ESI (Electronic Supplementary Information)

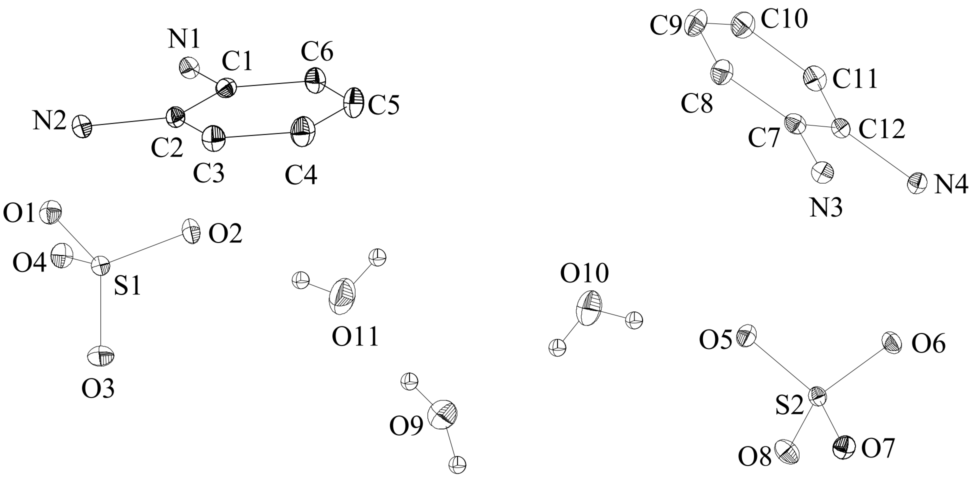
Title of the manuscript: **Sulphate anion helices formed by the assistance of a flip-flop water chain**

Authors: Pallepogu Raghavaiah, Sabbani Supriya and Samar K. Das*

A. **Crystallography.** Crystal data for compound $[C_6H_{10}N_2]\ SO_4 \cdot 1.5\ H_2O$ (**1**) were measured at 100(2) K on a Bruker SMART APEX CCD area detector system [λ(Mo-Kα) = 0.71073 Å], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 15 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction by SAINTPLUS (Software for the CCD Detector System, Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998), structure solution using SHELXS-97 (G. M. Sheldrick, Program for structure solution, University of Göttingen, Germany 1997) and refined using SHELXL-97 (G. M. Sheldrick, Program for crystal structure analysis, University of Göttingen, Germany 1997). All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms. The hydrogen atoms of protonated ammonium molecule and water molecules were located in the difference Fourier maps and their positions were refined isotropically.

ESI-Table 1. Crystal data and structure refinement parameters for compound **1**

Formula	$C_{12}H_{26}N_4O_{11}S_2$
Formula weight	466.49
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	26.946(2)
b/Å	9.5581(9)
c/Å	7.5203(7)
β/°	93.2080(10)
Z	4
V/Å^{-3}	1933.8(3)
D_c/g cm^{-3}	1.602
μ/mm^{-1}	0.342
F(000)	984
Total reflections	21667
Unique (R_{int})	4646 (0.0365)
Final R [I>2sigma(I)]^a	R_1 = 0.0382, wR_2 = 0.1009
R [all data]^b	R_1 = 0.0394, wR_2 = 0.1016
Largest diff. Peak and hole eÅ^{-3}	0.409 and –0.686 eÅ^{-3}



ESI-Fig. 1 Thermal ellipsoidal plot of $[C_6H_{10}N_2]$ $SO_4 \cdot 1.5$ H_2O (**1**) with atom labeling showing 50% thermal ellipsoids. The asymmetric unit contains two crystallographically independent orthophenylene diammonium sulphate compounds and three solvent water molecules. Water hydrogen's are shown and aromatic hydrogen's are not shown for clarity.

