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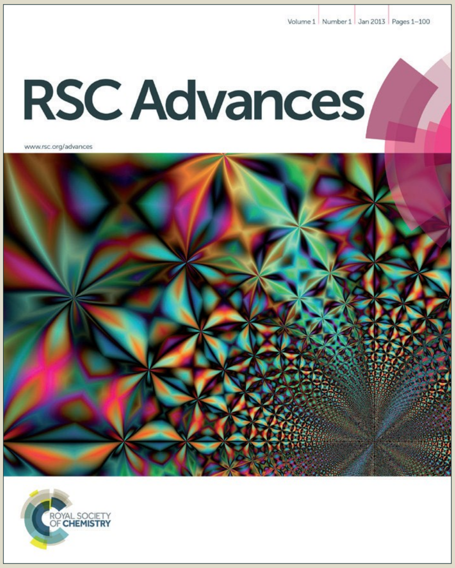

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Organically Templated Linear Metal Sulfites

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Organically-templated linear zinc and manganese sulfites have been prepared under mild reaction conditions and structurally characterized by single crystal X-ray diffraction. The linear zinc sulfites, with the compositions, $[(C_3H_{10}N)_2][Zn(SO_3)_2]$, **1**, $[C_3H_{12}N_2][Zn(SO_3)_2]$, **2**, $[C_4H_{14}N_2][Zn(SO_3)_2]$, **3**, $[C_6H_{18}N_2][Zn(SO_3)_2]$, **4** and $[C_4H_{12}N_2][Zn(SO_3)_2].H_2O$, **5** possessing the chain topologies consists of ZnO_4 tetrahedra and SO_3 pyramidal units forming four-membered rings which are connected through their vertices giving rise to 1D-chain structures. The linear manganese sulfite **6,** with the composition $[C_4H_{12}N_2][Mn(SO_3)_2(H_2O)_2].2H_2O$ has the kronkite type topology through corner sharing of four-membered rings formed by the MnO_6 octahedron and SO_3 pyramidal units. In all these structures the amine molecules are sitting between the interchain spaces. The compounds have been characterized by powder X-ray diffraction, infrared spectroscopy and thermogravimetric analysis.

Introduction

Although inorganic open-framework compounds are flooded with metal silicates[1-5] phosphates[6-11] and carboxylates[12], few open-framework compounds containing oxyanions of group 16 such as selenate,[13] selenite,[14-17] tellurites[18, 19] and sulfates[20-22] have been recently synthesized and characterized. Accordingly, open-framework structures of different dimensionality using the three-connected pyramidal unit of selenite and tellurite are reported in the literature.[14-19] The 3-connected centres has been proved to contribute large pore sizes and low framework density structures for zeolites (e.g., CLO, JDF-20), both of which are essential for desired applications.[23] There exist a number of different 3-connected inorganic building blocks, which includes planar BO_3^{3-} and CO_3^{2-} and pyramidal SnO_3^{4-}, SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}, and HPO_3^{2-}. Among these 3-connected units, HPO_3^{2-}, SeO_3^{2-} and SnO_3^{4-} have been studied.[24] The formation of BO_3^{3-} units faces competing processes to form other configurations such as BO_4^{5-} and associated cluster units.[25-30] There are also few limited successes with CO_3^{2-} but $SeO_3^{2-}$are well studied as Se is quite stable in +4 oxidation state.[31-36] In contrast, there have been very few studies on the use SO_3^{2-} as structural building units even though related tetrahedral SO_4^{2-} has been extensively studied.[37-44] This seems to be not surprising since the sulfur atom in the sulfite ion is in the 4+ oxidation state, which is relatively unstable under hydrothermal and acidic conditions and readily gets oxidized to the sulfate ion.[45] The presence of lone pair of electron in sulfite and many of the compounds analogous to the sulfites such as selenites and tellurites crystallize in noncentrosymmetric structures, with interesting nonlinear physical properties, such as second harmonic generation.[18, 46, 47] Organically templated metal sulphite chemistry is somewhat at a nascent state which needs to be explored.

We have been trying to prepare framework materials using sulfite ion as basic structural units and have discovered interesting frameworks.[48] In continuation to this theme, we have now been able to isolate six 1-D organically templated metal sulfites namely $[(C_3H_{10}N)_2]$ $[Zn(SO_3)_2]$, **1**, $[C_3H_{12}N_2]$ $[Zn(SO_3)_2]$, **2**, $[C_4H_{14}N_2]$ $[Zn(SO_3)_2]$, **3**, $[C_6H_{18}N_2]$ $[Zn(SO_3)_2]$, **4**, $[C_4H_{12}N_2]$ $[Zn(SO_3)_2].H_2O$, **5** and $[C_4H_{12}N_2]$ $[Mn(SO_3)_2(H_2O)_2].2H_2O$, **6** where the amine occupies the interchain spaces.

