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Ranjay K. Tiwari, Jitendra Kumar and J. N. Behera*

Three novel transition metal-sulfite coordination complexes $[(C_6N_4H_{18})NaCo(SO_3)_2(H_2O)_3]$, $[(C_3N_2H_{10})_2NaCo(SO_3)_2(H_2O)_2].H_2O$, **2** and $[(C_6N_4H_{18})Zn_3(SO_3)_3]$, **3** are synthesized using different amines and the role of H-bonding to provide 3D (for **1** & **2**) and 2D (for **3**) structures are discussed.

$[(C_6N_4H_{18})NaCo^{III}(SO_3)_2(H_2O)_3]$
1

$[(C_3N_2H_{10})_2NaCo^{III}(SO_3)_2(H_2O)_2].H_2O$
2

$[(C_6N_4H_{18})Zn_3^{II}(SO_3)_3]$
3

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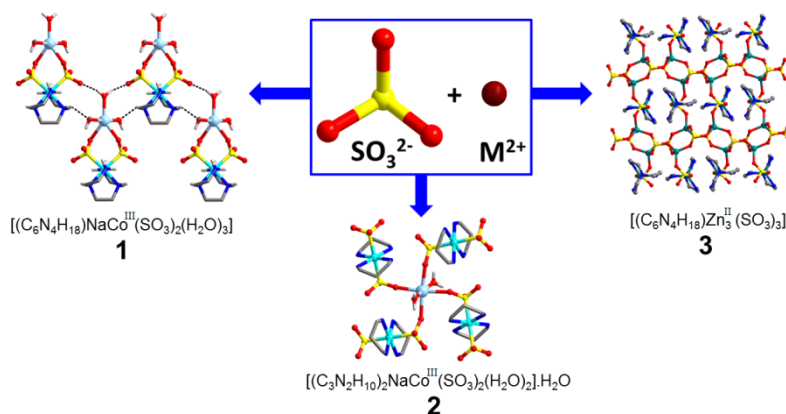
H–bond Supported Coordination Polymers of Transition Metal Sulfites with Different Dimensionalities

Ranjay K. Tiwari, Jitendra Kumar and J. N. Behera*

Three new transition metal-sufite coordination complexes namely $[(C_6N_4H_{18})NaCo(SO_3)_2(H_2O)_3]$, (**1**), $[(C_3N_2H_{10})_2NaCo(SO_3)_2(H_2O)_2].H_2O$, (**2**), and $[(C_6N_4H_{18})Zn_3(SO_3)_3]$, (**3**), have been synthesized under hydrothermal conditions in presence of various organic amines where the amine behaves as an organic ligand. The complexes were characterized by PXRD, TGA and FTIR techniques. **1** shows the formation of zero dimensional structure whereas **2** and **3** show two dimensional layer structures. The difference between **1** and **2** is due to the usage of different amines. The tetradentate amine in **1** dictates the coordination of sulfite groups in a *cis*–manner leading to the formation of zero dimensional structure whereas in **2** the bidentate amine forces the sulfite group coordination in a *trans*–manner resulting in a two dimensional structure. In **3**, the tetradentate amine caps one of the Zn centre, however the other two unique zinc ions coordinate with sulfite anion to form interconnected cyclic dimers which gives a two dimensional layer structure. The subtle changes in hydrogen bonding pattern and its consequence on the overall lattice to give a three dimensional network for **1** and **2** and two dimensional layer structure for **3** have been emphasized in details.

Introduction

Inorganic open–framework structures based on oxyanions like phosphate,[1] phosphite,[2-4] selenate,[5] selenite,[6-9] and sulfate[10-12] have been reported. Compared to other oxyanions, the use of noncentrosymmetric trigonal pyramidal sulfite anion for achieving open architecture materials based on transition metal ions is relatively less explored domain probably due to the inherent instability of sulfite anion in acidic as well as hydrothermal conditions.[13] The sulfite anion forms structures akin to selenite, tellurite and phosphite anions. However, in sulfite anion, the central sulfur atom with +4 oxidation state consists an active electron pair capable of metal coordination which induces crystallization in non-centrosymmetric space group and provides materials with possible nonlinear optical phenomenon.[14] The materials, thus obtained using sulfites are good candidates for simple harmonic generation. Apart from sulfur coordination, it also provides multitude of oxygen donor sites for metal coordination, thus exhibiting a range of coordination modes which can be exploited to synthesize complex inorganic materials.[15] Therefore, studying the metal-sulfite coordination complexes is an important area which opens up new avenue for generation of sulfite based inorganic

materials with fascinating properties.

We have been exploring sulfur based anionic complexes like sulfide, sulfite, sulfate, thiosulfate etc., as secondary building units for generating open-framework materials.[16-18] In continuation, we wish to study the coordination behavior of sulfite anion towards certain transition metal ions (Co(II) and Zn(II)) in presence of organic amines. The sulphite interaction and its coordination properties has been reported,[19, 20] however, very few literature reports are available describing Co–sulfite and Zn–sulfite coordination compounds.[21, 22] It has been observed that a range of precursors like sodium disulfite, ammonium sulfite and sodium sulfite can be used to incorporate SO_3^{2-} in the lattice structure. In the current study, sodium disulfite was employed as SO_3^{2-} source which readily dissolves in water and provides sulfite ion and sulfur dioxide after hydrolysis.