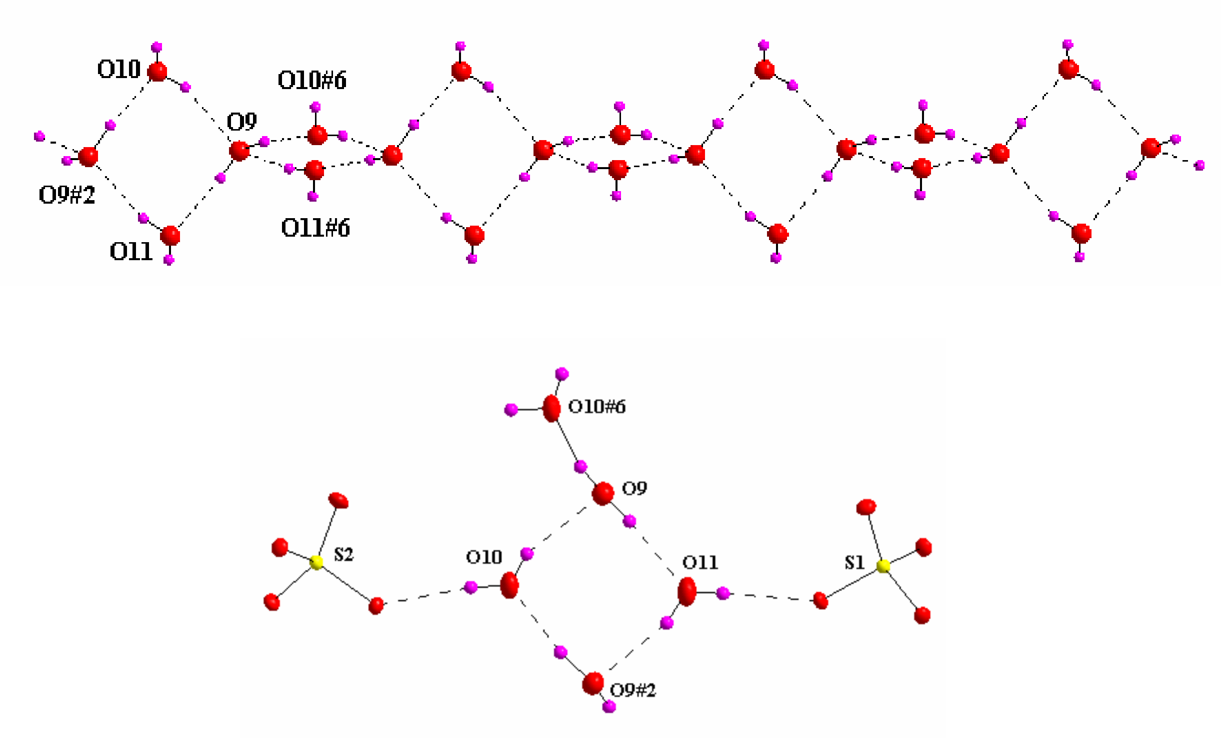
The relevant bond distances and angles are presented in ESI-Table 2.

ESI-Table 2. Bond lengths [Å] and angles [deg] for compound **1**

S(1)-O(3)	1.4598(12)	S(1)-O(4)	1.4736(11)
S(1)-O(1)	1.4876(11)	S(1)-O(2)	1.4989(11)
S(2)-O(8)	1.4597(11)	S(2)-O(7)	1.4742(11)
S(2)-O(6)	1.4866(11)	S(2)-O(5)	1.5037(11)
N(1)-C(1)	1.4548(19)	N(2)-C(2)	1.4626(19)
N(3)-C(7)	1.4591(19)	N(4)-C(12)	1.4633(19)
C(1)-C(2)	1.389(2)	C(1)-C(6)	1.390(2)
C(2)-C(3)	1.387(2)	C(3)-C(4)	1.392(2)
C(4)-C(5)	1.388(2)	C(5)-C(6)	1.392(2)
C(7)-C(8)	1.388(2)	C(7)-C(12)	1.389(2)
C(8)-C(9)	1.387(2)	C(9)-C(10)	1.391(2)
C(10)-C(11)	1.389(2)	C(11)-C(12)	1.389(2)

