Journal Name

ARTICLE

Supporting Information

Influence of organic and alkali metal cations over crystal lattice of benzenetrihydroxy trisulfonate ligand

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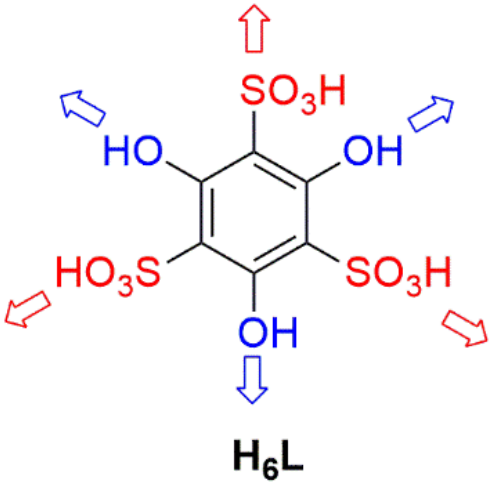

Fig. S1. Molecular structure of 2,4,6-trihydroxy-1,3,5-benzenetrisulfonic acid; $C_6H_6O_{12}S_3$ (H_6L) with various coordination sites.

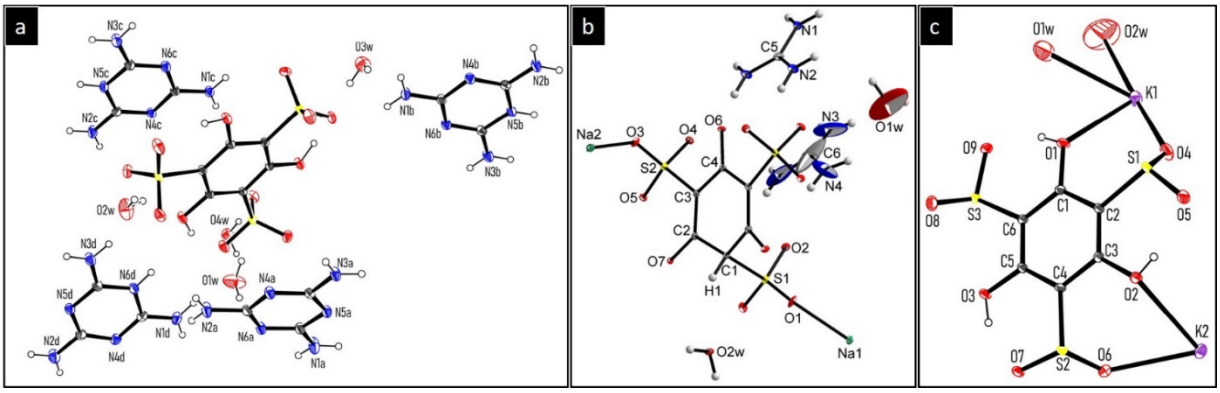

Fig. S2. Asymmetric unit of **1**, **2** and **3** as ORTEP representation drawn at 25 % ellipsoidal probability (selected atoms labeled, suffixes are used to define crystallographically unique melamine units in case of **1**; in case of 2, molecular structure is shown for clarity where unique atoms are labelled; in case of **3**, hydrogen atoms on water oxygen atoms were not located on fourier map).

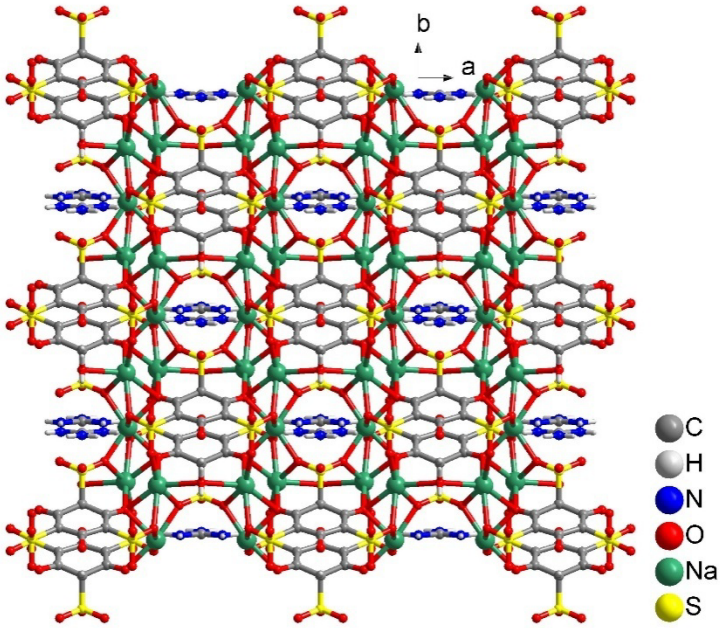

Fig. S3. 2D-layer structure in **2** with guanidium cations occupying the apparent cavity.

