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Supporting Information

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

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

Experimental

Materials and methods.

General. All the chemicals were purchased from standard chemical suppliers and used without further purification.

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 $CuK\alpha$ radiation (λ = 1.5418 Å). The phase transition (temperature and enthalpy changes) experiment was performed on Mettler Toledo DSC instrument. Heating and cooling were done at a rate of 10 K min^{-1} with the aid of Liq. N$_2$ under constant Ar flow (20 mL min^{-1}). The sample was taken in aluminum crucible and the experiment was carried out in the range of -120 ^{o}C to 180 ^{o}C. N$_2$ adsorption isotherm was performed on a Quantachrome Instrument version 3.01 at 77 K. Prior to the experiment, **2** was activated at 100 ^{o}C under reduced pressure. The frequency and temperature dependence dielectric and impedance properties of the compound was measured using an LCR Hi Tester (HIOKI,Model-3532) in the frequency range of 102–106 Hz from 25 to 75 °C. Single crystal data was collected on a Bruker AXS KAPPA-APEX II instrument at room temperature.

Synthetic procedures.

Synthesis of (NH$_3$CH$_2$CH$_2$NH$_3$)[Zn$_3$(SO$_3$)$_4$], (1). Zinc acetate dihydrate (220 mg) was dissolved in 3.0 mL water and sodium disulfite (389 mg) was added. Finally, ethylene diamine (60 μL) was added and the mixture was stirred 30 minutes. The reaction mixture having pH 5-6 was transferred to a polypropylene bottle (15 mL capacity), sealed and heated at 90 ^{o}C. After 72 h, the reaction mixture was cooled to room temperature and plate shape colourless crystals were obtained. The crystals were filtered and washed with *approx.* 5mL of water and dried in air. (Yield 56 % with respect to metal salt). Anal. Calc: C, 4.15; H, 1.74; N, 4.84; S, 22.17 % Found: C, 4.21; H, 1.68; N, 4.80; S, 22.09 %; IR data (KBr, cm^{-1}): 3307 br, 3012 m, 2920 m, 1635 m, 1530 m, 1385 w, 1145 s, 990-960 m, 925 s, 880 s, 645 m, 610 m, 530 m, 475 m.

Synthesis of (CN$_3$H$_6$)$_2$[Zn(SO$_3$)$_2$], (2). **2** was synthesized in a similar way as that of **1**, but guanidinium carbonate (300 mg) was used as a template. In this case, the reaction mixture having pH 6 was heated at 75°C. After 24 h plate shape colourless crystals were obtained after cooling the reaction mixture to room temperature. The crystals were filtered and washed with *approx.* 5mL of water and dried in air. (Yield 62 % with respect to Zn). Anal. Calc: C, 6.95; H, 3.50; N, 24.31; S, 18.55 % Found: C, 6.88; H, 3.58; N, 24.21; S, 18.69 %. IR data (KBr, cm^{-1}): 3430 br, 3185 s, 2791 w, 1670 s, 1117 m, 1045 s, 908 s, 834 s, 660 m, 620 m, 515 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[1] programs package. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS.[2] The graphic programs DIAMOND[3] and ORTEP[4] 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 **1–2** are given as Table S1 and S2, respectively.