O(3)-S(1)-O(4)	111.29(7)	O(3)-S(1)-O(1)	110.29(7)
O(4)-S(1)-O(1)	108.70(7)	O(3)-S(1)-O(2)	110.35(7)
O(4)-S(1)-O(2)	108.23(7)	O(1)-S(1)-O(2)	107.87(6)
O(8)-S(2)-O(7)	111.49(7)	O(8)-S(2)-O(6)	10.50(7)
O(7)-S(2)-O(6)	109.17(7)	O(8)-S(2)-O(5)	109.86(7)
O(7)-S(2)-O(5)	108.11(7)	O(6)-S(2)-O(5)	107.60(7)
C(2)-C(1)-C(6)	119.84(14)	C(2)-C(1)-N(1)	121.98(13)
C(6)-C(1)-N(1)	118.13(14)	C(3)-C(2)-C(1)	120.32(14)
C(3)-C(2)-N(2)	119.00(14)	C(1)-C(2)-N(2)	120.67(13)
C(2)-C(3)-C(4)	119.78(15)	C(5)-C(4)-C(3)	120.13(15)
C(4)-C(5)-C(6)	119.94(15)	C(1)-C(6)-C(5)	119.99(15)
C(8)-C(7)-C(12)	120.24(14)	C(8)-C(7)-N(3)	118.32(14)
C(12)-C(7)-N(3)	121.45(14)	C(9)-C(8)-C(7)	119.89(15)
C(8)-C(9)-C(10)	119.92(15)	C(11)-C(10)-C(9)	120.16(15)
C(10)-C(11)-C(12)	119.82(15)	C(11)-C(12)-C(7)	119.91(14)
C(11)-C(12)-N(4)	119.09(14)	C(7)-C(12)-N(4)	120.99(14)

B. Hydrogen bonding parameters for the water cluster.



ESI-Fig. 2 Top: Intermolecular hydrogen bonding interactions among solvent water molecules that lead to extended water structure. Bottom: The water chain is additionally hydrogen bonded to sulphate anion oxygen atoms. Colour code: S, yellow; O, red; H, purple. #2: x, 1.5-y, 0.5+z.; #6: x, 1.5-y, -0.5+z

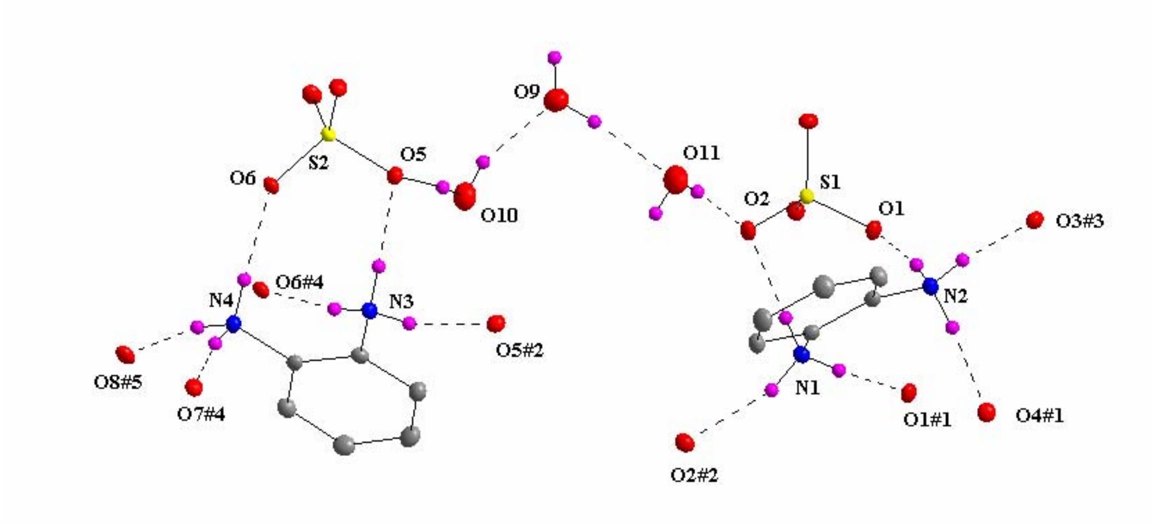
All three solvent water molecules interact among themselves and form an extended water structure, which is flip-flop in nature. This can be described as a water chain of corner-shared water tetramer. The corner-shared water oxygen has coordination number of four (donte two protons and accept two protons), where as, each of other two water oxygens donate two protons (one to water oxygen and second one to sulphate oxygen) and accept one proton from a water oxygen, thereby making coordination number of three. The hydrogen bonding parameters within the water chain are presented in ESI-Table 3 (see also ESI-Fig. 2).

