.0277(4) Å, β = 106.235(2)°, *V* = 1434.61(8) $Å^3$, *Z* = 4, D_{calc} = 2.678 g cm^{-3}, Total/Unique reflections 13392/2195 (R_{int} = 0.0331), *R*1 and R2 (all data) = 0.0253, 0.0576. Crystal data for **2**: $(CN_3H_6)_2[Zn(SO_3)_2]$ *Mr* = 345.67, orthorhombic, space group *Fdd*2, *a* = 14.4211(13), *b* = 12.1181(8), *c* = 14.0692(8) Å, *V* = 2458.7(3) $Å^3$, *Z* = 8, D_{calc} = 1.868 g cm^{-3}, Total/Unique reflections 9404/1109 (R_{int} = 0.1040), *R*1 and *R*2 (all data) = 0.0531, 0.0723. Both the compounds were further characterized by FTIR experiments which showed signature peaks of various functional groups present in the crystal lattice for all the complexes. FTIR spectra of **1–2** showed the characteristic peaks for SO_3^{2-} anion around 960, 908, 620 and 515 cm^{-1}. The peaks around 3430 cm^{-1} are attributed to NH stretching vibrations.[40]

§ Zinc acetate dihydrate (220 mg) and sodium disulfite (389 mg) were dissolved in 3.0 mL water followed by addition of ethylene diamine (60 μL). The reaction mixture was heated at 90 °C in a polypropylene bottle (15 mL capacity) for 72 h. Plate shape colourless crystals of **1** were obtained after cooling the reaction mixture to room temperature. **2** was synthesized in a similar manner as described for **1** however guanidinium carbonate (300 mg) was added as template and the reaction mixture was heated at 75°C for 24 h.

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Keywords: Metal-sulfite / Open-framework / H–bonding / Guanidinium / Diamondoid / Organically Templated

The crystallographic signatures and characterization data of two novel organically templated open-framework zinc-sulfite $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** and $(CN_3H_6)_2[Zn(SO_3)_2]$, **2** are reported for the first time, synthesized under hydrothermal conditions using different amines namely ethylenediamine and guanidine to generate 2D (for **1**) and 3D (for **2**) assemblies with 4, 6, 8 and 12-membered rings.