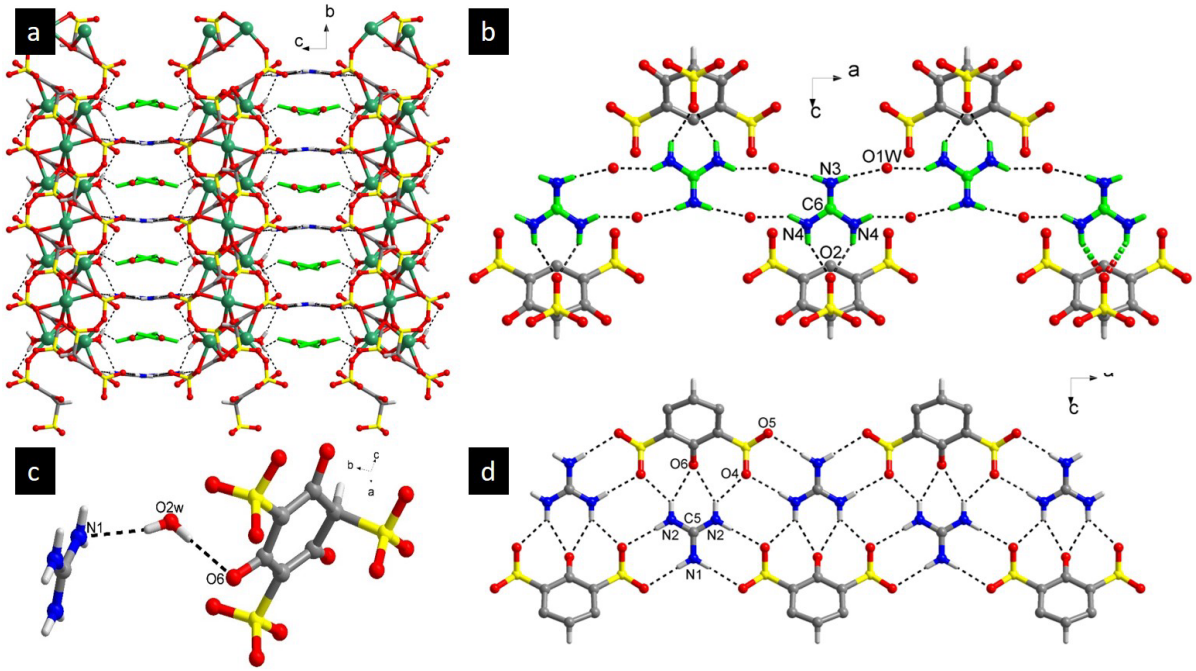

Fig. S4. (a) Interconnection of 2D-layers due to H-bonding interaction between $(HL)^{5-}$ anion and guanidinium cation; (b), (c) and (d) Various H-bonding pattern between $(HL)^{5-}$ anion, unique guanidinium cations, aqua ligand (O2w) and lattice water molecules. (Unique guanidinium cations are color coded).

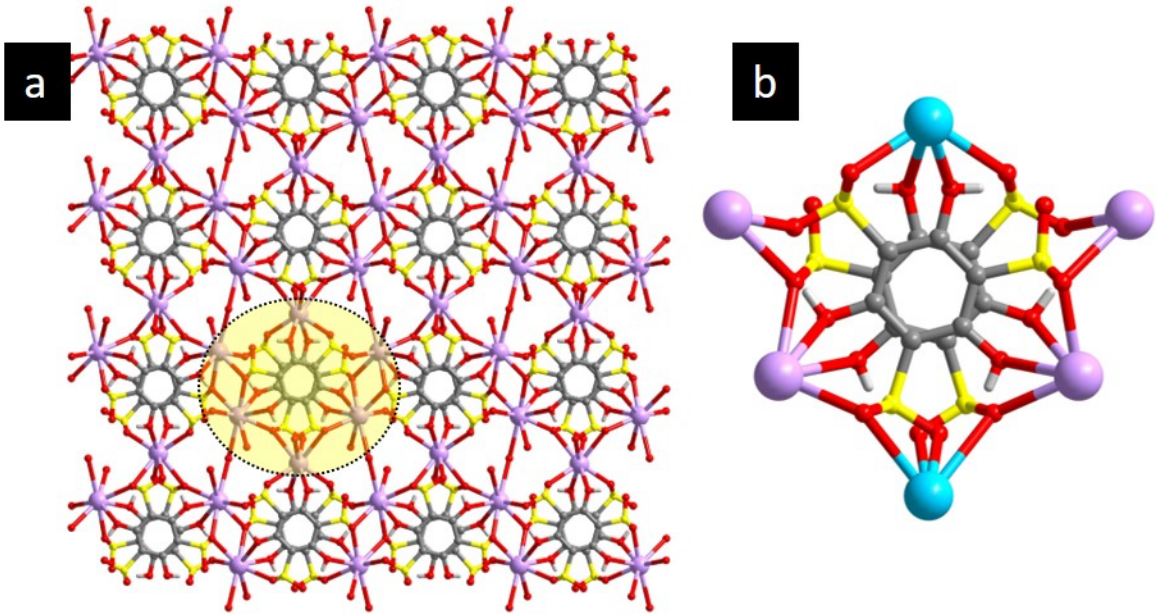

Fig. S5. (a) 3D crystal lattice of **3** as a result of K-O coordination as viewed along *a*-axis; (b) Structural unit present in the lattice with ligands stacked in ABAB fashion (color code: K1 ions: lavender and K2 ions: sky blue color).