Here we report three new sulfite based coordination complexes namely $[(C_6N_4H_{18})NaCo(SO_3)_2(H_2O)_3]$, (**1**), $[(C_3N_2H_{10})_2NaCo(SO_3)_2(H_2O)_2].H_2O$, (**2**) and $[(C_6N_4H_{18})Zn_3(SO_3)_3]$, (**3**) where sulfite acts as a bridging ligand as well as the counter anion for charge neutralization. During the reaction, *in–situ* oxidation of Co(II) to Co(III) species was observed similar to literature reports and it has been proposed that certain conditions promote such oxidation under hydrothermal conditions.[23] Co(III)/SO_3^{2-} complexes are interesting materials from the standpoint of their applications to the thermal and photochemical oxidation of sulfite to sulfate ions as metal sulfite materials promotes such oxidation which is of biological importance.[13, 23]

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† Footnotes relating to the title and/or authors should appear here.
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

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Results and discussion

The reaction of cobalt(II) or zinc(II) acetate with sodium disulfite in presence of bidentate or tetradentate amines afforded three novel metal-sulfite coordination complexes namely $[(C_6N_4H_{18})NaCo(SO_3)_2(H_2O)_3]$, (**1**), $[(C_3N_2H_{10})_2NaCo(SO_3)_2(H_2O)_2].H_2O$, (**2**) and $[(C_6N_4H_{18})Zn_3(SO_3)_3]$, (**3**). **1** and **2** differs with one another only in terms of organic amine but the structural outcomes are entirely different. **1** forms a zero dimensional coordination complex whereas **2** display the formation of a 2D polymer. The use of amines as structural directing groups has been demonstrated by several groups.[24, 25] However, the complexes reported herein have the organic amines coordinated with the metal ions as organic ligands similar to previous reports.[26-28] Such coordination also has influential outcome over the entire lattice adopted by metal sulfite complex. The subtle changes in the coordination pattern and the resultant changes in the hydrogen bonding patterns is worthy of detail discussion.

Structural analysis of $[(C_6N_4H_{18})NaCo(SO_3)_2(H_2O)_3]$, (1).

Rhombohedral orange color crystals of **1** crystalizes in monoclinic crystal system having $C2/c$ space group and displayed zero dimensional structure. The asymmetric unit of **1** consist of 13 non hydrogen atoms and contains one Co(III) ion and one Na(I) ion both with half occupancy which was neutralized by one SO_3^{2-} group which is shown in Fig. S1a and the corresponding refinement data is given in Table 1. The asymmetric unit also has half of triethylenetetraamine (TETA) ligand directly coordinated to cobalt ion and two aqua ligands out of which one is having half occupancy. The Co(III) cation, Na(I) and O1w molecule lie on a two-fold rotational axis of symmetry. The coordination environment of Co(III) ion is composed of four nitrogen atoms coming from tetradentate organic base (Co–N = 1.971(3) and 2.020(3) Å and its symmetry equivalents) which caps the Co(III) center and two sulfur atoms from two crystallographically symmetric sulfite anions coordinated in a *cis*-manner (Co1–S1 = 2.216(8) Å and its symmetry equivalent) leading to the octahedral geometry. The Na(I) ion has distorted trigonal bipyramidal geometry where the equatorial plane contains two O1 oxygens from crystallographically equivalent SO_3^{2-} anion (Na–O1 = 2.349(3) Å) and aqua ligand (Na–O1w = 2.281(4) Å) whereas the axial position is occupied by two crystallographically equivalent O2w ligand with bond length of 2.339(3) Å. The SO_3^{2-} anion is involved in $\eta^1:\eta^1$–O:S coordination mode. The Co–N, Co–S and Na–O bond lengths are in good agreement with the literature reports.[21, 22, 29, 30] Selected bond lengths for **1-3** are given in Table 2. The closest Co···Co distance in the complex is 8.7572(9) Å which are situated at the corners of a rhombus within the layer. Although, we have used Co(II) precursor for the synthesis of **1**, but in the lattice Co(III) species were found due to *in-situ* oxidation and such observations have been reported in the literature which facilitates the participation of sulfur loan pair in the coordination.[23] The bond valence calculation for Co ion in **1** is 3.35 which is closer to the expected value of 3.0 and 0.9729 for Na ion further confirms the observed +3 oxidation states of Co ion.[31-33]

Table 1. Crystal structure refinement parameters for **1–3**.

	1	**2**	**3**
Formula	$[(C_6N_4H_{18})NaCo(SO_3)_2(H_2O)_3]$	$[(C_3N_2H_{10})_2NaCo(SO_3)_2(H_2O)_2].H_2O$	$[(C_6N_4H_{18})Zn_3(SO_3)_3]$
Mr	442.33	444.35	582.53
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/c$	$P\text{-}1$
a/Å	10.2417(11)	8.7984(2)	10.061(5)
b/Å	14.2078(11)	13.7933(2)	10.157(5)
c/Å	10.7370(9)	13.9548(2)	10.260(5)
α/°	90	90	70.753(11)
β/°	98.190(10)	103.5570(10)	61.288(10)
γ/°	90	90	80.871(12)
V/Å³	1546.4(2)	1646.35(5)	868.1(7)
Z	4	4	2
Dx /Mg m⁻³	1.900	1.793	2.229
μ/ mm⁻¹	1.460	1.372	4.522
θ range (°)	2.47 to 28.33	2.11 to 30.04	2.12 to 25.50
Reflections collected	11868	26098	3226
Unique reflections [R(int)]	1935 [0.0844]	4817 [0.0352]	3226 [0.000]
Data /restraints /parameters	1935 / 6 / 127	4817 / 13 / 267	3226 / 7 / 242
GOF on F^2	1.041	1.043	1.020
$R1$ and $R2$ [$I>2\sigma(I)$]	0.0381, 0.0961	0.0318, 0.0764	0.0681, 0.1627
$R1$ and $R2$ (all data)	0.0567, 0.1205	0.0418, 0.0810	0.1226, 0.1966
Largest residual peaks (e.Å⁻³)	0.697 and -0.969	0.975 and -0.491	1.485 and -0.993
CCDC no	**1407003**	**1407004**	**1407005**