Results and discussion

The reaction of zinc(II) acetate or manganeses(II) acetate with sodium disulfite in presence of varying organic amines afforded six novel 1D-coordination polymers namely $[(C_3H_{10}N)_2]$ $[Zn(SO_3)_2]$, **1**, $[C_3H_{12}N_2]$ $[Zn(SO_3)_2]$, **2**, $[C_4H_{14}N_2]$ $[Zn(SO_3)_2]$, **3**, $[C_6H_{18}N_2]$ $[Zn(SO_3)_2]$, **4**, $[C_4H_{12}N_2]$ $[Zn(SO_3)_2].H_2O$, **5** and $[C_4H_{12}N_2]$ $[Mn(SO_3)_2(H_2O)_2].2H_2O$, **6** based on metal-sulfite coordination. **1-5** differs with one another only in terms of organic amine which acts as a template in all zinc based complexes but the basic unit for the formation of 1D polymer based on ZnO_4 tetrahedron remains same. In all the cases, Zn(II) ion is tetrahedrally coordinated with four sulfite anions and the ZnO_4 tetrahedra are joined together by their vertices to give 1D-polymer. In case of **6**, Mn(II) ion adopts octahedral

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Electronic Supplementary Information (ESI) available: [H-bonding interactions, complete bond lengths and bond angles as Tables, PXRD data as picture and X-ray crystallographic data in CIF format has been given as supporting information]. See DOI: 10.1039/x0xx00000x geometry and these octahedrons are joined with one another to give 1D-polymer. The use of amines as structural directing groups have been demonstrated by several groups.[49, 50] The crystal lattice of all the complexes is stabilized by intricate H-bonding interactions engendered by the presence of amino groups and/or water molecules. It is worthwhile to discuss the effect of these non-covalent interactions over entire crystal lattice because of their influential role which is imparted to the lattice to generate interesting topology with increased dimensionality.[51-55]

Table 1. Crystal structure refinement parameters for **1–6**.

	1	**2**	**3**	**4**	**5**	**6**
formula	$[(C_3H_{10}N)_2][Zn(SO_3)_2]$	$[C_3H_{12}N_2][Zn(SO_3)_2]$	$[C_4H_{14}N_2][Zn(SO_3)_2]$	$[C_6H_{18}N_2][Zn(SO_3)_2]$	$[C_4H_{12}N_2][Zn(SO_3)_2].H_2O$	$[C_4H_{12}N_2][Mn(SO_3)_2(H_2O)_2].2H_2O$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*bcn	*P*bcm	*C*2/c	*C*2/c	*P*-1	*P*-1
a [Å]	22.1708(7)	8.6326(3)	17.3344(9)	21.1872(13)	8.1135(2)	5.4228(3)
b [Å]	8.7244(2)	7.6916(3)	8.4890(3)	8.5354(4)	8.4917(2)	6.6958(4)
c [Å]	7.7214(2)	16.5072(5)	8.1660(3)	8.0784(4)	8.8022(3)	9.9304(5)
α [°]	90	90	90	90	87.946(2)	104.871(3)
β [°]	90	90	106.855(5)	109.333(4)	88.256(3)	95.917(3)
γ [°]	90	90	90	90	63.296(2)	99.602(3)
V [Å^3]	1493.53(7)	1096.05(7)	1150.02(8)	1378.53(13)	541.35(2)	339.56(3)
Z	4	4	4	4	2	1
Mr	345.73	301.64	315.66	343.71	331.66	375.28
Dx [g.cm^{-3}]	1.538	1.826	1.823	1.656	2.035	1.835
μ [mm^{-1}]	1.939	2.628	2.509	2.100	2.677	1.327
ϑ range [°]	3.61-30.50	3.42-30.53	3.49-28.71	3.48-30.57	2.32-30.56	2.15-30.49
reflections collected	12389	18464	8711	12033	9824	5916
unique reflections [R(int)]	2278 [0.0294]	1732 [0.0859]	1482 [0.0522]	2113 [0.0419]	3316 [0.0552]	2028 [0.0284]
data / restraint / parameters	2278 / 1 / 91	1732 / 1 / 79	1482 / 0 / 81	2113 / 0 / 90	3316 / 5 / 169	2028 / 3 / 112
R [$I>2\sigma(I)$]	*R*1 = 0.0282, *wR*2 = 0.0622	*R*1 = 0.0320, *wR*2 = 0.0674	*R*1 = 0.301, *wR*2 = 0.0701	*R*1 = 0.0310, *wR*2 = 0.0781	*R*1 = 0.0395, *wR*2 = 0.0759	*R*1 = 0.0313, *wR*2 = 0.0778
R (all data)	*R*1 = 0.0381, *wR*2 = 0.0653	*R*1 = 0.0517, *wR*2 = 0.0737	*R*1 = 0.0376, *wR*2 = 0.0737	*R*1 = 0.0385, *wR*2 = 0.0817	*R*1 = 0.0624, *wR*2= 0.0837	*R*1 = 0.0385, *wR*2 = 0.0806
Goodness of fit (*S*)	1.038	1.002	1.064	1.069	0.992	1.066
residual peak [e Å]	0.266 and -0.296	0.397 and -0.340	0.339 and -0.479	0.439 and -0.517	0.450 and -0.502	0.367 and -0.685
CCDC No	**1417645**	**1417646**	**1417647**	**1417648**	**1417649**	**1417650**

Structural analysis of $[(C_3H_{10}N)_2][Zn(SO_3)_2]$, (1).

Colorless crystals of **1** crystalize in orthorhombic crystal system having *P*bcn space group and displayed 1D-structure. The asymmetric unit of **1** consists of 9 non-hydrogen atoms which comprises of one Zn(II) ion with half occupancy and a protonated propyl amine which was neutralized by one SO_3^{2-} anion as shown in Fig. 1. The crystal structure refinement parameters for **1-6** are given in Table 1. The coordination environment of Zn(II) ion is composed of four oxygen atoms contributed by four sulfite anions (Zn–O1 = 1.9445(12) Å; Zn–O2 = 1.9683(12) Å and corresponding symmetry equivalents) which gives a distorted tetrahedral environment around Zn(II) center. The Zn–O bond lengths are within the acceptable limits as reported in literature for other similar complexes.[56-59] The selected bond lengths are given in Table 2.