1.   G. M. Sheldrick, *SHELXL-97, program for X-ray crystal structure refinement*, University of Göttingen, Germany, 1997.
2.   G. M. Sheldrick, *SADABS Siemens Area Correction Absorption Program*, University of Göttingen, Göttingen, Germany, 1994.
3.   W. T. Pennington, *J. Appl. Crystallogr.*, 1999, **32**, 1028-1029.
4.   L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565-565.
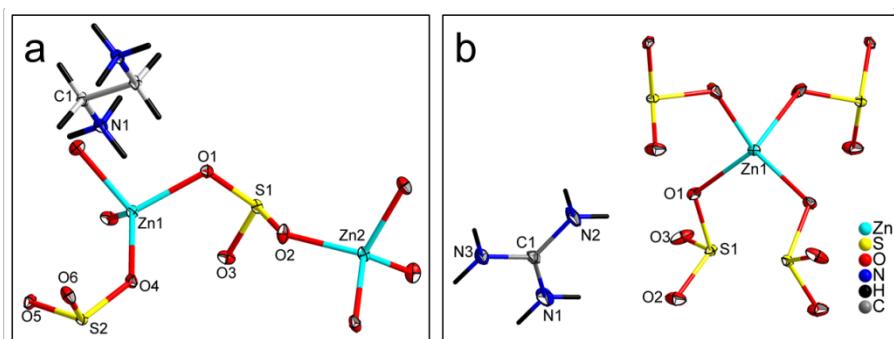
Fig. S1 (a) Molecular structure of (a) $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** at 25 % ellipsoid probability and (b) $(CN_3H_6)_2[Zn(SO_3)_2]$, **2** at 15 % ellipsoid probability, where unique atoms are labelled.
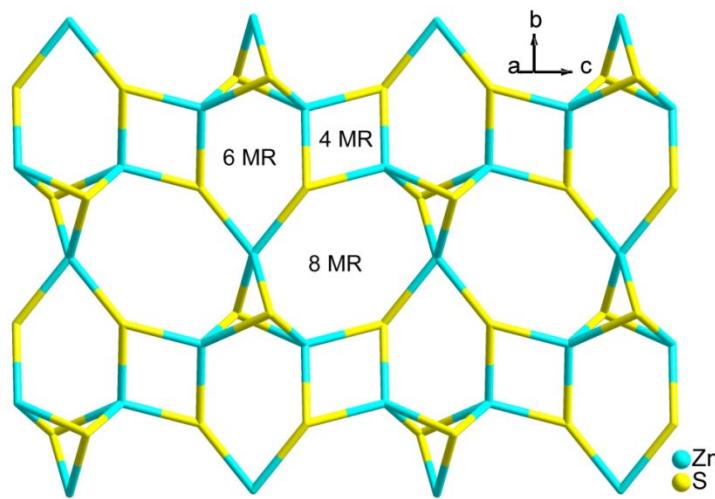