ESI-Table 3. Hydrogen bonding parameters for the water chain

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O10–H10A···O9	0.79(5)	2.06(5)	2.811(2)	159(4)
O9–H9B···O11	0.84(5)	1.93(5)	2.764(2)	174(5)
O11–H11B···O9#2	0.81(4)	2.04(4)	2.824(2)	164(4)
O9–H9A···O10#6	0.95(6)	1.82(6)	2.755(2)	170(5)

#2: x, 1.5-y, 0.5+z.; #6: x, 1.5-y, -0.5+z

C. Hydrogen bonding situation among $–NH_3^+$ groups, $SO_4^{2–}$ anions and H_2O.



ESI-Fig. 3 Hydrogen bonding interactions that involve $–NH_3^+$ groups, $SO_4^{2–}$ anions and H_2O molecules in **1**. Colour code: C, gray; O, red; N, blue; H, purple. #1: 1-x, 2-y, 1-z; #2: x, 1.5-y, 0.5+z; #3: x, 2.5-y, 0.5+z; #4: -x, 1-y, 1-z; #5: x, 0.5-y, 0.5+z.

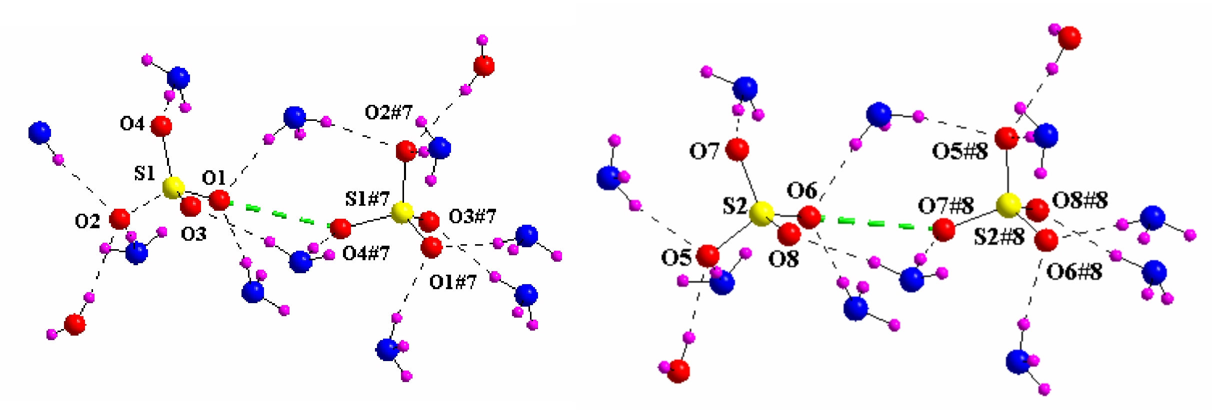
Interestingly, all hydrogen atoms on $–NH_3^+$ groups participate in hydrogen bonding interactions exclusively with sulphate oxygen atoms. Each sulphate anion is hydrogen bonded to one solvent water molecule. The relevant hydrogen bonding parameters are described in ESI-Table 4.