Although the complex has zero dimensional structure, it is worth to emphasize the role of hydrogen bonding interactions engendered by the coordinated aqua ligands which lead to 3D structure.[34] The favorable interactions like hydrogen bonding and π–π interaction along with metal coordination have been shown to generate novel coordination frameworks with interesting topology and applications due to significant advantages offered by such coordination polymers over pure coordination polymers.[35, 36] Part of the crystal lattice of **1** consists of molecular structure of similar orientation in *ab*–plane is shown in Fig. 1. The non-coordinated sulfite oxygen O3 interacts in an intermolecular manner with the O1w molecule (O1w–H1w1···O3; $d_{O···H}$ = 2.00(4) Å) of adjacent molecular unit whereas the coordinated aqua ligands (O2w and its symmetry equivalent) offer one of its hydrogens to strongly interact in intramolecular manner with one of the remaining non–coordinated sulfite oxygens (O2w–H2w2···O2; $d_{O···H}$ = 1.98(3) Å), thus extending the lattice in *ab*–plane.

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Table 2. Selected bond lengths [Å] for **1-3**.[#]

[(C₆N₄H₁₈)NaCo(SO₃)₂(H₂O)₃], 1					
Co1–N1	2.020(3)	Co1–S1	2.216(8)	Na1–O1w	2.281(4)
Co1–N2	1.971(3)	Na1–O1	2.349(3)	Na1–O2w	2.339(3)

[(C₃N₂H₁₀)₂NaCo(SO₃)₂(H₂O)₂].H₂O, 2					
Co1–N1	1.988(1)	Co2–N4	1.987(2)	Na1–O4	2.389(1)
Co1–N2	1.978(1)	Co2–S2	2.273(4)	Na1–O5[b]	2.401(1)
Co1–S1	2.259(4)	Na1–O1	2.319(2)	Na1–O1w	2.337(2)
Co2–N3	1.971(1)	Na1–O3[a]	2.379(1)	Na1–O2w	2.563(2)

[(C₆N₄H₁₈)Zn₃(SO₃)₃], 3					
Zn1–O1	1.925(7)	Zn2–O3[d]	1.962(7)	Zn3–N1	2.262(9)
Zn1–O4	1.977(8)	Zn2–O5	1.954(7)	Zn3–N2	2.024(9)
Zn1–O6[c]	1.953(7)	Zn2–O9[e]	1.936(7)	Zn3–N3	2.058(9)
Zn1–O7	1.939(7)	Zn3–O8	2.037(8)	Zn3–N4	2.077(8)
Zn2–O2	1.934(8)				

#Symmetry transformations used to generate equivalent atoms: (a) -x+1, y-1/2, -z-1/2; (b) x, -y+1/2, z-1/2; (c) -x, -y, -z+1; (d) -x-1, -y, -z+1; (e) -x, -y, -z
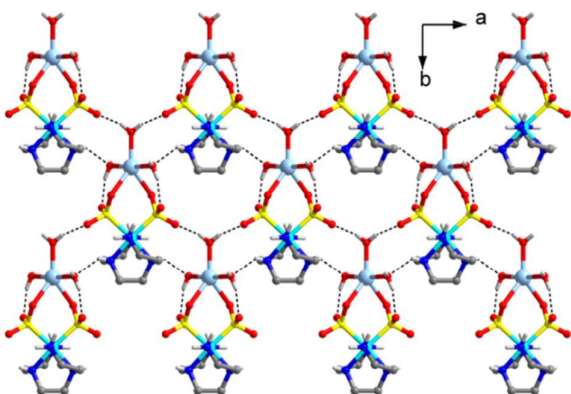

Fig. 1 Crystal lattice of [(C₆N₄H₁₈)NaCo(SO₃)₂(H₂O)₃], (**1**) with H–bonding (fragmented bonds) scheme in *ab*-plane.
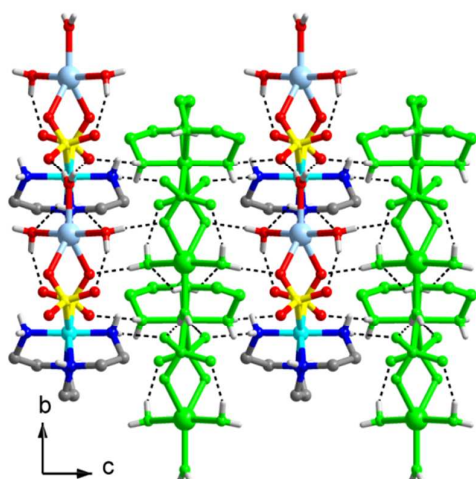

Fig. 2 Crystal lattice of [(C₆N₄H₁₈)NaCo(SO₃)₂(H₂O)₃], (**1**) with H-bonding scheme in *bc*–plane. Symmetrically equivalent structures are highlighted with colour code which constitutes different layers in the crystal lattice; the hydrogen atoms on carbon have been omitted for clarity.

The crystal lattice of **1** viewed along *a*–axis is shown in Fig. 2 along with hydrogen bonding schemes. The lattice contains molecular structure of opposite orientation in layer arrangements along *c*-axis as highlighted with different color code. The O2w molecule present in one layer offers the remaining hydrogen towards the O1 oxygen of sulfite anion present in adjacent layer for hydrogen bonding and extends the lattice in *c*–direction (O2–H1w2···O1; $d_{O···H}$ = 1.96(2) Å). Thus, the overall dimensionality of the crystal structure increases from 2D to 3D as a result of intricate hydrogen bonding schemes demonstrated by aqua ligands. Additionally, the amino group also displays variety of hydrogen bonding schemes to add to the strength of the crystal lattice (see Table S1).