Fig. S2 A 2D layer structure in case of $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** with embedded 4, 6 and 8 membered rings (MR); excluding the oxygen atoms (ignoring the intervening sulfite oxygen atoms).
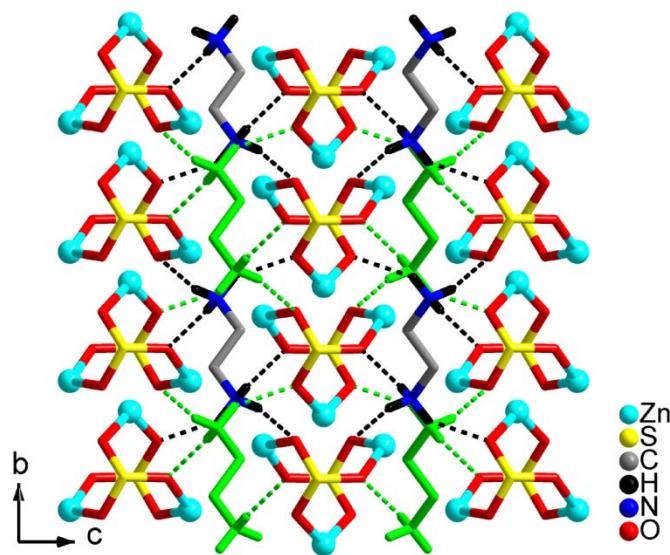
Fig. S3 Interconnection of triangular node in **1** *via* H-bonding interaction shown with fragmented bonds (part of the lattice is omitted and protonated ethylene diamine is shown with different color for clarity).
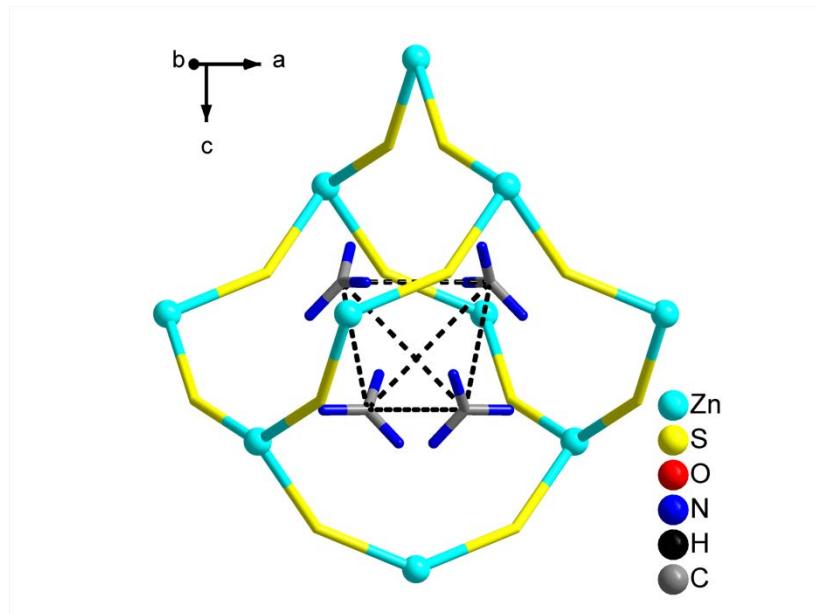
Fig. S4 12-membered ring with Zn-S atoms in an adamantane topology in case of **2** (part of the lattice is omitted and protonated ethylene diamine is shown with different color for clarity).
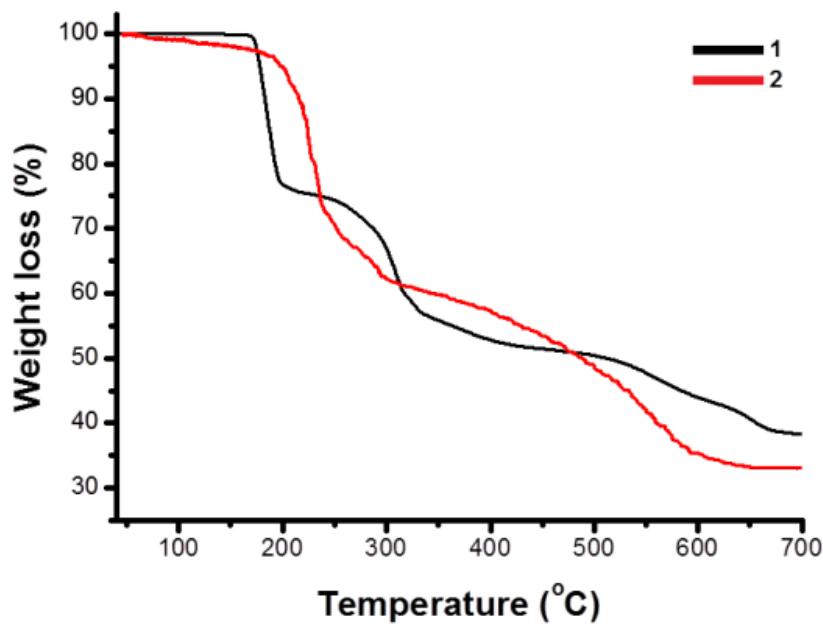
Fig. S5 Thermogravimetric analysis for $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** and $(CN_3H_6)_2[Zn(SO_3)_2]$, **2**.
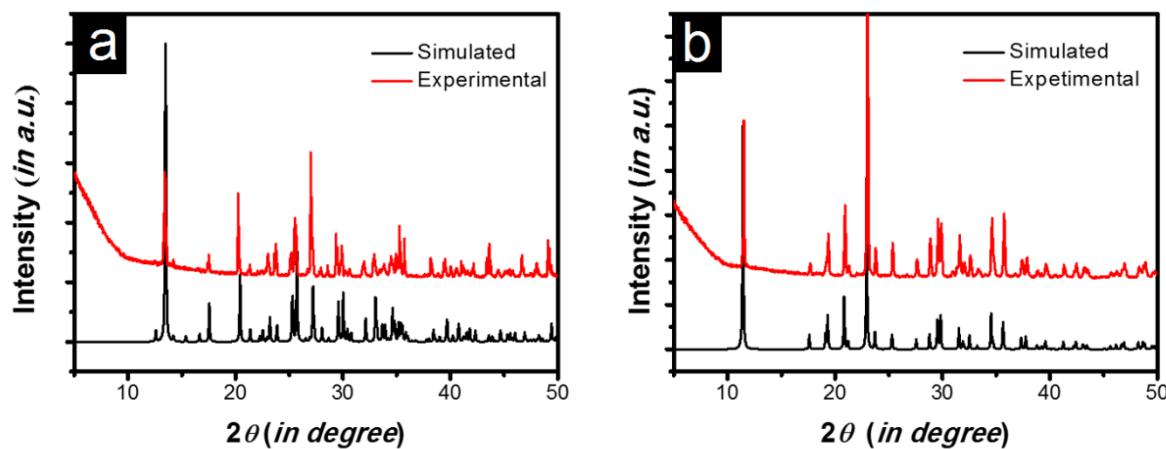
Fig. S6 PXRD pattern for (a) $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** and (b) $(CN_3H_6)_2[Zn(SO_3)_2]$, **2**.
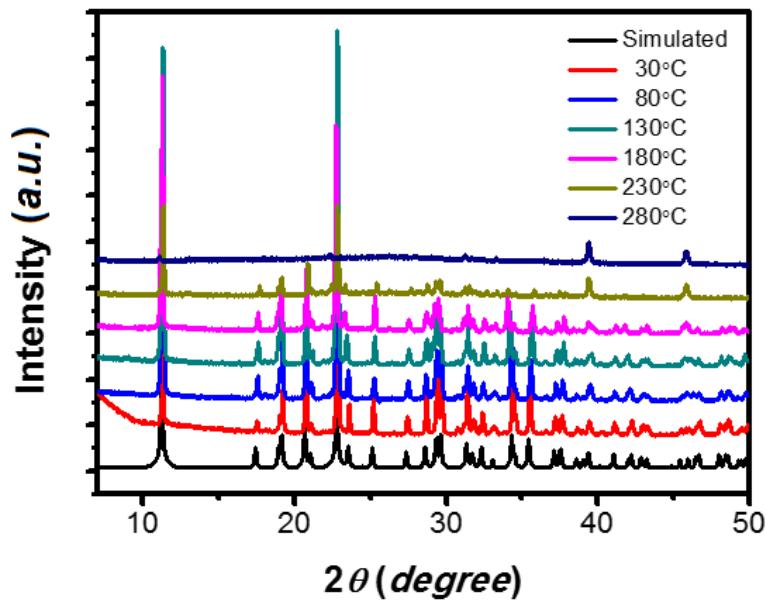
Fig. S7 Temperature dependent PXRD pattern of $(CN_3H_6)_2[Zn(SO_3)_2]$, **2**.