ESI-Table 4. Hydrogen bonding parameters for the H-bonds that involve $-NH_3^+$ groups, SO_4^{2-} anions and H_2O in **1** (see ESI-Fig. 3)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O11–H11A··· O2	0.75(3)	2.11(3)	2.857(19)	174(3)
O10–H10B···O5	0.80(3)	2.03(3)	2.831(18)	172(3)
N2–H2C···O1	0.90(2)	1.91(2)	2.7953(18)	171(2)
N3–H3B···O5	0.91(3)	1.90(3)	2.8059(18)	176(2)
N4–H4A···O6	0.88(3)	1.97(3)	2.8394(18)	171(2)
N1–H1C···O2	0.89(2)	2.03(2)	2.8709(18)	156(2)
N1–H1B···O1#1	0.88(3)	1.94(3)	2.8001(18)	165(2)
N2–H2A···O4 #1	0.93(3)	1.81(3)	2.7449(18)	174(2)
N1–H1A···O2#2	0.90(3)	1.92(3)	2.8113(18)	167(2)
N3–H3A···O5#2	0.91(2)	1.98(2)	2.8680(18)	164(2)
N2–H2B···O3 #3	0.88(3)	2.02(3)	2.8809(19)	165(2)
N3–H3C···O6#4	0.89(3)	1.95(3)	2.8344(18)	171(2)
N4–H4C···O7#4	0.91(3)	1.83(3)	2.7280(18)	170(2)
N4–H4B···O8#5	0.92(2)	1.94(2)	2.8469(18)	168(2)

#1: 1-x, 2-y, 1-z.; #2: x, 1.5-y, 0.5+z.; #3: x, 2.5-y, 0.5+z.; #4: -x, 1-y, 1-z; #5: x, 0.5-y, 0.5+z; #6 x, 1.5-y, -0.5+z.

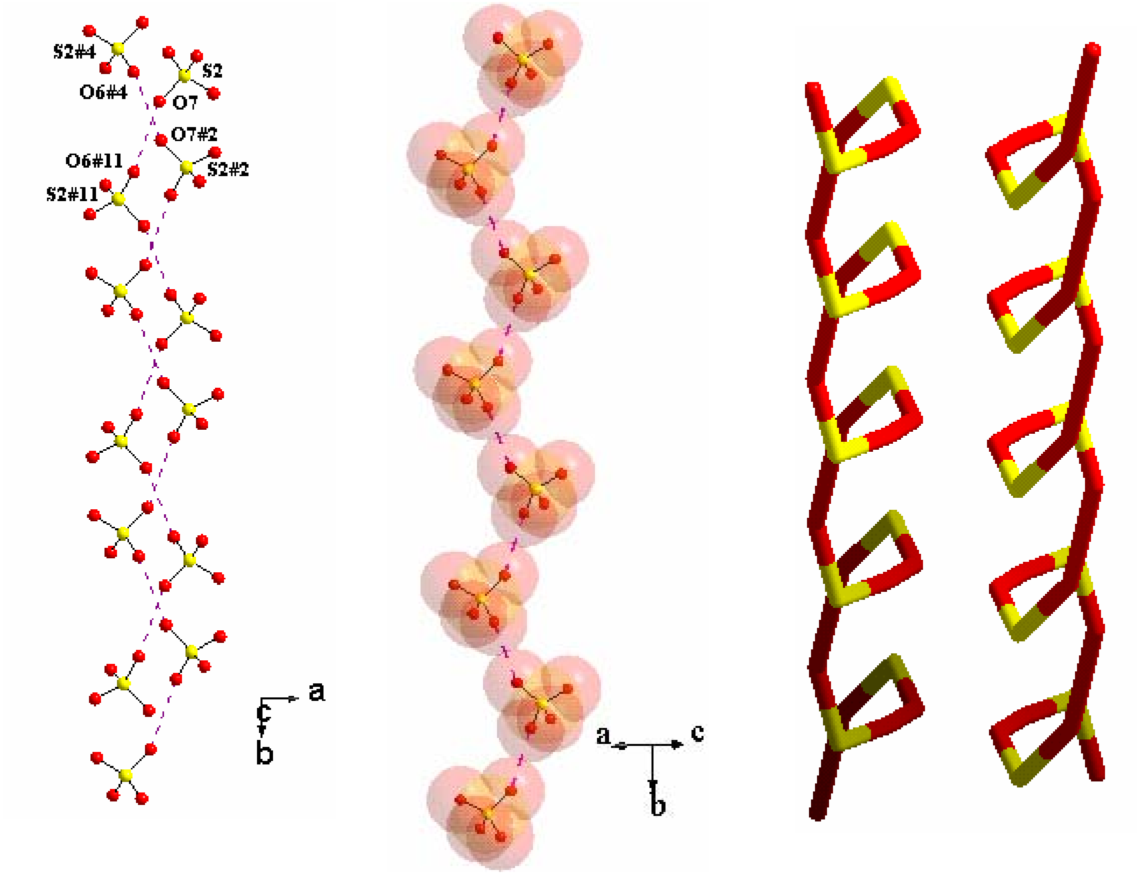
D. Why sulphate anion-sulphate anion aggregation? Hydrogen bonding environments around sulphate anion oxygen atoms.