Structural analysis of [(C₃N₂H₁₀)₂NaCo(SO₃)₂(H₂O)₂].H₂O, (2).

When the organic base is changed from TETA to 1,3–diamino propane, **2** was obtained. Thus, **1** and **2** owe their difference in terms of organic amine but the resultant crystal structure differs significantly. Rhombohedral shape orange color single crystals of **2** suitable for X–ray crystallography were synthesized hydrothermally and crystal structure refinement analysis showed that it belongs to monoclinic crystal system having *P*2₁/c space group. The asymmetric unit (Fig. S1b), consists of 24 non hydrogen atoms which contains two crystallographically unique Co(III) ions (namely Co1 and Co2) each having 0.5 occupancy, two SO₃²⁻ anions and two 1,3–diaminopropane units coordinated to Co(III) ion in a chelate manner. The crystal lattice was further neutralized by the presence of Na(I) ion. Three water molecules were also found in the crystal lattice out of which two (namely O1w and O2w) are coordinated with Na(I) ion whereas the third water molecule (O3w) is trapped in the lattice as solvent of crystallization (Fig. S1b). In this case also, the *in–situ* auto-oxidation of Co(II) precursor to Co(III) species is observed. The bond valence sum calculation, in case of **2**, for Co1 is 3.3152, for Co2 is 3.3094 and for Na is 1.2245 again confirm the +3 oxidation state of Co ion.[31-33] The difference between the crystal structure of **1** and **2** is due to the different coordination mode of the amine to the metal ion. In **2**, the two bidentate amine ligands coordinate the metal center and occupies the equitorial positions, consequently, the coordinated sulfur atom of sulfite anion occupies the axial site which are further bridged by Na(I) coordination facilitating the formation of layer structure but in case of **1**, the coordination from tetradentate amine forces the sulfur coordination with Co(III) center in a *cis*–manner which is bridged by Na(I) ion leading to the formation of zero dimensional coordination complex.

Both the Co(III) ions are situated at crystallographic inversion center and have octahedral geometries. The coordination sphere of each Co(III) ion consists of four amino nitrogen atoms from the organic base which forms the equatorial plane and two sulfur atom from the two crystallographically identical SO₃²⁻ occupying the axial sites. The Co–N bond lengths range between 1.978(1)–1.988(1) Å whereas the Co–S bond length are 2.259(4) Å (for Co1–S1) and 2.273(4) Å (for Co2–S2) which is in agreement with the literature reports.[21, 22] The

coordination geometry of Na(I) ion is also octahedral consisting only oxygen atoms where four oxygen atoms are contributed by four SO_3^{2-} anions forming the equatorial plane and aqua ligands occupy the axial sites. The Na–O bond lengths are in the range of 2.319(2)–2.563(2) Å which are in good agreement with the literature reports of similar compounds.[21, 22] A complete list of bond lengths and bond angles are given as Table S2.
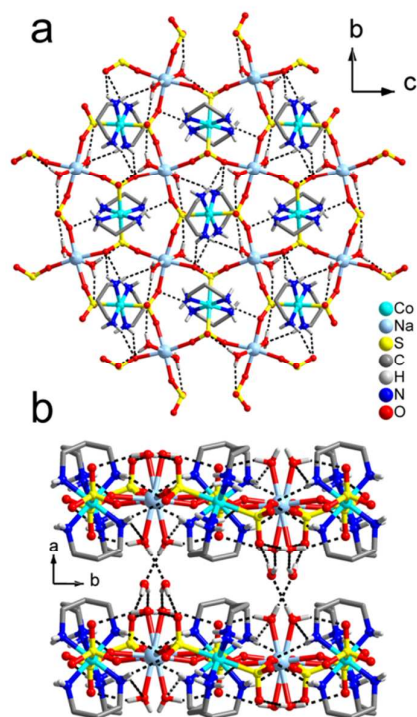

Fig. 3 (a) View of the two dimensional layer of $[(C_3N_2H_{10})_2NaCo(SO_3)_2(H_2O)_2].H_2O$, **2**, with H–bonding scheme (fragmented bonds). (b) Interconnection of different layers *via* H-bonding as viewed along *c*-axis. Part of the crystal lattice has been omitted for clarity.

In the crystal lattice of **2**, Co(III) and Na(I) coordination to SO_3^{2-} anion forms an infinite 2D layer in the *bc*–plane where each SO_3^{2-} anion is coordinated with two Na(I) ions and one Co(III) anion (Fig. 3a) *via* $\eta^1:\eta^1:\eta^1$–O:O:S mode, respectively. The distance between adjacent Co(III) ion is 6.8966(1) along *b*–axis and 6.9774(1) Å along *c*–axis respectively, thus the Co(III) ions are situated on the corners of a perfect rectangle. Within the 2D layer, the *trans*-coordination with sulfur atom of sulfite ion with Co ions generate a $[Co(SO_3)_2]^-$ unit which extends in two dimension by bridging Na(I) ions in almost orthogonal fashion as shown in Fig. 3a. Cobalt(II) sulfite complexes under acidic pH was reported but contrary to our results no oxidation to Co(III) and consequent coordination to sulfur atom was observed.[21]