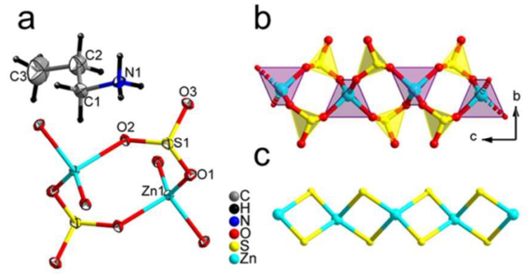

Fig. 1 (a) Molecular structure of **1** at 25% ellipsoid probability level with unique atoms labelled, (b) Formation of 1D chain due to Zn(II)-sulfite coordination (part of the lattice is omitted for clarity). (c) Interconnected Zn_2S_2 dimeric units to generate 1D chain (ignoring the oxygen atom).

Part of the crystal lattice of **1** is shown in Fig. 1b which shows the formation of infinite 1D-chain extending along crystallographic *c*-axis as a result of μ^2-η^1:η^1-O:O coordination mode from SO_3^{2-} anion. These linear chains consist of ZnO_4 tetrahedrons interlinked through vertices by two O-S-O bridges of two SO_3^{2-} anions. Thus, sulfite anion coordination with Zn metal ions, results in the formation of interconnected dimeric unit Zn_2S_2 (not considering the bridging oxygen atom) to generate a 1D-chain along *c*-axis as shown in Fig. 1c. The adjacent Zn···Zn distance within the $[Zn(SO_3)]_\infty$ chain is 3.8735(1) Å.

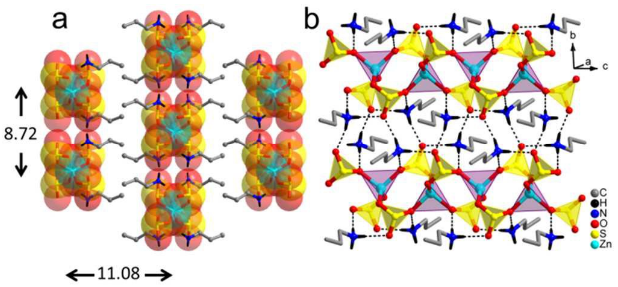

Fig. 2 (a) Crystal lattice of **1** as viewed along *c*-axis showing the interchain space, (b) 2D layer structure as a result of H-bonding interaction (shown with fragmented bonds).

Table 2. Selected bond lengths [Å] for **1-6**.#

1	Zn1–O1	1.9445(12)	Zn1–O2^{i}	1.9683(11)
2	Zn1–O1	1.9403(15)	Zn1–O3^{ii}	1.9687(15)
3	Zn1–O1	1.9641(16)	Zn1–O2^{iii}	1.9383(17)
4	Zn1–O1	1.9623(13)	Zn1–O3^{iv}	1.9402(15)
5	Zn1–O1	1.945(2)	Zn1–O3^{v}	1.968(2)
	Zn1–O4	1.9798(19)	Zn1–O5^{vi}	1.9532(19)
6	Mn1–O1	2.1902(11)	Mn1–O2^{vii}	2.2008(12)
	Mn1–O1w	2.1861(15)		

#Symmetry transformations used to generate equivalent atoms: (i) -x+1,-y,-z+2; (ii) -x+1,-y,-z+1; (iii) x,-y,z +1/2; (iv) -x,-y,-z; (v) -x,-y+1,-z+2; (vi) -x,-y+1,-z+1 and (vii) -x+1,-y+2,-z.

The crystal lattice of **1** is shown in Fig. 2 where anionic interchain space is occupied by the protonated amines which acts as an organic template and also balances the charge required for neutralization of the crystal lattice. The interchain M···M distance along *b*-axis is 8.72 Å and the interplanar distance consisting Zn(II) ions along *a*-axis is 11.08 Å, which also reflects in the unit cell parameters of **1**. The H-bonding interactions engendered by the protonated amine interconnect the chains along *b*-axis thus; extend the lattice in *bc*-plane leading to a 2D-layer as shown in Fig. 2b. Interestingly, the three S-O distances of sulfite anion are not equal and one of the S-O bonds is only 1.484 Å which shows double bond character for O3 oxygen atom which in-turn suggests an uneven electron distribution. This O3 oxygen remain non-coordinated and takes part in strong bifurcated H-bonding interaction by simultaneously acting as acceptor for N–H1A and N–H1C hydrogen atoms with $d_{N1–H1A\cdots O3}$ = 1.932(16) and $d_{N1–H1C\cdots O3}$ = 1.91(2) Å respectively which are contributed by two different protonated amines. The organic appendage of amine is situated in between the 2D layers along *a*-axis. The third hydrogen is involved in a H-bonding interaction with O2 oxygen of the sulfite anion with distance of $d_{N1—H1B\cdots O2}$ = 1.97(2) Å which further strengthens the lattice. The complete list of various hydrogen bonding interactions are given in Table S1.

After having access to crystal structure with mono amine, we wished to incorporate *bis*-substituted amine into the crystal lattice and studied its influence on the crystal lattice. We employed acyclic as well as cyclic amines for this purpose.

Structural analysis of $[C_3H_{12}N_2][Zn(SO_3)_2]$, (2), $[C_4H_{14}N_2][Zn(SO_3)_2]$, (3) and $[C_6H_{18}N_2][Zn(SO_3)_2]$, (4).

Crystallographic analysis of **2-4** suggest almost similar crystal packing however they vary with respect to the diamino alkane, which differ with one another in terms of the intervening methylene units, as the organic template and in all the cases both the amine groups are protonated. All the three complexes form 1D-chain structure akin to **1** as shown in Fig. 1b. Crystallographic analysis for colorless crystals of $[C_3H_{12}N_2][Zn(SO_3)_2]$, (**2**) suggested orthorhombic crystal system with *P*bcm space group whereas $[C_4H_{14}N_2][Zn(SO_3)_2]$, (**3**) and $[C_6H_{18}N_2][Zn(SO_3)_2]$, (**4**) adopts monoclinic crystal system with *C*2/c space group.