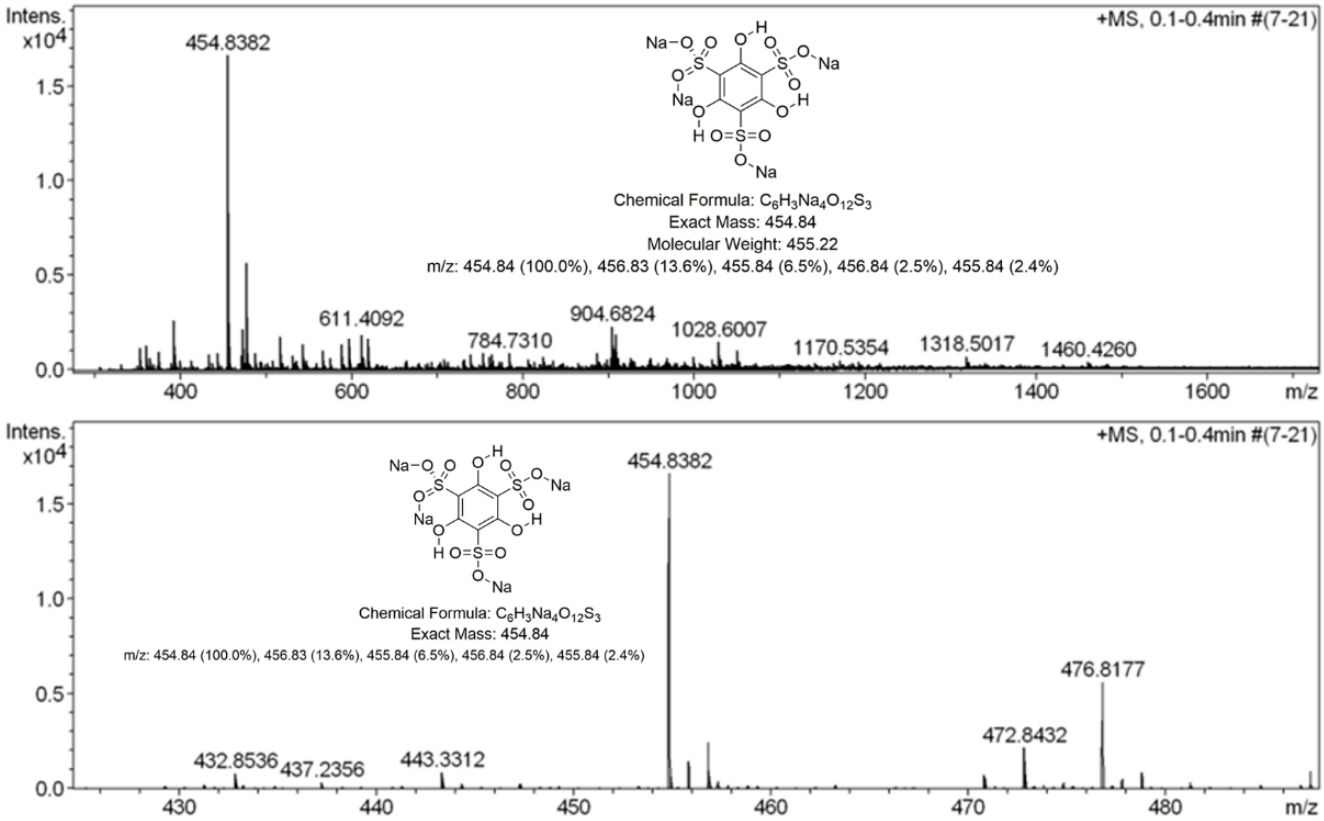

Fig. S6. HRMS data of synthesized sodium salt of 2,4,6-trihydroxy-1,3,5-benzenetrisulfonic acid ligand.

FTIR

FT-IR spectrum of **1**, the broad peak at 3548 cm^{-1} corresponds water molecules in the framework, aromatic O-H stretching of the ligand and N-H stretching of melamine. The bands corresponding to the aromatic ring are observed between 615-810 cm^{-1} and 1289-1615 cm^{-1}. Finally, bands corresponding to the fundamental and spilt S-O stretching modes are found in the region 1030-1270 cm^{-1}. FT-IR spectrum of **2**, the broad peak at 3548 cm^{-1} represents the framework's water molecules, the ligand's O-H stretching, and the guanidinium's N-H stretching. There is C-H extending between 2848-3000 cm^{-1} range. The ligand's C-H stretching vibration is represented by the band at 2848 and 2915 cm^{-1}. The 1000–1240 cm^{-1} region contains bands that correspond to the fundamental and split S-O stretching modes. FT-IR spectrum of **3**, the broad peak at 3510 cm^{-1} corresponds to the presence of water molecules in the framework and aromatic O-H stretching of the ligand. The bands corresponding to the aromatic ring are observed between 590-780 cm^{-1} and 1300-1630 cm^{-1}. The bands corresponding to the fundamental and spilt S-O stretching modes are found in the region 990-1215 cm^{-1} (Fig. S7).

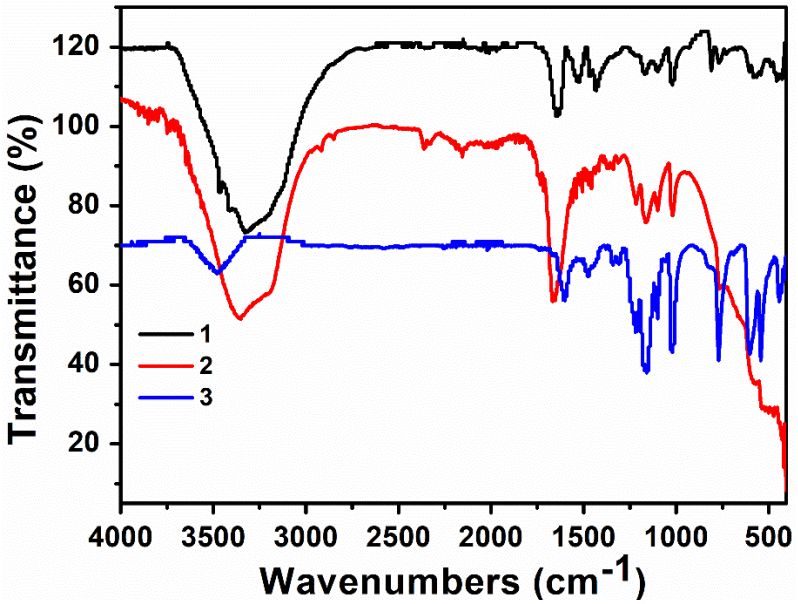

Fig. S7. FTIR spectra of **1-3**.

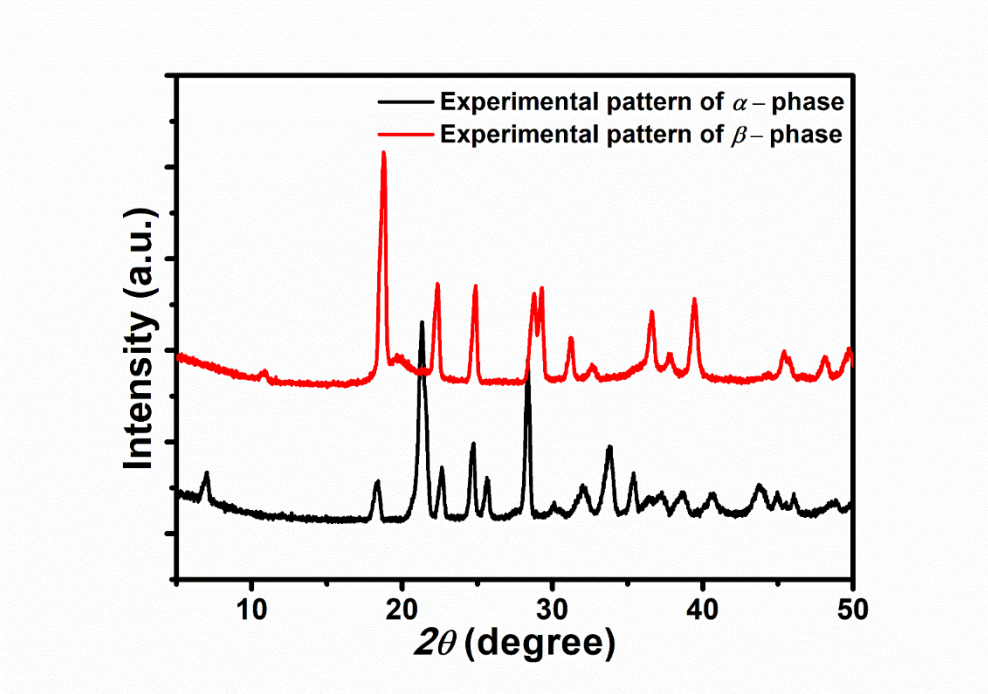

Fig. S8. PXRD patterns for α-phase and β-phase of $Na_3(H_3L)$ salt.