Although the metal-sulfite coordination result in a 2D polymer in case of **2**, it is important to give some emphasis on the intricate hydrogen bonding interactions displayed by amino groups, aqua ligands and water molecule. In the crystal lattice, both the coordinated aqua ligands (O1w and O2w) show

different hydrogen bonding schemes. The O2w ligand acts as donor and offers both of its hydrogen atoms for O2 (O2w–H2w2···O2; $d_{O···H}$ = 2.34(2) Å) and O6 (O2w–H1w2···O6; $d_{O···H}$ = 2.17(3) Å) oxygen atoms of sulfite anion present in the same layer. Interestingly, the O2 and O6 oxygen atoms of sulfite anions are not involved in coordination with Na(I) cation contrary to the remaining oxygen atoms present in SO_3^{2-} anions. In the crystal lattice, non-coordinated water molecule O3w plays a crucial role which occupies the interlayer space as shown in Fig. 3b. The trapped O3w molecule interconnects the 2D layers through strong hydrogen bonding by simultaneously acting as donor atom for O6 atom (O3w–H2w3···O6; $d_{O···H}$ = 2.00(2) Å) of sulfite anion and O2w ligand (O3w–H1w3···O2w; $d_{O···H}$ = 2.09(3) Å) present in one layer and as acceptor for O1w ligand present in another layer (O1w–H1w1···O3w; $d_{O···H}$ = 1.979(19) Å) as shown in Fig. S2. This interaction results in the increase in the dimensionality of the crystal lattice by extending it along *a*–axis, eventually generating a 3D lattice. The remaining hydrogen atom on O1w exhibits H–bonds with the O2 oxygen of sulfite anion (O1w–H2w1···O2; $d_{O···H}$ = 2.15(2) Å) of the same layer. The amino groups also display significant H–bonding interactions within the 2D layer which further strengthens the crystal lattice of **2** (see Table S2).

Structural analysis of $[(C_6N_4H_{18})Zn_3(SO_3)_3]$, (3).

Plate shaped colourless crystals of **3** crystalizes in triclinic crystal system and *P*–1 space group. The asymmetric unit consist of 25 non hydrogen atoms and have three Zn(II) ion, three SO_3^{2-} ion and one *tris*–(2–aminoethyl) amine molecule which is shown in Fig. S1c. The Zn(II) ion has two different coordination geometry in the complex where two crystallographically unique Zn(II) ions (namely Zn1 and Zn2) possess distorted tetrahedral geometry where the coordination sphere is composed of four sulfite oxygen with average Zn–O bond length of 1.925(7) and 1.977(8) Å, respectively, which is comparable to the literature reports on other zinc(II)–sulfite complexes.[26-28, 30] The third Zn(II) (namely Zn3) has distorted trigonal bipyramidal geometry where the equitorial sites are occupied by terminal amino groups of *tris*–(2–aminoethyl)amine with average bond length of 2.057 Å and the axial sites are occupied by tertiary amine group of organic ligand (Zn3–N1 = 2.262(9) Å) and sulfite oxygen (Zn3–O8 = 2.037(8) Å) which is again in good agreement with literature reports.[26] The bond valence sum calculation for Zn1, Zn2 and Zn3 is 2.0713, 2.0734 and 2.1139 respectively which further suggest the +2 oxidation state of metal ions in **3**.

In the crystal lattice, Zn(II) coordination with sulfite oxygen generates a 2D layer utilizing only Zn1 and Zn2 ions whereas the third crystallographically unique zinc ion namely Zn3 coordinates with the organic amine which is protruding outside the 2D layer occupying the inter layer space (Fig. 4). Since there are three unique sulfite anions present in the crystal lattice, the coordination engendered towards zinc ions differ. Two sulfite anions (with sulfur atom S1 and S2) coordinate with Zn1 and Zn2 metal ions, leading to the formation of a dimeric unit Zn_2S_2 (not considering the bridging oxygen atom) with Zn···Zn distance of 3.818 Å. These dimeric

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units are interconnected with sulfite oxygen to generate a 1D chain along *a*–axis as highlighted with grey color rectangle in Fig. 4a. These 1D chains are further connected with each other by another sulfite anion (with S3 sulfur atom) to generate a 2D layer structure in *ac*–plane. The extension of lattice through Zn3 center is not observed as the coordinated amine caps the metal center (Fig. 4b). Thus, in the crystal lattice, each sulfite anion is coordinated with three Zn(II) ions in a $\eta^1\mu^3$ coordination mode as shown in Fig. 4c.
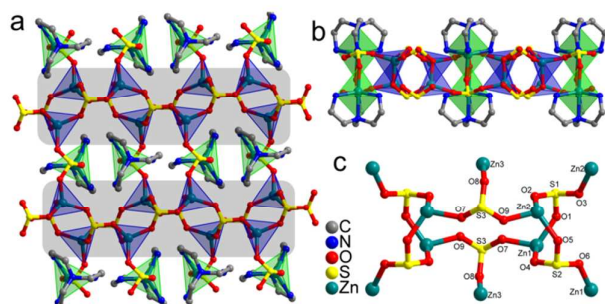

Fig. 4 (a) View of the 2D layer in [(C$_6$N$_4$H$_{18}$)Zn$_3$(SO$_3$)$_3$], **3**, as viewed close to *b*–axis (green polyhedra represent the Zn3 ions and blue polyhedra represent Zn1 or Zn2 ions, respectively) (b) View of the crystal lattice along *a*–axis showing the position of coordinated organic amines. (c) Coordination of sulfite anions in the crystal lattice of **3**.