The asymmetric unit of **2** and **3** consist of 8 non-hydrogen atoms each having one Zn(II) ion with half occupancy, one SO_3^{2-} anion and half of protonated diaminopropane (for **2**; Fig. 3a) and diaminobutane (for **3**; Fig. 3b) cation. The asymmetric unit of **4** consist of 9 non-hydrogen atoms with similar occupancy for Zn(II) and SO_3^{2-} ions however the extra atom is due to the presence of half of the protonated diaminohexane cation as shown in Fig. 3c. The coordination environment of Zn(II) ion in **2-4** is composed of four oxygen atoms coming from four sulfite anions similar to **1** which gives a tetrahedral arrangement around Zn(II) ions. The Zn-O bond lengths for the zinc tetrahedron for **2-4** ranges between 1.938-1.969 Å (Table 2).

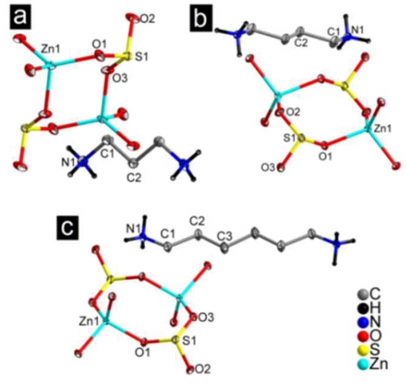

Fig. 3 Molecular structure of **2** (a), **3** (b) and **4** (c) with unique atoms labelled (ellipsoid probability is 25 % in all cases).

Part of the crystal lattice of **2-4** is shown in Fig. 4 where the interchain spaces are occupied by the *bis*-amino alkane template. As intended, the presence of organic template increases the separation between the planes of 1D chains along *b*-axis (for **2**) and along *c*-axis (for **3** and **4**) as the intervening methylene units are increased in the template. The interplanar distances increases from 8.25 Å to 8.67 Å to 10.59 Å as the template changes from propyl- to butyl- and finally to hexyl diamine. All the three hydrogens on protonated amine are involved in H-bonding from both ends leading to a 3D-network which has been shown in Fig. 5 for **2-4**. In all the cases, the non-coordinated oxygen atom of sulfite group is involved in bifurcated hydrogen bonding to provide strong interaction with H-bond distance of $d_{\mathrm{N1–H1A\cdots O2}}$ 1.93(4) and $d_{\mathrm{N1–H1C\cdots O2}}$ 1.88(2) for **2**; $d_{\mathrm{N1–H1B\cdots O3}}$ 1.94(3) and $d_{\mathrm{N1–H1C\cdots O3}}$ 1.90(4) for **3** and $d_{\mathrm{N1–H1B\cdots O2}}$ 1.90(3) and $d_{\mathrm{N1–H1C\cdots O2}}$ 1.95(3) for **4**. The remaining hydrogen of protonated amine is involved in hydrogen bonding with one of coordinated sulfite oxygen with the distance of $d_{\mathrm{N1–H1B\cdots O3}}$ 1.97(3) for **2**; $d_{\mathrm{N1–H1A\cdots O1}}$ 2.03(3) for **3** and $d_{\mathrm{N1–H1A\cdots O1}}$ 2.06(4) for **4**. These interactions extend the lattice in orthogonal plane with respect to 1D-polymeric chain resulting in a 3D-structure.

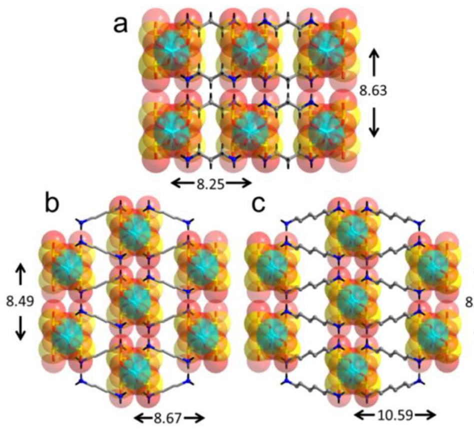

Fig. 4 Part of the crystal lattice of (a) **2** as viewed along *b*-axis; (b) **3** as viewed along *c*-axis; (c) **4** as viewed along *c*-axis;

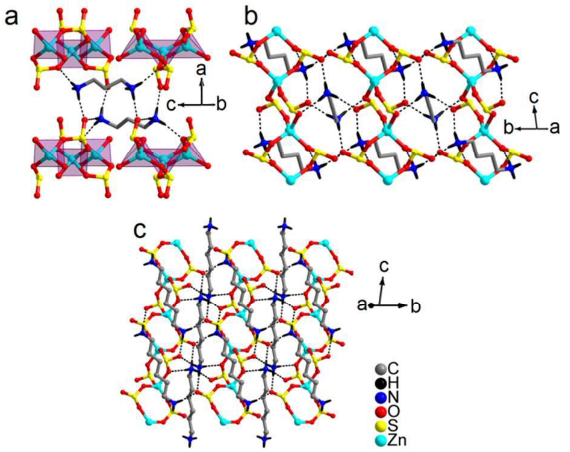

Fig. 5 H-bonded 3D-lattice of (a) **2;** (b) **3**; (c) **4**; (part of the lattice is omitted for clarity).