Index #		FOM	Mtc	nM	%	Source	ID	...	...	I/...	...	Name	Formula
✓	1	0.53	4	0	97	PDF2010	PDF 01-075-0576	...	...	5.53	...	Zinc Oxide	Zn O
	2	0.67	4	0	74	PDF2010	PDF 01-070-8071	...	...	4.89	...	Zinc Lithium Oxide	(Zn0.914 Li0.086) O0.957
	3	0.74	4	0	66	PDF2010	PDF 01-070-8070	...	...	5.36	...	Zincite, syn	Zn O
	4	0.74	4	0	66	PDF2010	PDF 01-071-6424	...	...	5.21	...	Zincite, syn	Zn O
	5	0.77	4	0	47	PDF2010	PDF 00-003-0891	...	...		...	Zincite	Zn O
	6	0.80	4	0	64	PDF2010	PDF 01-089-7102	...	...	5.33	...	Zincite, syn	Zn O
	7	0.82	4	0	62	PDF2010	PDF 01-075-7918	...	...	5.36	...	Zinc Iron Oxide	(Zn0.97 Fe0.03)0.989 O
	8	0.83	4	0	38	PDF2010	PDF 00-003-0888	...	...		...	Zinc Oxide	Zn O
	9	0.83	4	0	77	PDF2010	PDF 00-001-1136	...	...		...	Zincite	Zn O