The 2D layer itself consists two sheets depending on the position of zinc ions which are organized in a hexagonal arrangement (as differentiated with color code) with Zn···Zn distance ranging between 5.83–6.03 Å resulting in a honeycomb structure as shown in Fig. 5a. The Zn3 ions coordinated to the sulfite ions constituting the green sheet are roughly situated at the center of hexagonal arrangement of grey sheet and *vice-versa* (Fig. 5b). Further strength of the crystal lattice comes from the hydrogen bonding interaction shown by coordinated amino group and sulfite oxygen atoms which is involved in bifurcated hydrogen bonding and ranges between 2.2–2.6 Å as shown in Fig. 5b however the hydrogen bonding is restricted within the layer and no increase in dimensionality due to H–bonding was observed contrary to **1** and **2**.
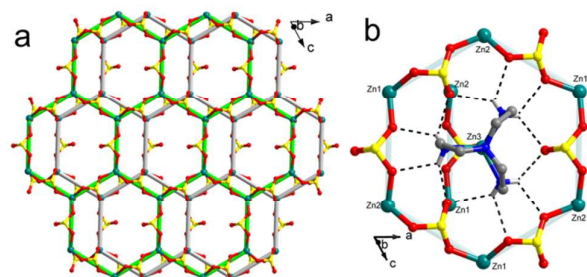

Fig. 5 (a) Interconnected sheets of honeycomb structure within two dimensional layer of [(C$_6$N$_4$H$_{18}$)Zn$_3$(SO$_3$)$_3$], **3**, composed of alternate Zn1 and Zn2 ions, (b) Position of amine coordinated Zn3 ion in hexagonal space.

The complexes were further characterized by FTIR, PXRD and TGA experiments. FTIR spectra showed signature peaks of various functional groups present in the crystal lattice for all the complexes. FTIR spectra of **1–3** showed the characteristic peaks for SO$_3$$^{2-}$ anion around 970, 930, 620 and 470 cm^{-1}. The peaks around 3250–3500 cm^{-1} are attributed to OH and NH stretching vibrations of water molecule and amino groups respectively.[37, 38] 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. S3). A representative PXRD pattern of **2** along with its simulated pattern is given in Fig. 6.
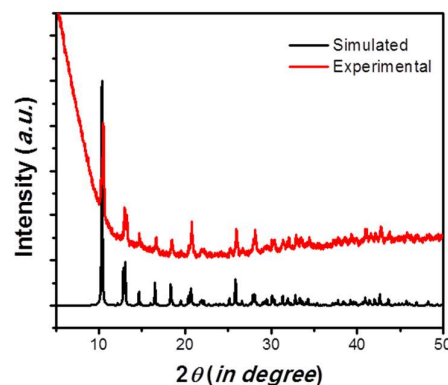

Fig. 6 PXRD pattern of [(C$_3$N$_2$H$_{10}$)$_2$NaCo(SO$_3$)$_2$(H$_2$O)$_2$].H$_2$O, **2** showing the phase purity of as synthesized materials.
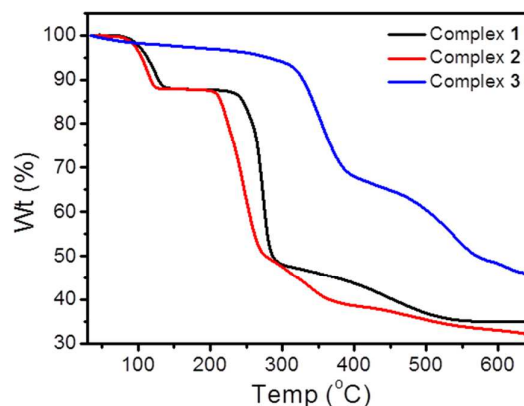
Fig. 7 Thermogravimetric analysis for [(C$_6$N$_4$H$_{18}$)NaCo(SO$_3$)$_2$(H$_2$O)$_3$], **1**; [(C$_3$N$_2$H$_{10}$)$_2$NaCo(SO$_3$)$_2$(H$_2$O)$_2$].H$_2$O, **2** and [(C$_6$N$_4$H$_{18}$)Zn$_3$(SO$_3$)$_3$], **3**.

The TGA analyses of the samples were performed in order to establish the thermal stability of the complexes which is shown in Fig. 7. **1** shows multi–step decomposition where the first stage is dehydration in the temperature range 80 to 130 °C showing the loss of water molecules which accounts for ~11.79 % (calc. as 12.20 %) weight loss. The second step is due to decomposition of TETA ligand in the range of 200 to 280 °C which accounts nearly 37 % (calc 38.20 %) of weight loss. And finally decomposition of SO$_3$ group shows 19 % (calc 18.08 %) weight loss in the temperature range of 280 to 670 °C. **2** also

shows multi–step decomposition in TGA and again the first step is dehydration in the temperature range 75 to 140 °C showing the loss of water molecules which is found to be 11.90 % (calc 12.15 %). The second step is due to the decomposition of 1,3–diaminoprpane in the range of 220 to 300 °C which accounts nearly 39.18 % (calc 38.48 %) weight loss. Similar to **1**, loss of sulfite group as sulfur dioxide molecule due to decomposition shows 19 % (18.00 %) weight loss in the 400 to 600 °C range. **3** also shows two major decomposition steps where the first step corresponds to the loss of *tris*–(2–ethylamino)amine ligand which accounts for 25.06 % weight loss (calc 25.94 %) in the temperature range of 200-300 °C. This also indicates that **3** is more thermally stable compared to **1** and **2** due to absence of water molecules in the crystal structure. Further decomposition of **3** is due to loss of sulfite ligands in the temperature range of 415-570 °C and accounts for 13.07 % (14.18 %) weight loss. The PXRD analysis of the calcined product of **1** and **2** corresponds to the cobalt oxide (PDF-00-043-1004) whereas in case of **3**, it corresponds to zinc oxide (PDF-01-075-0576) as shown in Fig. S4.