After accessing the crystal structure with acyclic *bis*-substituted amine, we turned our attention towards *bis*-substituted cyclic amine. For this purpose, we employed piperazine as our organic template of choice under similar conditions as given in Table 3 and accessed **5**. The Mn(II) crystals (**6**) were also obtained in this case to investigate the effect of metal ions over the lattice with interesting results.

Structural analysis of [$C_4H_{12}N_2$][Zn(SO_3)$_2$].H_2O, (5) & [$C_4H_{12}N_2$][Mn(SO_3)$_2$(H_2O)$_2$].2H_2O, (6).

Colorless crystals of **5** crystalize in triclinic crystal system having *P*-1 space group and displayed 1D-structure. The asymmetric unit of **5** consist of 15 non-hydrogen atoms with one Zn(II) ion, two sulfite anions and two halves of protonated piperazine moiety as shown in Fig. 6a. The asymmetric unit also has one water molecule trapped in the lattice as solvent of crystallization. The coordination environment of Zn(II) ion is composed of four oxygen atoms coming from four sulfite anions (Zn1–O1 = 1.945(2); Zn1–O3 = 1.968(2); Zn1–O4 = 1.9798(19) and Zn1–O5 = 1.9532(19) Å) which gives a tetrahedral environment around Zn(II) center (Table 2). Although the basic 1D structure of Zn-SO_3 chain remains same, but there is a slight difference between the bindings of sulfite grouping with Zn ions in **5** compared to **1-4** as shown in Fig. 6c.

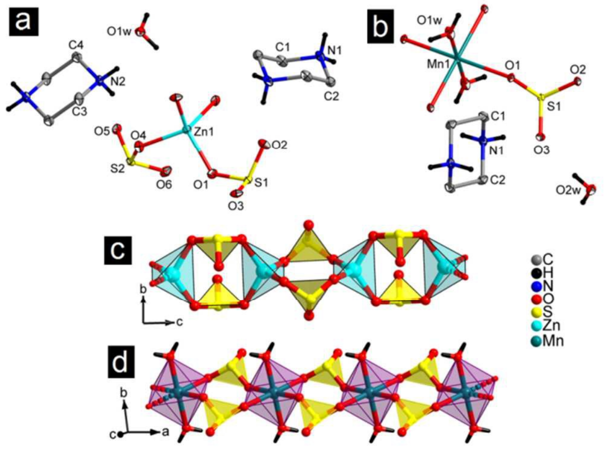

Fig. 6 Molecular structure of (a) **5** and (b) **6** at 25 % ellipsoid probability level (unique atoms are labelled); View of 1D-structure with interconnected ZnO_4 tetrahedron for **5** (c) and MnO_6 octahedron for **6** (d).

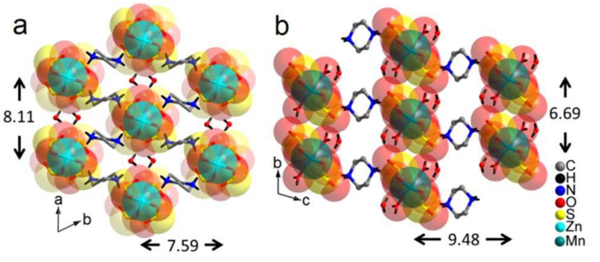

Fig. 7 Part of the crystal lattice of (a) **5**; (b) **6** showing the positions and orientations of water and protonated piperazine molecules.

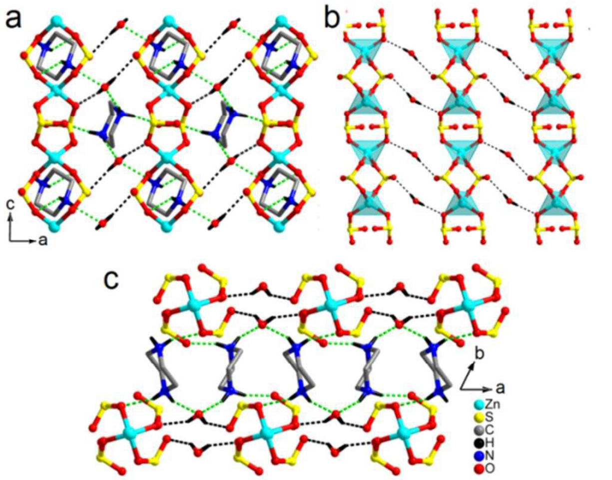

Fig. 8 (a) H-bonded lattice of **5**; (b) water molecule mediated hydrogen bonding in the lattice as viewed close to *b*-axis; (c) involvement of piperazine molecules in the lattice as shown with green colour fragmented bonds (H-bonds are represented with fragmented bonds).

When the metal ion is changed from Zn to Mn, **6** was obtained. Crystallographic analysis of **6** revealed a triclinic system with *P*-1 space group which also displayed 1D-polymeric chain. The asymmetric unit of **6** consist of 10 non-hydrogen atoms with one Mn(II) ion of half occupancy, one SO_3^{2-} anion and half of protonated piperazine cation occupying the interchain spaces. The crystal lattice also has one water molecules as solvent of crystallization and one aqua ligand coordinated to the Mn(II) center. The coordination environment of Mn(II) ion is composed of six oxygen atoms where the four oxygen atom comes from four sulfite anions (Mn–O1 = 2.1902(11); Mn–O2 = 2.2008(12) Å and corresponding symmetry equivalents) forming the equitorial plane and two aqua ligands (Mn–O1w = 2.1861(15) and its symmetry equivalents) occupying the axial sites, thus giving an octahedral arrangement around Mn(II) center (Table 2). The Mn–O bond lengths are again within the range as reported previously.[60]

Part of the crystal lattice of **5** and **6** is shown in Fig. 7 which also demonstrates the position of protonated piperazine molecules present in between the 1D-chains. The interplanar distance between the 1D-chains situated along *a*-axis for **5** and *b*-axis for **6** is 7.59 A and 9.48 A respectively. Although, the organic template is same in both cases, the distances vary significantly which can be attributed to the different geometries adopted by the metal ions, the orientation of piperazine molecule and the trapped lattice water molecule.