Fig. S8 Post calcination PXRD analysis of both $(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$, **1** and $(CN_3H_6)_2[Zn(SO_3)_2]$, **2** showing formation of ZnO (PDF-01-075-0576) species.
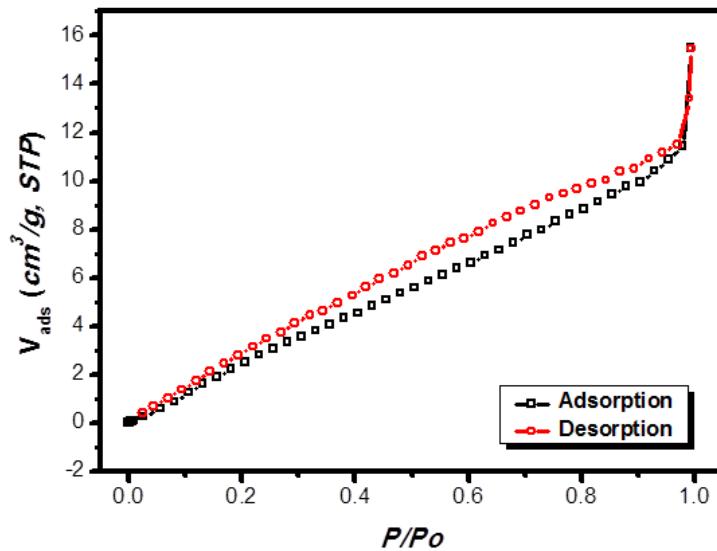
Fig. S9 N_2 Sorption isotherm for $(CN_3H_6)_2[Zn(SO_3)_2]$, **2**.
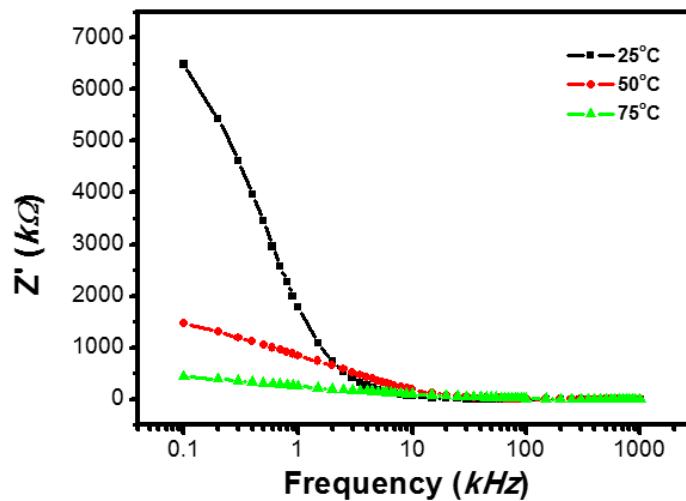
Fig. S10 Frequency dependence impedance (real part) spectra of $(CN_3H_6)_2[Zn(SO_3)_2]$, **2** at different temperatures.

**Table S1.** Crystal structure refinement parameters for **1–2**.

	1	2
Empirical formula	$(NH_3CH_2CH_2NH_3)[Zn_3(SO_3)_4]$	$(CN_3H_6)_2[Zn(SO_3)_2]$
Mr	578.47	345.67
crystal system	Monoclinic	Orthorhombic
space group	*C 2/c*	F*dd2*
a/Å	13.7379(4)	14.4211(13)
b/Å	8.3487(3)	12.1181(8)
c/Å	13.0277(4)	14.0692(8)
α/°	90	90
β/°	106.235(2)	90
γ/°	90	90
Volume/ Å^3	1434.61(8)	2458.7(3)
Z	4	8
Dx /Mg m^{-3}	2.678	1.868
μ/ mm^{-1}	5.623	2.365
θ range for data collection/ °	2.89 to 30.52	2.63 to 27.52
Reflections collected	13392	9404
unique reflections	2195	1109
R(int)	0.0331	0.1040
Data / restraints / parameters	2195 / 0 / 117	1109 / 1 / 79
$R1$ and $R2$ [$I>2\sigma(I)$]	0.0225, 0.0564	0.0380, 0.0669
$R1$ and $R2$ (all data)	0.0253, 0.0576	0.0531, 0.0723
Goodness-of-fit on F^2	1.095	1.029
Largest diff. peak and hole/e.Å^{-3}	0.457 and -0.764	0.307 and -0.347
CCDC no	**1424543**	**1424544**

Table S2. Complete list of bond lengths [Å] and bond angles [°] for complex **1-2**[#]

(NH$_3$CH$_2$CH$_2$NH$_3$)[Zn$_3$(SO$_3$)$_4$] (1)