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 **1-3** were calculated by considering $r_{o(Co-N)} = 1.790$; $r_{o(Co-S)} = 1.980$; $r_{o(Na-O)} = 1.803$; $r_{o(Zn-N)} = 1.770$ and $r_{o(Zn-O)} = 1.704(Å)$.[31-33]

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.

Synthesis of [(C₆N₄H₁₈)NaCo(SO₃)₂(H₂O)₃], (1). A mixture of cobalt acetate tetrahydrate (0.248 g, 1.0 mmol), sodium disulfite (0.380 g, 2.0 mmol) and triethylenetetraamine (TETA) (0.300 mL, 2.0 mmol) were dissolved in 2.0 mL of distilled water. The mixture was transferred in polypropylene bottle of 15 mL capacity. The reaction mixture was stirred for 25 minutes. to get a homogeneous solution. The pH of the solution was 9.0 initially and there was no significant change after the hydrothermal reaction. The reaction mixture was sealed and heated at 75 °C for 72 h after that the solution was cooled down naturally to room temperature. The clear orange solution thus obtained was filtered and left undisturbed for slow evaporation which provided rhombohedral shaped orange crystals of **1** suitable for single crystal X-ray diffraction

within 2 days. (Yield 74% with respect to Co). Anal. Calc: C, 16.29; H, 5.47; N, 12.67; S, 14.50 % Found: C, 16.26; H, 5.51; N, 12.64; S, 14.45 % IR data (KBr, cm^{-1}): 3412 br, 3006 m, 1588 s, 1470 m, 1225 s, 1033 s, 979 m, 928s, 616 m, 479 m.

Synthesis of [(C₃N₂H₁₀)₂NaCo(SO₃)₂(H₂O)₂].H₂O, (2). The orange color rhombohedral shape single crystals of **2** was obtained in a similar manner as that of **1** except 1,3–diamino propane (0.166 mL, 2.0 mmol) was added as base instead of TETA and pH of the solution was 8.0 initially which remains almost same after hydrothermal reaction. (Yield 61% with respect to Co). Anal. Calc: C, 16.22; H, 5.90; N, 12.61; S, 14.43 %. Found: C, 16.18; H, 5.96; N, 12.57; S, 14.40 %. IR data (KBr, cm^{-1}): 3406 br, 2985 m, 1595 s, 1467 m, 1237 s, 1030 s, 965 m, 934m, 621 m, 473 m.

Synthesis of [(C₆N₄H₁₈)Zn₃(SO₃)₃], (3). The plate shape colorless single crystals of **3** suitable for X-ray diffraction was obtained in a similar manner as that of **2** using zinc acetate tetrahydrate (0.219 g, 1.0 mmol), sodium disulfite (0.380 g, 2.0 mmol) and *tris*–(2–aminoethyl)amine (0.104 mL, 1.0 mmol). The pH of the colorless solution was 6.0 initially which has no observable change after the hydrothermal reaction. (Yield 68% with respect to Zn). Anal. Calc: C, 12.37; H, 3.11; N, 9.62; S, 16.51% Found: C, 12.32; H, 3.16; N, 9.58; S, 16.48 %. IR data (KBr, cm^{-1}): 3424br, 2997m, 1580 s, 1472 m, 1086 b, 969 s, 932s, 623 m, 486 m.

Crystallography.

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[39] programs package. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS.[40] The graphic programs DIAMOND[41] and ORTEP[42] 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 positions. Details of crystal structure refinement parameters and H–bonding parameters for **1–3** are given as Table 1 and S1, respectively.

Conclusions

In conclusion, hydrothermal synthesis of three new metal sufite complexes based on Co and Zn metal ions are reported where the sulfite coordination and hydrogen bonding interactions result in a novel topology. The role of weak interaction in dictating the crystal structure and the crucial role to increase the dimensionality of crystal structure has

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been discussed. On the basis of present studies it appears that many more open framework metal sulfite with more complex two and three dimensional structures can be synthesized.

Acknowledgements

Notes and references

‡ CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC **1407003** (**1**), **1407004** (**2**), & **1407005** (**3**). 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].