The various hydrogen bonding interaction in case of **5** and **6** leading to a 3D-structure are shown in Fig. 8 and 9 respectively, which need to be highlighted. It is interesting to note that in case of **5**, the lattice water molecule acts as a donor to interact with sulfite oxygen atoms present in 1D-chain structures with $d_{\mathrm{O1w–H1w\cdots O6}}$ = 2.16(3) and $d_{\mathrm{O1w–H2w\cdots O3}}$ = 2.01(5) resulting in the formation of 2D-structure in *ac*-plane as shown in Fig. 8b. Further, the protonated piperazine molecules acts as a donor for sulfite oxygen present in the 1D-chain and for the water molecule to extend the lattice in *ab*-plane as shown in Fig. 8c. Thus, the water molecule is involved in quadrupole hydrogen bonding and giving hydrogen bonded 3D-assembly consisting metal-sulfite chains (Table S1).

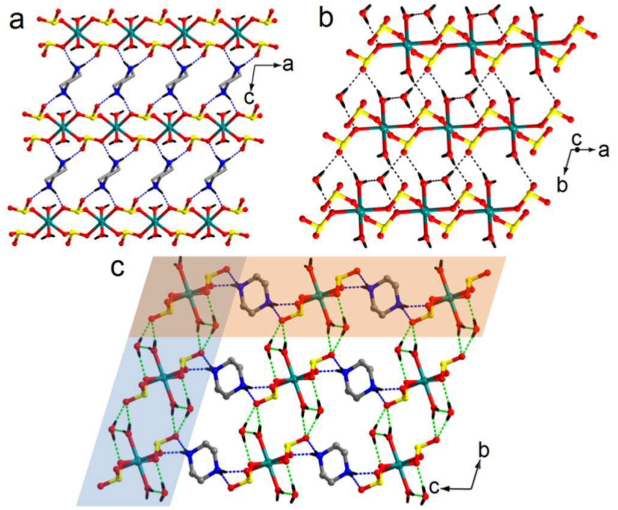

Fig. 9 (a) H-bonding in **6** through piperazine molecules giving 2D layer in *ac*-plane; (b) water molecule mediated H-bonding in the lattice; (c) H-bonded lattice of **6** highlighting the extension through water and piperazine H-bonding as represented with different colour rectangle (H-bonds are represented with fragmented bonds).

Similarly, part of the lattice of **6** is given in Fig. 9. The interconnected Mn(II)-sulfite octahedrons are running along *a*-axis which are interconnected *via* H-bonding interactions involving the protonated piperazine molecules which extend the lattice in *ac*-plane as shown in Fig. 9a. Additionally, the lattice water molecule and the coordinated aqua ligands interconnect the 1D-chain structures through H-bonding along *b*-axis which extend the lattice in *ab*-plane (Fig. 9b, Table S1). In combination, these two types of hydrogen bonding interactions namely, N–H···O and O–H···O, along with metal-sulfite coordination, thus, generate a 3D-assembly which has been also highlighted in Fig. 9c with different colour rectangle where the N–H···O interactions extends the lattice in *c*-direction (light brown rectangle) whereas the O–H···O interaction extends the lattice in *b*-direction (light blue rectangle).

The bond valence sum calculation value for Zn ion in case of **1-5** is 2.023, 2.033, 2.052, 2.051 and 1.996 respectively which suggest +2 oxidation state of Zn ion in all five complexes whereas the value for Mn ion in case of **6** is 2.023 which again suggests +2 oxidation state of Mn ion as well. The complexes were further characterized by FTIR, PXRD and TGA experiments. Synthesis of **1**, only afforded few crystal suitable for X-ray crystallography and attempts to increase the yield has failed for this complex. Hence, we were not able to perform other characterization of this complex however; characterization data for all other complexes are given. FTIR spectra showed signature peaks of various functional groups present in the crystal lattice for the complexes. FTIR spectrum of **2-6** showed the characteristic peaks for SO_3^{2-} anion around

970, 930, 620 and 470 cm^{-1} (Fig. S1). The peaks around 3250–3500 cm^{-1} are attributed to OH and NH stretching vibrations of water molecule and amino group respectively.[61, 62] Further the PXRD analysis of as synthesized material showed the phase purity of the complexes which is in good agreement with simulated patterns (supporting information Fig. S2). A representative PXRD pattern for **2** is given in Fig. 10 to show the phase purity of as synthesized materials.

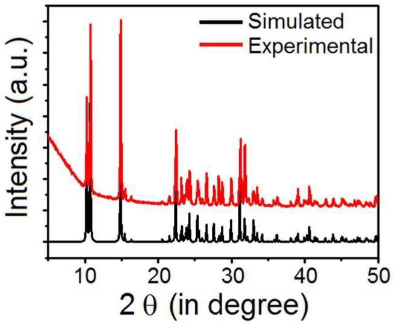

Fig. 10 PXRD pattern of complex **2** showing the phase purity of as synthesized material.

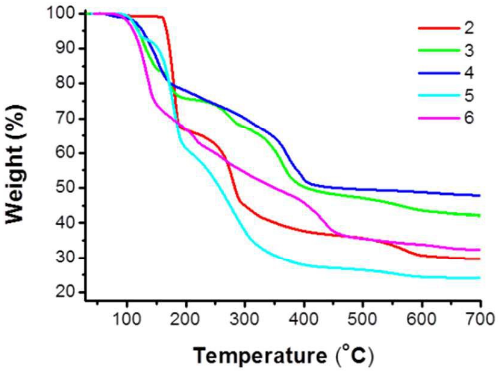

Fig. 11 Thermogravimetric analysis for **2-6**.