ESI-Fig. 4 Hydrogen bonding situation of sulphate anion oxygen atoms. Left: the hydrogen bonding interactions around two S1 sulphate anions involved in the formation of non-covalent non-hydrogen bonding O···O interactions; right: : the hydrogen bonding interactions around two S2 sulphate anions involved in the formation of non-covalent non-hydrogen bonding O···O interactions. Colour code: S, yellow; O, red; N, blue; H, purple. Black dashed lines represent N–H···O hydrogen bonds and green dashed lines are non-covalent non-hydrogen bonded O···O interactions leading to sulphate anion helices. #7: 1-x, 0.5+y, 0.5-z; #8: -x, -0.5+y, 0.5-z

Notably in both crystallographically independent sulphate anions (S1 and S2 sulphates), the two oxygen atoms that connect two sulphate anions in sulphate anion helices are dissimilar in terms of their hydrogen bonding environments. In the S1 sulphate helices, O(1) atom accepts two protons two different $-\mathrm{NH}_3^+$ groups, where as the O(4) atom accept one proton from one $-\mathrm{NH}_3^+$ group. Similarly, in the case of S2 sulphate helices, O(6) is hydrogen bonded to two $-\mathrm{NH}_3^+$ groups and O(7) atom is hydrogen bonded to one $-\mathrm{NH}_3^+$ group. As shown in above figure (ESI-Fig. 4) sulphate anions are alternatively hydrogen bonded to 5 and 6 $-\mathrm{NH}_3^+$ groups of ortho-phenylenediammonium cations (see ESI-Fig. 3 and ESI-Table 4 for the relevant hydrogen bonding parameters). This causes the drift of a considerable amount of electron density from a sulphate anion towards surrounding $-\mathrm{NH}_3^+$ cations and thereby reduces the negative charge of each sulphate anion to a great extent. The reduction of negative charge apparently makes the sulphate anion-sulphate anion aggregation possible.