Zn1–O1	1.9755(14)	Zn2–O6[c]	1.9644(15)	S2–O5	1.5227(14)
Zn2–O2	1.9486(14)	S1–O1	1.5275(14)	S2–O6	1.5308(15)
Zn1–O3[a]	1.9530(14)	S1–O2	1.5295(15)	C1–N1	1.485(2)
Zn1–O4	1.9596(14)	S1–O3	1.5330(15)	C1–C1[d]	1.515(4)
Zn1–O5[b]	2.0028(14)	S2–O4	1.5363(14)		
O1–Zn1–O3[a]	109.98(6)	O2–Zn2–O6[f]	108.23(7)	N1–C1–C1[d]	109.90(19)
O1–Zn1–O4	111.25(6)	O6[c]–Zn2–O6[f]	121.28(9)	S1–O1–Zn1	113.25(8)
O1–Zn1–O5[b]	101.50(6)	O1–S1–O2	103.57(9)	S1–O2–Zn2	126.29(9)
O3[a]–Zn1–O4	118.72(6)	O1–S1–O3	102.24(8)	S1–O3–Zn1[a]	127.20(9)
O3[a]–Zn1–O5[b]	93.39(6)	O2–S1–O3	102.68(9)	S2–O4–Zn1	131.64(8)
O4–Zn1–O5[b]	119.68(6)	O5–S2–O6	103.61(8)	S2–O5–Zn1[b]	118.00(8)
O2–Zn2–O2[e]	121.06(9)	O5–S2–O4	105.45(8)	S2–O6–Zn2[f]	120.59(8)
O2–Zn2–O6[c]	99.76(6)	O6–S2–O4	103.52(8)		

(CN$_3$H$_6$)$_2$[Zn(SO$_3$)$_2$] (2)

Zn1–O1	1.950(3)	S1–O2	1.478(4)	C1–N2	1.323(6)
Zn1–O3[g]	1.952(3)	S1–O3	1.523(3)	C1–N3	1.319(7)
S1–O1	1.553(3)	C1–N1	1.301(7)		
O1–Zn1–O1[h]	112.0(2)	O1–S1–O2	105.5(2)	S1–O3–Zn1[j]	123.8(2)
O1–Zn1–O3[g]	116.92(17)	O1–S1–O3	100.38(19)	N1–C1–N2	120.6(5)
O1–Zn1–O3[i]	108.31(15)	O2–S1–O3	106.0(3)	N1–C1–N3	120.4(5)
O3[g]–Zn1–O3[i]	93.4(2)	S1–O1–Zn1	120.09(19)	N2–C1–N3	119.0(5)

[#]Symmetry transformations used to generate equivalent atoms: (a) -x+1, -y+1, -z; (b) -x+1, y, -z+1/2; (c) x, -y+2, z-1/2; (d) -x+1/2, -y+1/2, -z; (e) -x+1, y, -z-1/2; (f) -x+1,-y+2,-z; (g) -x+1/4, y-1/4, z-1/4; (h) -x+1/2, -y-1/2, z; (i) x+1/4, -y-1/4, z-1/4; (j) -x+1/4, y+1/4, z+1/4

Table S3. Hydrogen bonding table for complexes **1-2**.[#]

D–H···A	Symmetry of A	D–H	H···A	D–A	∠D–H···A
(NH₃CH₂CH₂NH₃)[Zn₃(SO₃)₄] (1)					
N1–H1A···O1	1/2+x,-1/2+y,z	0.88(4)	2.43(4)	3.016(2)	125(3)
N1–H1A···O6	1/2-x,-1/2+y,1/2-z	0.88(4)	2.12(4)	2.884(2)	145(3)
N1–H1B···O5	-x,-y,-z	0.92(3)	2.04(3)	2.936(2)	164(2)
N1–H1C···O4	1/2-x,1/2-y,-z	0.90(3)	2.15(3)	2.981(2)	154(2)
C1–H1E···O4		0.97	2.59	3.337(3)	133
(CN₃H₆)₂[Zn(SO₃)₂] (2)					
N1–H1A···O3		0.86	2.13	2.984(7)	174
N1–H1B···O2	1/4+x,3/4-y,-1/4+z	0.86	2.20	2.987(7)	152
N2–H2A···O1	1/4+x,3/4-y,-1/4+z	0.86	2.27	3.114(6)	168
N2–H2B···O2	-x,1/2-y,-1/2+z	0.86	2.28	3.008(7)	143
N3–H3A···O1		0.86	2.07	2.928(6)	173
N3–H3B···O2	-x,1/2-y,-1/2+z	0.86	2.17	2.928(6)	147

[#]Where 'D' is donor and 'A' is acceptor, the bond lengths are in (Å) and angles are in (°).