The TGA analysis of **2-6** was performed under constant flow of N_2 gas at a heating rate of 5 °C/min in the temperature range 30-700 °C (Fig. 11). **2** shows multi-step decomposition where the first stage is loss of 1,3-diaminopropane moiety in the temperature range of 160-200 °C which accounts 31.3% (calc. 25.24%) weight loss. Finally, decomposition of SO_3 group shows 26.86 % (calc. 26.52%) weight loss in the temperature range of 240-400 °C. Similarly, **3** shows two major decomposition steps where first step is the degradation of incorporated 1,4-diaminobutane moiety which is 24.14 % (calc. 28.51%) in the range of 95-195 °C. Further decomposition of sulfite in the temerature range of 290-390 °C accounts for 18.46 % (calc. 20.27 %) weight loss. In **4**, there was a two step weight loss corresponding to the loss of amine (HMDA) in the range of 110-200 °C (obs. = 34.53 %, calc. = 33.8%), followed by the decomposition of SO_3 in the range of 220-600 °C (obs. = 40.7%, calc. = 41.8 %). In **5**, there was a three step weight loss corresponding to the water in the temperature range of 85-135 °C (obs. = 6.0%, calc. = 5.8%), the amine molecules in the range 140-200 °C (obs. = 28.0%, calc. = 26.0 %), the decomposition of sulfite in the range 230-700 °C (obs. = 44.0 %, calc. 42.4%). In case of **6**, gradual decomposition with varying slopes was observed. The total weight loss observed between temperature range of 100-700 °C is 67.66 % which is less than the combined weight loss of water, piperazine and SO_2 molecules (calc 76.83 %) indicating the formation of Mn_3O_4 species along with MnO species as confirmed by the PXRD analysis of calcined product. The PXRD analysis of the calcined product of **2-5** corresponds to the zinc oxide (PDF-01-075-0576) whereas in **6** it corresponds to MnO (PDF 01-077-2929) /Mn_3O_4 (PDF 01-080-0382) mixture as shown in Fig. S3.

Experimental

Materials and methods.

General. All the chemicals were purchased from standard chemical suppliers and used without further purification. The bond valence sums for different metal ions in **1-6** were calculated by considering r_o(Zn-O) = 1.704(Å) and r_o(Mn-O) = 1.790(Å).[63]

Physical Measurements. Infrared spectra were recorded on a ‘Perkin Elmer FTIR spectrometer’ equipped with an attenuated total reflectance accessory. Thermogravimetric analyses (TGA) were carried out at a ramp rate of 5 °C/min under a flow of nitrogen using a Discovery TGA by TA Instruments-Waters Lab. 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 *CuKα* radiation (λ = 1.5418 Å). Single crystal data was collected on a Bruker AXS KAPPA-APEX II instrument at room temperature.

Synthetic procedures.

Syntheses of 1-6. The syntheses of amine templated metal sulfite **1-6** were done by hydrothermal method at mild condition using sodium disulfite as the source of sulfite. In a typical synthesis of **1**, zinc acetate dihydrate (0.219 g) was dissolved in water (3.0 mL) under constant stirring. Sodium disulfite (0.380 g) followed by *n*-propyl amine (0.224 mL) were added to this solution. The mixture was again stirred for 25 minutes to form a clear solution. The final mixture with molar compositions of $Zn(OAc)_2$/3.0 $Na_2S_2O_5$/*n*-PA/155 H_2O were transfer into a 15 mL polypropylene bottle, which was then tightly closed and heated at 100 °C for 72 h. The pH of the initial solution was approximately 6.0 which remained almost same during the reaction. After the reaction, few X-ray quaity colorless single crystals were obtained but the yield was poor hence other characterization of this particular complex has not been performed. The other zinc-sulfite coordination polymers **2-5** were synthesized in moderate yeilds by following similar protocol with the addition of different organic amine and sulfite source and the details for the respective molar compositions and reaction temperature are given in Table 3. For the preparation of **6**, manganese acetate tetrahydrate (0.245 g) was dissolved in water (3 mL) under constant stirring. Sodium disulfite (0.570 g) followed by piperazine (0.172 g) were added to this solution. The resultant mixture with the molar compositions of $Mn(OAc)_2$/3.0 $Na_2S_2O_5$/2.0 PIP/155 H_2O with pH 6 was stirred for 15 minute and transferred into a 15 mL polypropylene bottle which was then tightly closed and heated at 100 °C for 120 h. After cooling to room temperature, transparent crystals were obtained in 62% yield.