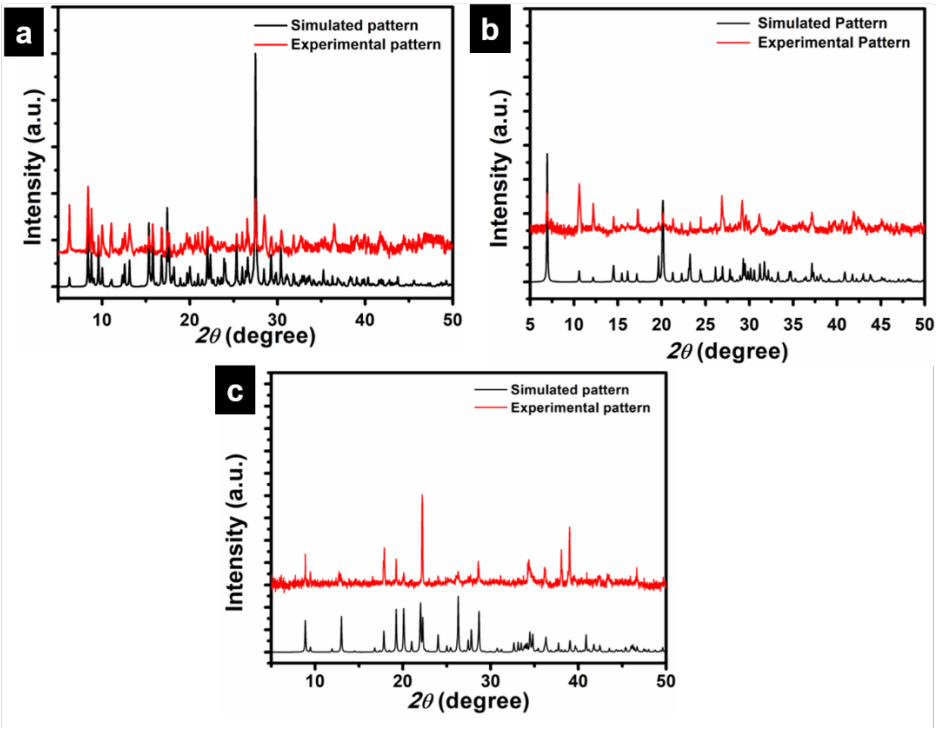

Fig. S9. PXRD patterns for (a) $[(C_3N_6H_7)_3(C_6H_3O_{12}S_3).(C_3N_6H_6).4(H_2O)]$, **1**, (b) $[(CN_3H_6)_2[Na_3(C_6HO_{12}S_3)\ (H_2O)].2(H_2O)]$, **2** and (c) $[K_3(C_6H_3O_{12}S_3)(H_2O)_2]$, **3**.

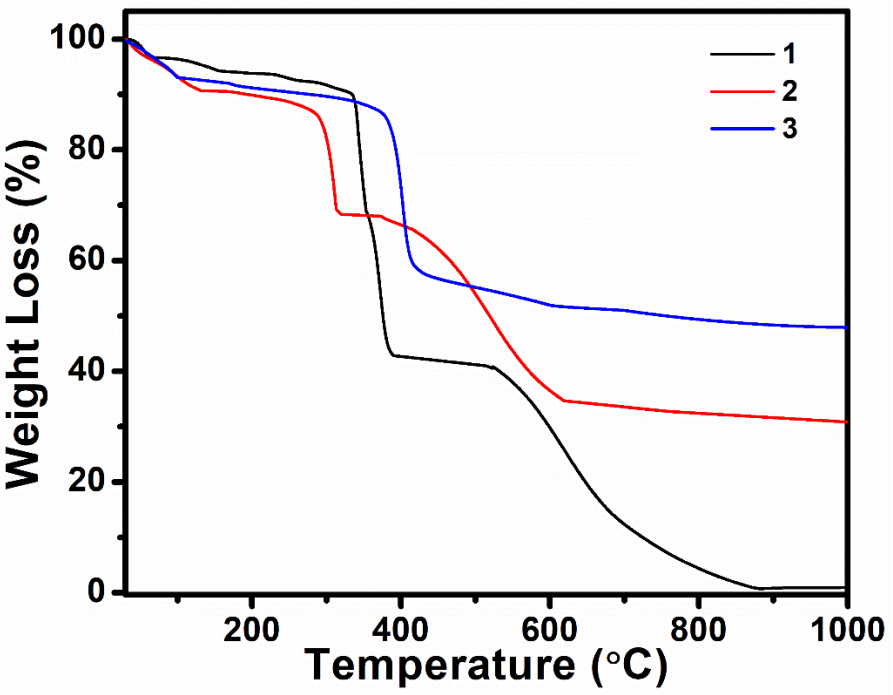

Fig. S10. TGA profile for **1-3**.