Table S4. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å×10^3) for **1-2** U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

	X	y	Z	U(eq)		x	Y	Z	U(eq)
(NH$_3$CH$_2$CH$_2$NH$_3$)[Zn$_3$(SO$_3$)$_4$] (1)									
Zn1	4630(1)	6250(1)	950(1)	17(1)	O1	3799(1)	7168(2)	-411(1)	24(1)
Zn2	5000	9929(1)	-2500	19(1)	O2	4779(1)	8781(2)	-1283(1)	28(1)
S1	4320(1)	7108(1)	-1304(1)	17(1)	O3	5251(1)	6065(2)	-809(1)	24(1)
S2	6627(1)	7536(1)	2654(1)	16(1)	O4	5865(1)	7507(2)	1537(1)	21(1)
C1	2681(2)	1776(2)	352(2)	19(1)	O5	6393(1)	6052(2)	3221(1)	22(1)
N1	3089(1)	552(2)	-244(2)	22(1)	O6	6252(1)	8917(2)	3216(1)	25(1)
(CN$_3$H$_6$)$_2$[Zn(SO$_3$)$_2$] (2)									
Zn1	2500	-2500	10190(1)	21(1)	N3	4517(4)	1929(4)	12073(4)	57(2)
S1	1631(1)	-1337(1)	11886(1)	23(1)	C1	3837(4)	1202(5)	12066(4)	40(1)
O1	2214(2)	-1210(3)	10965(2)	28(1)	N2	3805(4)	460(4)	11377(4)	55(2)
O2	2239(3)	-956(4)	12665(3)	51(1)	N1	3199(4)	1227(4)	12720(4)	68(2)
O3	917(3)	-427(3)	11738(3)	47(1)					

Table S5. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for complex **1-2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12		U11	U22	U33	U23	U13	U12
(NH₃CH₂CH₂NH₃)[Zn₃(SO₃)₄] (1)													
Zn1	18(1)	14(1)	18(1)	0(1)	4(1)	0(1)	**O1**	21(1)	31(1)	20(1)	5(1)	8(1)	7(1)
Zn2	24(1)	15(1)	17(1)	0	3(1)	0	**O2**	43(1)	16(1)	26(1)	4(1)	12(1)	-1(1)
S1	21(1)	16(1)	14(1)	0(1)	3(1)	2(1)	**O3**	21(1)	16(1)	34(1)	-2(1)	4(1)	3(1)
S2	14(1)	18(1)	16(1)	0(1)	4(1)	-2(1)	**O4**	22(1)	26(1)	14(1)	-2(1)	2(1)	-7(1)
C1	21(1)	17(1)	19(1)	1(1)	5(1)	2(1)	**O5**	25(1)	17(1)	25(1)	5(1)	11(1)	3(1)
N1	23(1)	19(1)	23(1)	0(1)	5(1)	4(1)	**O6**	31(1)	20(1)	19(1)	-5(1)	0(1)	6(1)
(CN₃H₆)₂[Zn(SO₃)₂] (2)													
Zn1	21(1)	24(1)	18(1)	0	0	1(1)	**N3**	75(4)	53(4)	43(3)	-19(3)	19(3)	-29(3)
S1	25(1)	25(1)	20(1)	2(1)	4(1)	1(1)	**C1**	49(3)	40(3)	30(3)	-13(2)	9(2)	-13(3)
O1	34(2)	24(2)	27(2)	0(1)	16(1)	6(1)	**N2**	52(3)	60(4)	55(3)	-36(3)	23(2)	-22(3)
O2	48(2)	76(3)	31(2)	-3(2)	-9(2)	-1(2)	**N1**	80(4)	69(4)	54(3)	-30(3)	37(3)	-27(3)
O3	40(2)	64(3)	36(2)	23(2)	17(2)	33(2)							