Anal for $[C_3H_{12}N_2][Zn(SO_3)_2]$, (**2**); calc (found): C, 11.94 (11.85); H, 4.01 (4.05); N, 9.29 (9.11); S, 21.26 (21.17). Anal for $[C_4H_{14}N_2][Zn(SO_3)_2]$, (**3**); calc (found): C, 15.22 (15.11); H, 4.47 (4.59); N, 8.87 (8.73); S, 20.31 (20.23). Anal for $[C_6H_{18}N_2][Zn(SO_3)_2]$, (**4**); calc (found): C, 20.96 (20.92); H, 5.28 (5.25); N, 8.15 (8.20); S, 18.66 (18.58); Anal for $[C_4H_{12}N_2][Zn(SO_3)_2].H_2O$, (**5**); calc (found): C, 14.48 (14.42); H, 4.25 (4.30); N, 8.45 (8.42); S, 19.33 (19.23); Anal for $[C_4H_{12}N_2][Mn(SO_3)_2(H_2O)_2].2H_2O$, (**6**) calc (found): C, 12.80 (12.72); H, 5.37 (5.42); N, 7.46 (7.50); S, 17.09 (17.01);

FTIR (KBr, cm^{-1}) for **2**: 3431 br, 2924 m, 1638 s, 1532 m, 1478 s, 1413 s, 1221 s, 1144 b, 992 s, 968 s, 932 s, 884 s, 643 m, 490 m; for **3**: 3332 br, 2945 m, 1645 s, 1523 m, 1160 b, 960 s, 928 s, 616 m, 512 m; for **4**: 3323 br, 3018 m, 1616 s, 1472 m, 1112 b, 932 s, 875 s, 618 m, 512 m; for **5**: 3354 br, 3030 m, 1595 s, 14770 m, 1096 b, 969 s, 904 s, 618 m, 489 m; for **6**: 3258 br, 3020 m, 1628 s, 1458 m, 1096 b, 961 s, 910s, 636 m, 496 m.

Table 3. Synthetic conditions and molar ratios for the preparation of 1-6.#

	Starting composition (in mM)[#]	T[°C]	t[h]	pH	M/S	Formula	Yield (%)
1	$Zn(OAc)_2.2H_2O$:3.0 $Na_2S_2O_5$:4.0 PA:155 H_2O	100	72	6	1:2	$[(C_3H_{10}N)_2][Zn(SO_3)_2]$	2-3%
2	$Zn(OAc)_2.2H_2O$:2.0 $Na_2S_2O_5$:1.0 DAP:155 H_2O	90	72	6	1:2	$[C_3H_{12}N_2][Zn(SO_3)_2]$	70
3	$Zn(OAc)_2.2H_2O$:2.0 $Na_2S_2O_5$:1.0 DAB:155 H_2O	90	72	6	1:2	$[C_4H_{14}N_2][Zn(SO_3)_2]$	68
4	$Zn(OAc)_2.2H_2O$:2.0 $Na_2S_2O_5$:1.0 HMDA:155 H_2O	90	72	6	1:2	$[C_6H_{18}N_2][Zn(SO_3)_2]$	56
5	$Zn(OAc)_2.2H_2O$:2.0 $Na_2S_2O_5$:2.56 PIP:155 H_2O	75	24	6	1:2	$[C_4H_{12}N_2][Zn(SO_3)_2].H_2O$	65
6	$Mn(OAc)_2.4H_2O$:3.0 $Na_2S_2O_5$:2.0 PIP:155 H_2O	100	120	6	1:2	$[C_4H_{12}N_2][Mn(SO_3)_2(H_2O)_2].2H_2O$	62

[#]PA= *n*-propylamine; DAP = 1, 3-diaminopropane; DAB = 1, 4-diaminobutane; HMDA = hexamethylenediamine and PIP = piperazine

Single-Crystal Structure Determination.

A suitable single crystal of each complex was carefully selected under a polarizing microscope and mounted at the tip of the thin glass fibre using cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (*Mo-Kα* radiation, λ = 0.71073Å) operating at 50 kV and 30 mA. Structures were solved by the direct method using SHELXS-97 and refined on F^2 by a full-matrix least-squares technique using the SHELXTL-PLUS[64] programs package. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS[65] The graphic programs DIAMOND[66] and ORTEP[67] were used to draw the structures. Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. During refinement, water and amine hydrogen atoms were located on Fourier map however, constrains were applied to fix the distance and angle. Details of crystal structure refinement parameters and H–bonding parameters for complex **1-6** are given as Table 1 and S1, respectively.

Conclusions

This article reports six organically templated 1D metal sulfites linear chain structures synthesized under mild hydrothermal conditions using sodium disulfite as the source of sulfite. From the results, the sulfites anion show strong tendencies to form 1D chains with the metals having both tetrahedral and octahedral coordination. These compounds are the first members of the organically templated metal sulfite 1D coordination polymer. On the basis of the present studies, it appears that many more open-framework materials of metal sulfite with more complex two- and 3D-structures can be synthesized and their NLO properties can be studied. Our future efforts will be to prepare both -layered and 3D-open-framework sulfites to demonstrate the rich synthetic and structural chemistry of metal sulfites.

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Notes and references

‡ PXRD and FTIR data as pictures, H-bonding interactions, complete bond lengths and bond angles as tables and X-ray crystallographic data in CIF format has been given as supporting information. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC 1417645 (**1**); 1417646 (**2**); 1417647 (**3**); 1417648 (**4**); 1417649 (**5**) and 1417650 (**6**). 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].

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Journal Name

ARTICLE

Table of Contents for

Organically Templated Linear Metal Sulfites

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Keywords: Metal-sulfite / Open-framework / H–bonding / Linear coordination polymer / One dimensional

Here, six novel organically templated linear transition metal-sulfite coordination polymers [($C_3H_{10}N)_2$] [Zn($SO_3)_2$], **1**, [$C_3H_{12}N_2$] [Zn($SO_3)_2$], **2**, [$C_4H_{14}N_2$] [Zn($SO_3)_2$], **3**, [$C_6H_{18}N_2$] [Zn($SO_3)_2$], **4**, [$C_4H_{12}N_2$] [Zn($SO_3)_2$].H_2O, **5** and [$C_4H_{12}N_2$] [Mn($SO_3)_2$ ($H_2O)_2$].2H_2O, **6** are synthesized using different amines and the role of H-bonding to provide 2D (for **1**) and 3D (for **2-6**) structures with increased dimensionality are discussed.