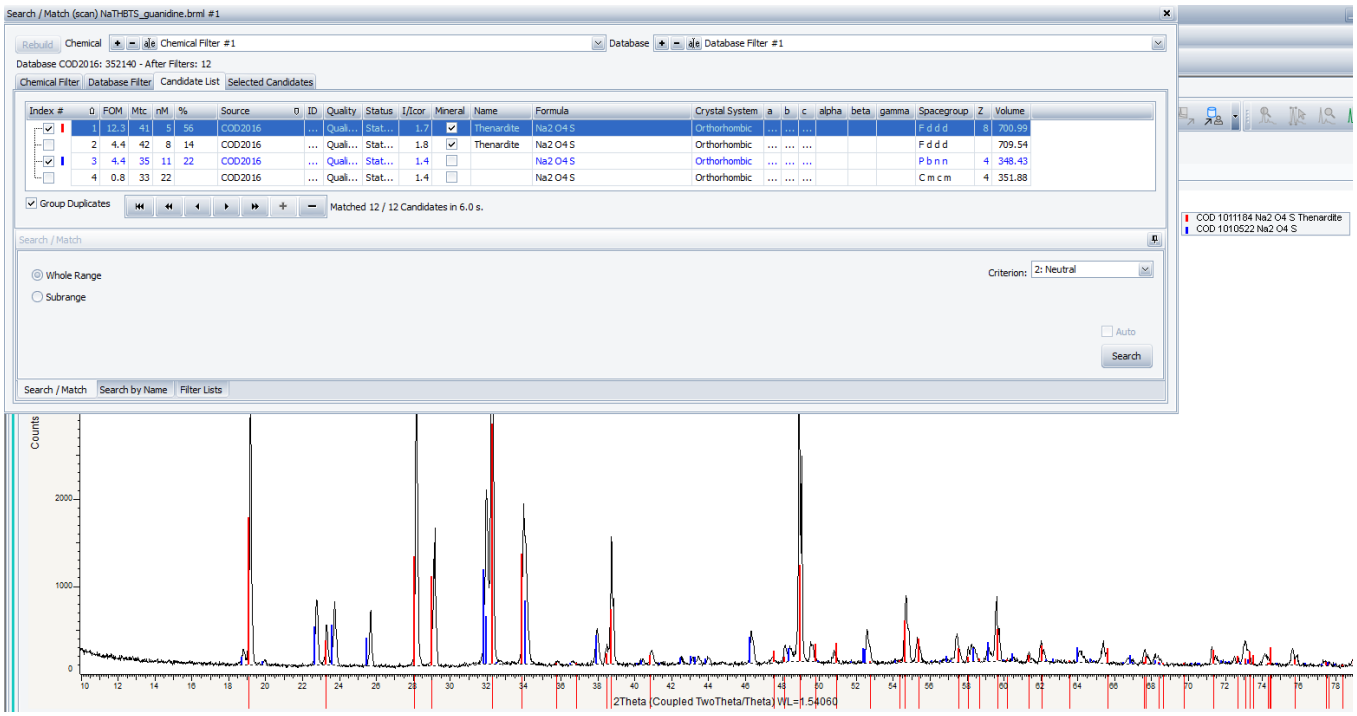

Fig. S11. Post calcination PXRD analysis of **2** showing formation of Na_2SO_4 thenardite (COD-1011184) and Na_2SO_4 (COD-1010522).

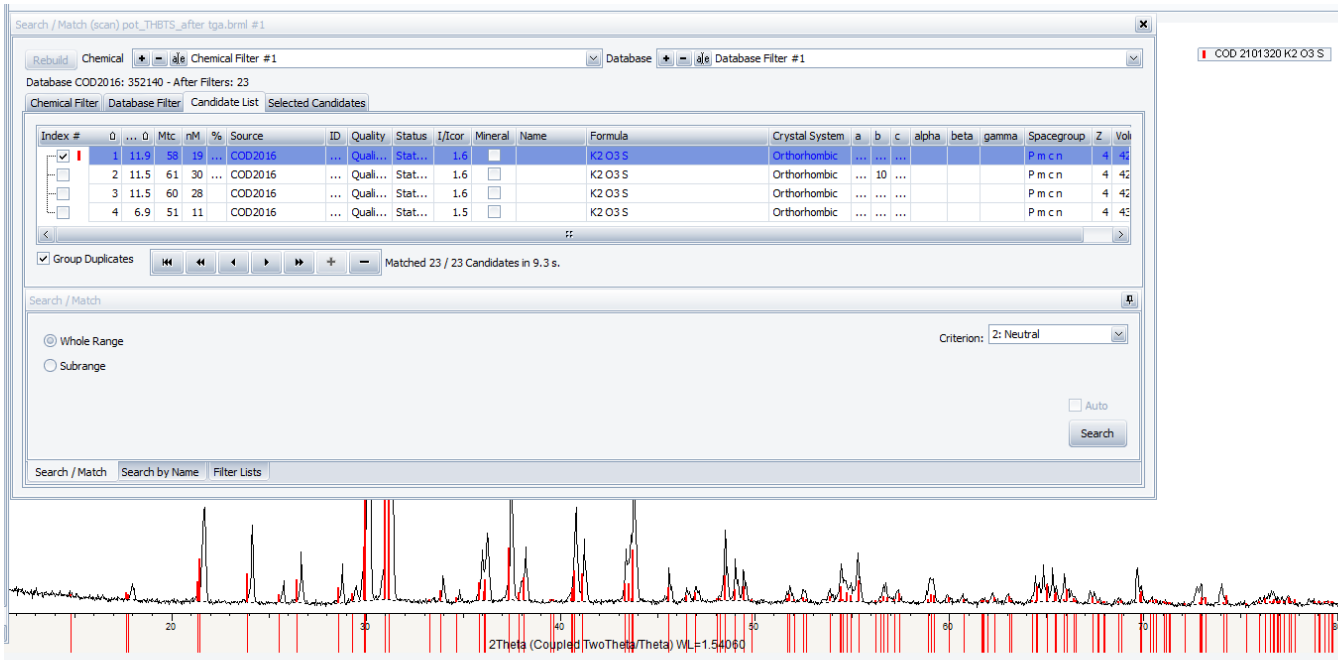

Fig. S12. Post calcination PXRD analysis of **3** showing formation of K_2SO_3 (COD-2101320).

Impedance analysis of 3

An impedance measurement was carried out on a pristine crystalline powder sample of **3**. The pristine crystalline powder sample of 3 was first ground into a uniform powder using a mortar and pestle to construct the pellet. After that, the powders were put into a regular 13 mm die, positioned between two anvils, and compressed for five minutes at 700 kg/cm^2. The diameter of the pellet was 13 mm. After that, both sides of the pellet were made contact to copper wires with conducting silver paste. The proton conductivity of the pellet was then tested by a four-probe electrochemical cell, and an applied AC voltage. The impedance experiment was performed by using a OrigaLys Potentiostat Galvanostat (Model OGF+01A EIS) electrochemical workstation operating at 1 Hz to 1 MHz and alternating potentials of 0.1 V at 298 K. The bulk proton conductivity σ in S cm^{-1} was calculated by using equation:

$$\sigma = \frac{L}{RA}$$

Where L is the thickness of pellet in cm, R is the impedance in Ω and A is the facial area of the pellet in cm^2.

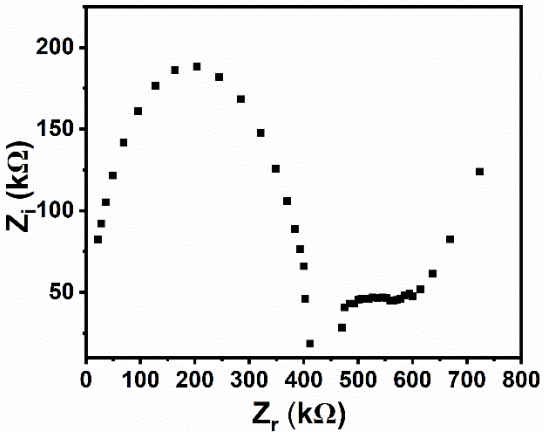

Fig. S13. Nyquist plot for **3** at room temperature.