1.	R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja and C. N. R. Rao, *Chem. Rev.*, 2008, **108**, 3549-3655.
2.	C.-M. Wang, T.-Y. Chang, L.-W. Lee, H.-M. Lin, K.-L. Lu and K.-H. Lii, *Chem. Commun.*, 2015, **51**, 7824-7826.
3.	X.-M. Jing, Y.-B. Tan, L.-W. Xiao and Y.-L. Liu, *Inorg. Chem. Commun.*, 2015, **57**, 75-77.
4.	J. Tian, B. Li, X. Zhang and J. Zhang, *CrystEngComm*, 2014, **16**, 1071-1078.
5.	I. Pasha, A. Choudhury and C. N. R. Rao, *J. Solid State Chem.*, 2003, **174**, 386-391.
6.	A. J. Howarth, M. J. Katz, T. C. Wang, A. E. Platero-Prats, K. W. Chapman, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 7488-7494.
7.	G. S. Papaefstathiou, K. S. Subrahmanyam, G. S. Armatas, C. D. Malliakas, M. G. Kanatzidis and M. J. Manos, *CrystEngComm*, 2014, **16**, 3483-3486.
8.	I. Pasha, A. Choudhury and C. N. R. Rao, *Inorg. Chem.*, 2003, **42**, 409-415.
9.	D. Udayakumar and C. N. R. Rao, *J. Mater. Chem.*, 2003, **13**, 1635-1638.
10.	S. Natarajan and S. Mandal, *Angew. Chem. Int. Ed.*, 2008, **47**, 4798-4828.
11.	A. Choudhury, J. Krishnamoorthy and C. N. R. Rao, *Chem. Commun.*, 2001, 2610-2611.
12.	G. Paul, A. Choudhury, E. V. Sampathkumaran and C. N. R. Rao, *Angew. Chem. Int. Ed.*, 2002, **41**, 4297-4300.
13.	B. Meyer, *Sulfur, energy, and environment*, Elsevier, 2013.
14.	R.-L. Zhong, H.-L. Xu, Z.-R. Li and Z.-M. Su, *J. Phys. Chem. Lett.*, 2015, **6**, 612-619.
15.	H. N. Miras, G. I. Chilas, L. Cronin and T. A. Kabanos, *Eur. J. Inorg. Chem.*, 2013, **2013**, 1620-1630.
16.	C. N. R. Rao, J. N. Behera and M. Dan, *Chem. Soc. Rev.*, 2006, **35**, 375-387.
17.	S. R. Marri and J. N. Behera, *J. Solid State Chem.*, 2014, **210**, 15-21.
18.	J. N. Behera, J. Bhattacharjee, S. Horike, S. R. Marri and P. P. Dahiya, *RSC Adv.*, 2014, **4**, 50435-50442.
19.	P.-X. Li and J.-G. Mao, *Dalton Trans.*, 2010, **39**, 107-112.
20.	B. Nyberg, *Acta Crystallogr., B*, 1978, **34**, 1418-1421.
21.	G. I. Chilas, N. Lalioti, T. Vaimakis, M. Kubicki and T. Kabanos, *Dalton Trans.*, 2010, **39**, 8296-8305.
22.	G. I. Chilas, M. Stylianou, M. Kubicki, T. Vaimakis, P. Kögerler, A. D. Keramidas and T. A. Kabanos, *Inorg. Chem.*, 2008, **47**, 4451-4453.
23.	M. V. Alipázaga, D. Lowinsohn, M. Bertotti and N. Coichev, *Dalton Trans.*, 2004, 267-272.
24.	P.-X. Li, H.-L. Jiang, M.-L. Feng and J.-G. Mao, *Inorg. Chem.*, 2007, **46**, 8302-8308.
25.	P.-X. Li and J.-G. Mao, *Cryst. Growth Des.*, 2008, **8**, 3385-3389.
26.	K. P. Rao and C. N. R. Rao, *Inorg. Chem.*, 2007, **46**, 2511-2518.
27.	D.-T. Nguyen, E. Chew, Q. Zhang, A. Choi and X. Bu, *Inorg. Chem.*, 2006, **45**, 10722-10727.
28.	C. Austria, J. Zhang, H. Valle, Q. Zhang, E. Chew, D.-T. Nguyen, J. Y. Gu, P. Feng and X. Bu, *Inorg. Chem.*, 2007, **46**, 6283-6290.
29.	B. F. Abrahams, M. G. Haywood and R. Robson, *Cryst. Growth Des.*, 2008, **8**, 1288-1293.
30.	P.-X. Li, C.-L. Hu, Q.-P. Lin, N. Zhao and J.-G. Mao, *Inorg. Chem.*, 2009, **48**, 5454-5461.
31.	G. J. Palenik, *Inorg. Chem.*, 1997, **36**, 122-122.
32.	N. E. Brese and M. O'Keeffe, *Acta Crystallogr., B*, 1991, **47**, 192-197.
33.	I. D. Brown, *Structure and bonding in crystals*, 1981, **2**, 1-30.
34.	R. F. D'Vries, V. A. de la Peña-O'Shea, A. n. Benito Hernández, N. Snejko, E. Gutierrez-Puebla and M. A. Monge, *Cryst. Growth Des.*, 2014, **14**, 5227-5233.
35.	G. R. Desiraju, *Cryst. Growth Des.*, 2011, **11**, 896-898.
36.	J. Kumar and S. Verma, *J. Chem. Sci.*, 2011, **123**, 927-935.
37.	K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, Wiley Online Library, 1986.
38.	B. Nyberg and R. Larsson, *Acta Chem. Scand.*, 1973, **27**, 63-70.
39.	G. M. Sheldrick, *Journal*, 1997.
40.	G. M. Sheldrick, *University of Göttingen, Göttingen, Germany*, 1994.
41.	W. T. Pennington, *J. Appl. Crystallogr.*, 1999, **32**, 1028-1029.
42.	L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565-565.

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H−bond Supported Coordination Polymers of Transition Metal Sulfites with Different Dimensionalities

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Three novel transition metal-sulfite coordination complexes [(C$_6$N$_4$H$_{18}$)NaCo(SO$_3$)$_2$(H$_2$O)$_3$], **1**, [(C$_3$N$_2$H$_{10}$)$_2$NaCo(SO$_3$)$_2$(H$_2$O)$_2$].H$_2$O, **2** and [(C$_6$N$_4$H$_{18}$)Zn$_3$(SO$_3$)$_3$], **3** are synthesized using different amines and the role of H−bonding to provide 3D (for **1** & **2**) and 2D (for **3**) structures are discussed.

[(C$_6$N$_4$H$_{18}$)NaCo^{III}(SO$_3$)$_2$(H$_2$O)$_3$]
1

[(C$_3$N$_2$H$_{10}$)$_2$NaCo^{III}(SO$_3$)$_2$(H$_2$O)$_2$].H$_2$O
2

[(C$_6$N$_4$H$_{18}$)Zn$_3^{II}$(SO$_3$)$_3$]
3