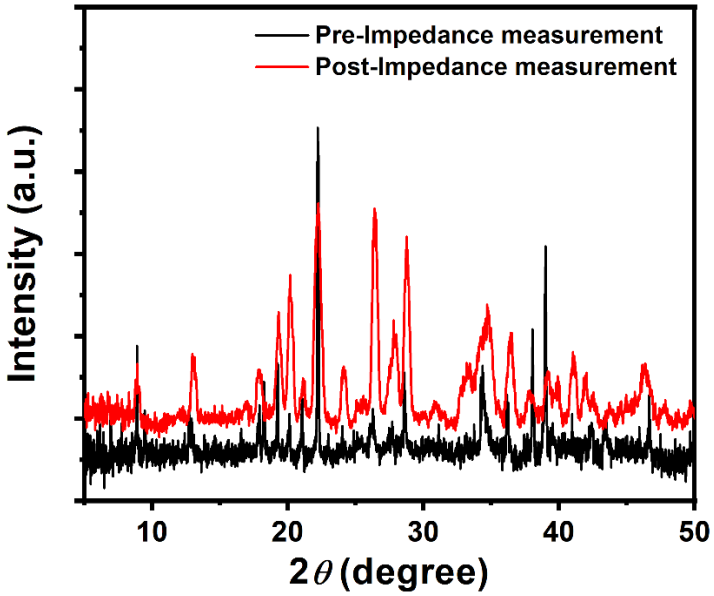

Fig. S14. PXRD pattern Pre- and Post-Impedance measurement.

EuroEA Elemental Analyser

AutoRun name	:	Calibration-27022025 (102)
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Time of Analysis	:	14:19:46
Analysed By	:	EVR
Signed By	:	EVR
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	TRISMELA
Sample position #	:	32
Type	:	Smp
Sample weight	:	1.147 (mg)
Calibration type	:	Linear

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (ºC)	Rear (ºC)	Oven (ºC)
120	80	15	35	6	360	980	Off	100

Chromatogram

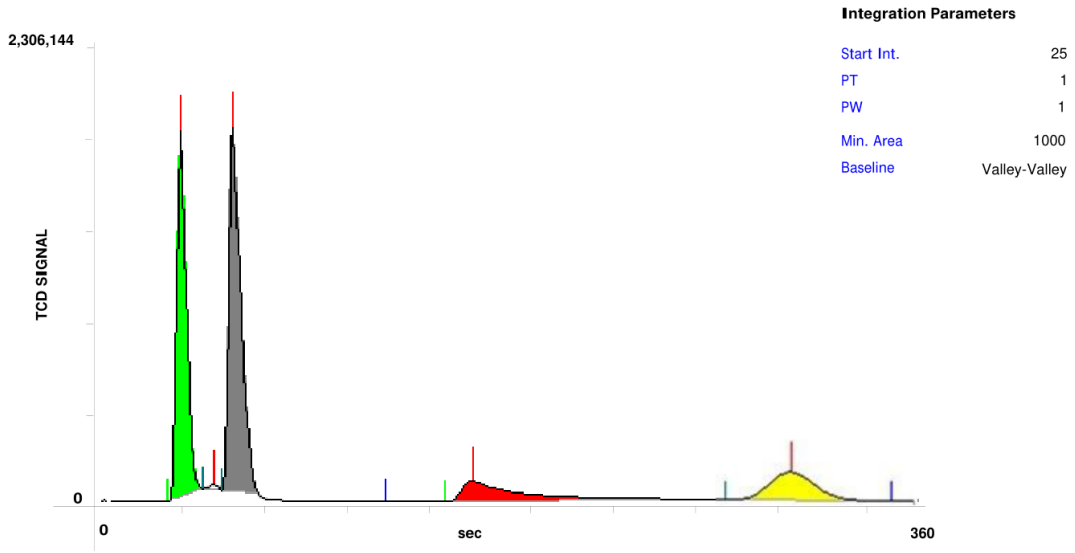

Fig. S15. C, H, N, S elemental analysis profile graph of **1**. Color code green for nitrogen atom, grey for carbon atom, red for hydrogen atom yellow for sulfur atom.

EuroEA Elemental Analyser

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Date of Analysis	:	27 Feb 2025
Time of Analysis	:	14:19:46
Analysed By	:	EVR
Signed By	:	EVR
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	NaTRISGUN
Sample position #	:	30
Type	:	Smp
Sample weight	:	0.564 (mg)
Calibration type	:	Linear

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (ºC)	Rear (ºC)	Oven (ºC)
120	80	15	35	6	360	980	Off	100

Chromatogram

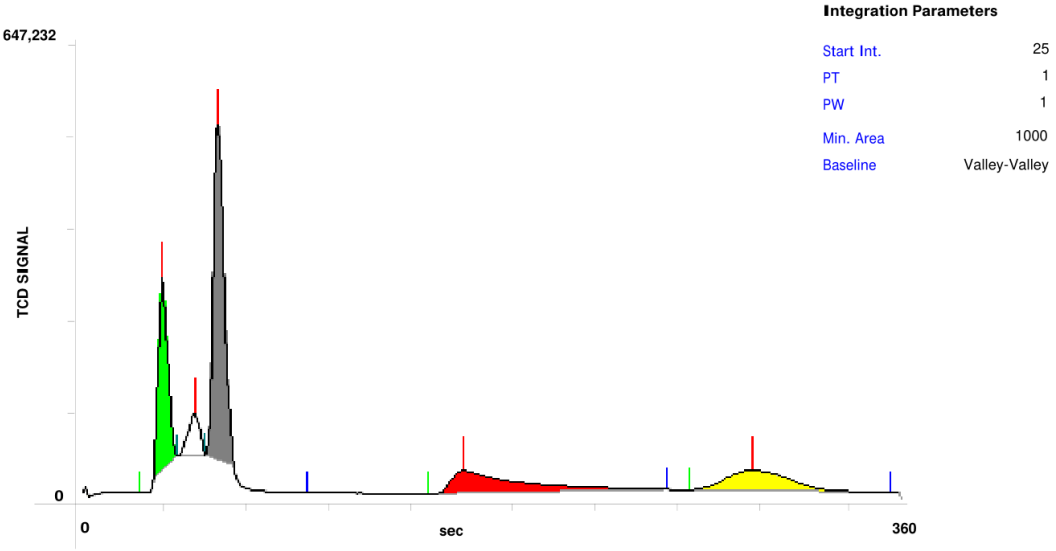

Fig. S16. C, H, N, S elemental analysis profile graph of **2**. Color code green for nitrogen atom, grey for carbon atom, red for hydrogen atom yellow for sulfur atom.

EuroEA Elemental Analyser

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Time of Analysis	:	14:19:46
Analysed By	:	EVR
Signed By	:	EVR
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	KTRIS
Sample position #	:	31
Type	:	Smp
Sample weight	:	0.594 (mg)
Calibration type	:	Linear

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (ºC)	Rear (ºC)	Oven (ºC)
120	80	15	35	6	360	980	Off	100

Chromatogram

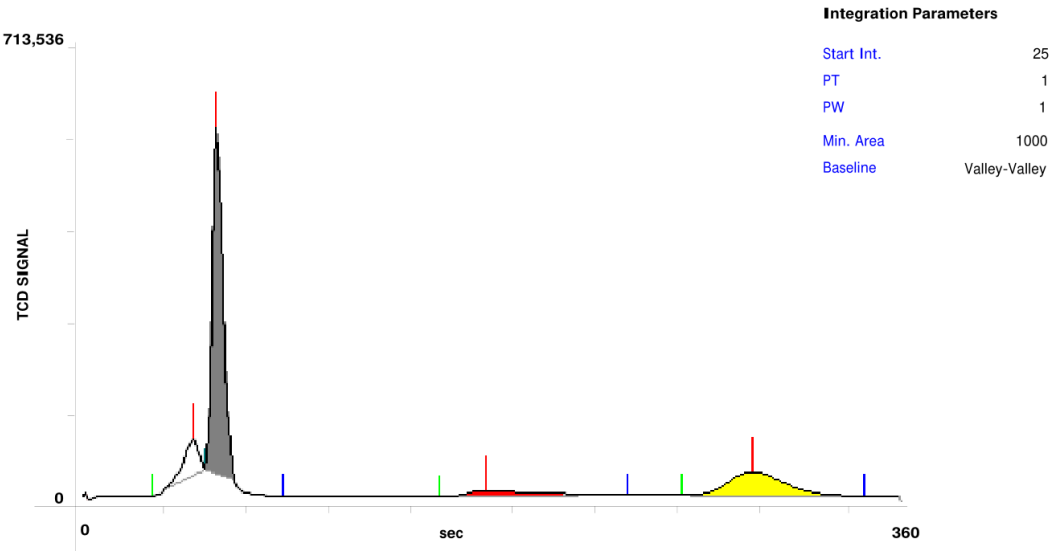

Fig. S17. C, H, S elemental analysis profile graph of **3**. Color code green for grey for carbon atom, red for hydrogen atom yellow for sulfur atom.

Table S1: Selected bond length (in Å) tables for **1-3**.

$(C_3N_6H_7)_3(C_6H_3O_9S_3)$. $(C_3N_6H_6).4(H_2O)$, **1**					
C1-C2	1.403(3)	C2-C3	1.400(3)	C3-C4	1.392(3)
C4-C5	1.407(3)	C5-C6	1.398(3)	C1-C6	1.408(3)
C1-S1	1.768(2)	C3-S2	1.770(2)	C5-S3	1.764(2)
O1-S1	1.4526(18)	O4-S2	1.4683(17)	O7-S3	1.4518(17)
O2-S1	1.4398(18)	O5-S2	1.4390(18)	O8-S3	1.4522(18)
O3-S1	1.4622(18)	O6-S2	1.4382(18)	O9-S3	1.4559(18)
C2-O10	1.337(3)	C4-O11	1.353(3)	C6-O12	1.344(3)
$(CN_3H_6)_2[Na_3(C_6HO_{12}S_3)$ $(H_2O)].2(H_2O)$, **2**					
C(1)-C(2)	1.513(3)	C(2)-C(3)	1.396(4)	C(3)-C(4)	1.453(3)
C(1)-S(1)	1.826(4)	C(3)-S(2)	1.755(3)	C(2)-O(7)	1.263(3)
C(4)-O(6)	1.263(5)	O(1)-S(1)	1.449(2)	O(2)-S(1)	1.442(3)
O(3)-S(2)	1.463(2)	O(4)-S(2)	1.461(2)	O(5)-S(2)	1.461(2)
Na1-O1	2.256(2)	Na1-O5[1]	2.436(2)	Na1-O7[2]	2.346(2)
Na2-O1[3]	2.370(3)	Na2-O3	2.337(2)	Na2-O5[4]	2.518(2)
Na2-O7[5]	2.401(2)	Na2-O7[4]	2.441(2)	Na2-O2w[3]	2.5745(18)
$K_3(C_6H_3O_{12}S_3)(H_2O)_2$, **3**					
C1-C2	1.409(4)	C2-C3	1.390(4)	C3-C4	1.401(4)
C4-C5	1.403(4)	C6-C5	1.402(4)	C6-C1	1.399(5)
C2-S1	1.773(3)	C4-S2	1.774(3)	C6-S3	1.776(3)
C1-O1	1.343(4)	C3-O2	1.353(4)	C5-O3	1.352(4)
O4-S1	1.435(2)	O5-S1	1.470(3)	O6-S2	1.440(2)
O7-S2	1.460(2)	O8-S3	1.4421(19)	O9-S3	1.472(2)
K1-O1	2.9972(18)	K1-O3[6]	3.0455(16)	K1-O4	2.690(2)
K1-O4[7]	2.7559(19)	K1-O7[8]	2.7667(16)	K1-O8[9]	2.6995(19)
K1-O1w	3.002(3)	K1-O2w	3.004(4)	K2-O2	2.9017(15)
K2-O6	2.689(2)	K2-O(8)[10]	2.964(2)	K2-O9[11]	2.7659(14)

Symmetry of atoms: (1). x+1/2,-y+1/2,-z+2; (2). x-1/2,y+1/2,z; (3). -x+1,-y+1,-z+2; (4) -x+1/2,y+1/2,z; (5) x,-y+1,-z+2; (6) x-1/2,y,-z+3/2;

(7) -x-1/2,-y+1/2,-z+1; (8) -x,-y+1/2,z-1/2; (9) x-1/2,y,-z+3/2; (10) x-1/2,y-1/2,z; (11) x+1/2,y+1/2,z

Table S2: Hydrogen bonding distances [Å] and bond angles [°] for **1-3**.

D—H···A	Symmetry of A	D—H	H···A	D···A	∠D—H···A
$(C_3N_6H_7)_3(C_6H_3O_9S_3).(C_3N_6H_6).4(H_2O)$, **1**					
N1A—H1A1···O1	1/2-x,1/2+y,1/2-z	0.86	2.16	2.994(3)	162
N1A—H1A2···O2w	-x,1-y,-z	0.86	2.23	3.000(4)	150
N2A—H2A1···O7	1/2-x,-1/2+y,1/2-z	0.86	2.23	3.037(3)	157
N2A—H2A2···O6	1/2-x,1/2+y,1/2-z	0.86	2.44	3.167(3)	143
N2A—H2A2···O10	1/2-x,1/2+y,1/2-z	0.86	2.53	3.218(3)	137
N3A—H3A1···O2	1/2-x,-1/2+y,1/2-z	0.86	2.41	3.064(3)	133
N3A—H3A1···O12	1/2-x,-1/2+y,1/2-z	0.86	2.34	3.087(3)	145
N3A—H3A2···N5D	-x,-y,-z	0.86	2.17	3.024(3)	172
N1B—H1B1···O3w	1-x,1-y,1-z	0.86	2.17	2.922(3)	145
N1B—H1B2···O4	1/2+x,1/2-y,1/2+z	0.86	2.16	2.973(3)	158
N2B—H2B1···N6C	x,1+y,z	0.86	2.12	2.981(3)	174
N2B—H2B2···O5	x,1+y,z	0.86	2.10	2.815(3)	140
N3B—H3B1···N4C		0.86	2.20	3.055(3)	177
N3B—H3B2···O8		0.86	2.31	3.126(3)	159
N3B—H3B2···O8	1-x,1-y,-z	0.86	2.58	3.073(3)	118
N5B—H5B···O4w	1/2-x,1/2+y,1/2-z	0.86	2.06	2.901(3)	167
N1C—H1C1···O4w	1/2+x,1/2-y,-1/2+z	0.86	2.22	3.008(3)	152
N1C—H1C2···O5	1-x,-y,-z	0.86	2.55	3.075(3)	121
N2C—H2C1···N6B		0.86	2.10	2.960(3)	179
N2C—H2C2···O4	1/2+x,1/2-y,1/2+z	0.86	2.42	3.018(3)	127
N2C—H2C2···O11	1/2+x,1/2-y,1/2+z	0.86	2.45	3.159(3)	140
N5C—H5C···O9	1/2+x,1/2-y,1/2+z	0.86	2.18	2.939(3)	147
N5C—H5C···O11	1/2+x,1/2-y,1/2+z	0.86	2.54	3.247(3)	140
N3C—H3C1···N4B	x,-1+y,z	0.86	2.23	3.084(3)	174
N3C—H3C2···O9	1/2+x,1/2-y,1/2+z	0.86	2.16	2.935(3)	150
N6D—H6D···O3	1/2-x,-1/2+y,1/2-z	0.86	2.36	3.079(3)	141
N1D—H1D1···O3		0.86	2.21	2.967(3)	147
N1D—H1D2···O1w	1/2-x,-1/2+y,1/2-z	0.86	1.99	2.812(4)	159
N2D—H2D1···O2	1/2+x,1/2-y,-1/2+z	0.86	2.31	3.141(3)	162
N3D—H3D1···N5A	-x,-y,-z	0.86	1.99	2.845(3)	173
N3D—H3D2···O3	1/2-x,-1/2+y,1/2-z	0.86	2.02	2.823(3)	156
O10—H10···O1		0.86(3)	1.77(3)	2.582(2)	157(2)
O10—H10···N6A	1/2-x,-1/2+y,1/2-z	0.86(3)	2.60(3)	2.971(3)	107.2(19)
O11—H11···O4		0.95(4)	1.67(4)	2.526(2)	148(3)
O12—H12···O7		0.90(4)	1.76(4)	2.588(2)	153(3)
O12—H12···N4A	1/2-x,1/2+y,1/2-z	0.90(4)	2.58(4)	3.018(3)	111(3)
O1w—H1w1···N4D		0.81(3)	2.23(3)	2.937(3)	146(3)
O1w—H1w2···N6A		0.79(4)	2.13(4)	2.895(4)	163(5)
O2w—H2w1···O1	1/2-x,1/2+y,1/2-z	0.83(4)	2.55(6)	3.273(4)	145(5)
O2w—H2w1···O3	1/2-x,1/2+y,1/2-z	0.83(4)	2.34(5)	3.012(3)	139(4)
O2w—H2w2···O9		0.83(4)	2.39(6)	3.032(3)	165(5)
O3w—H3w2···O2w	1/2-x,-1/2+y,1/2-z	0.81(4)	2.08(4)	2.891(4)	175(4)
O3w—H3w1···O6	1/2-x,1/2+y,1/2-z	0.83(2)	1.99(3)	2.798(3)	166(5)
O4w—H4w1···O8	1/2-x,-1/2+y,1/2-z	0.83(3)	2.08(3)	2.864(3)	157(5)
O4w—H4w2···O3w		0.85(4)	2.11(4)	2.945(4)	166(5)

$(CN_3H_6)_2[Na_3(C_6HO_{12}S_3)(H_2O)].2(H_2O)$, 2					
N1—H1A···O5		0.86	2.14	3.002(3)	178
N2—H2A···O4	1/2-x,y,1/2-z	0.86	2.19	2.843(3)	132
N2—H2A···O6	1/2-x,y,1/2-z	0.86	2.38	3.141(4)	148
N2—H2B···O4		0.86	2.08	2.938(3)	177
N3—H3A···O1w	1/2-x,y,1/2-z	0.80	1.94	2.71(3)	160
N4—H4A···O1w		0.86	1.96	2.74(3)	150
N4—H4A···O1w	1/2-x,y,1/2-z	0.86	2.31	2.985(18)	135
N4—H4B···O2		0.86	2.17	2.821(9)	133
O1w—H1w2···O3	1/2-x,1/2+y,z	0.85	1.92	2.695(10)	151
O1w—H1w1···O4		0.90	2.53	3.081(12)	120
O2w—H2w1···N1	-1/2+x,1/2-y,-z	0.83(6)	2.20(6)	3.005(5)	165(5)
O2w—H2w2···O6	x,-y,-z	0.83(7)	2.13(7)	2.960(5)	179(8)
C1—H1···O2W		0.98	2.44	3.290(5)	145
$K_3(C_6H_3O_{12}S_3)(H_2O)_2$, 3					
O1—H1···O9	---	0.76	1.83	2.540(3)	156
O2—H2···O5	---	0.75	1.81	2.531(4)	163
O3—H3···O7	---	0.85	1.77	2.561(3)	155

[b]Where D is donor and A is acceptor