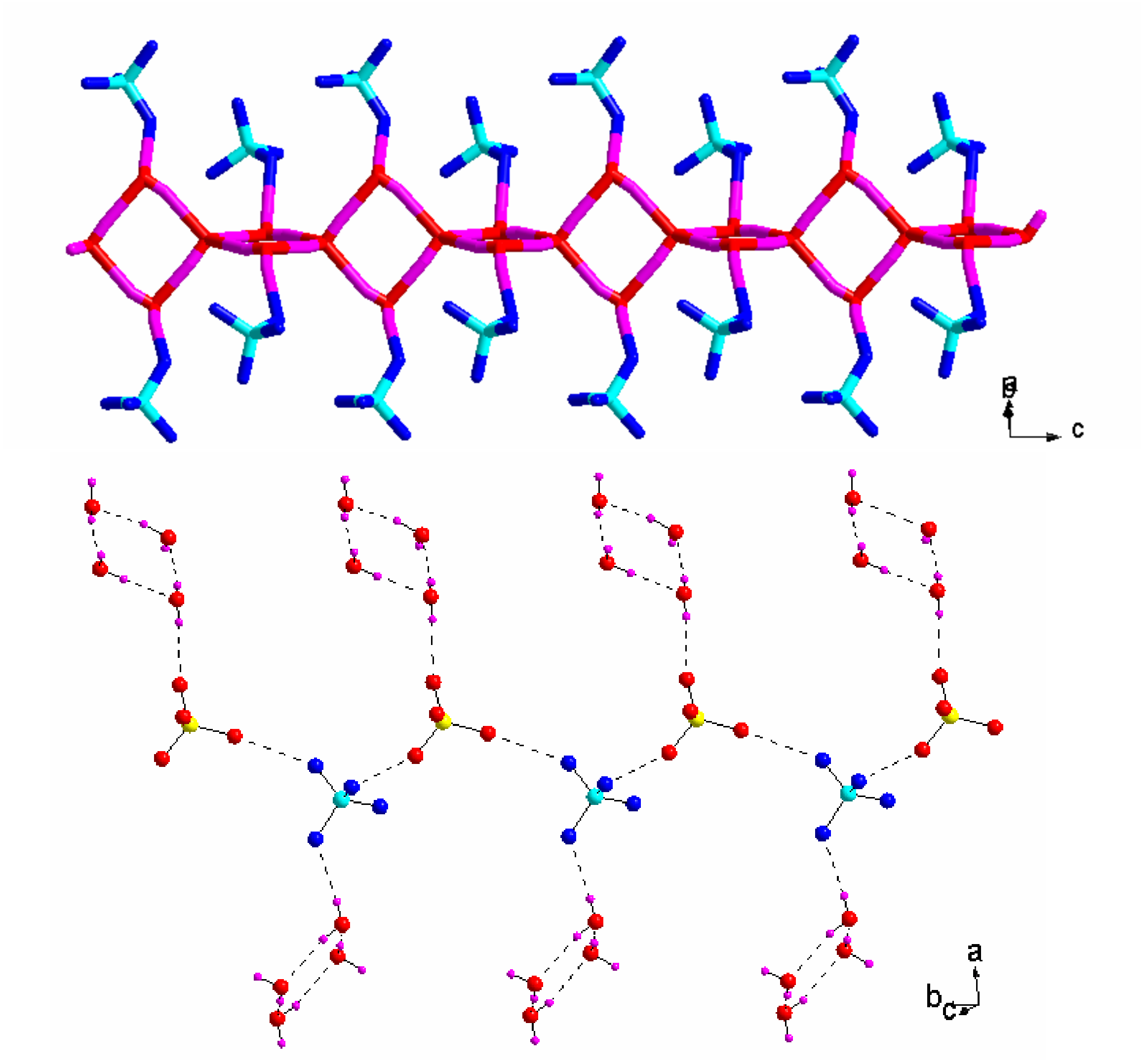
E. Sulphate anion helices from S2 sulphate.



ESI-Fig. 5 Sulphate helices: left, ball-and-stick representation of left and right handed helices; middle, superimpose space-filling model of a left-handed sulphate helix; right: wire-frame representation of helical back bones of left and right handed sulphate helices. Colour code: S, yellow; O, red. #2: x, 1.5-y, 0.5+z; #4: -x, 1-y, 1-z; #11: -x, 0.5+y, 0.5-2.

Both S1 sulphate and S2 sulphate froms left and right handed helices independently. S1 sulphate helices (left and right handed) are shown in the manuscript and S2 sulphate helices are presented here as ESI (ESI-Fig. 5). The non-covalent non-hydrogen bonded O···O separation in S1 sulphate anion helices is 2.9413(16) Å and that in S2 sulphate anion helices is 2.9463(16) Å.

F. How is helicity induced among sulphate anion aggregations? The role of the flip-flop water chain.

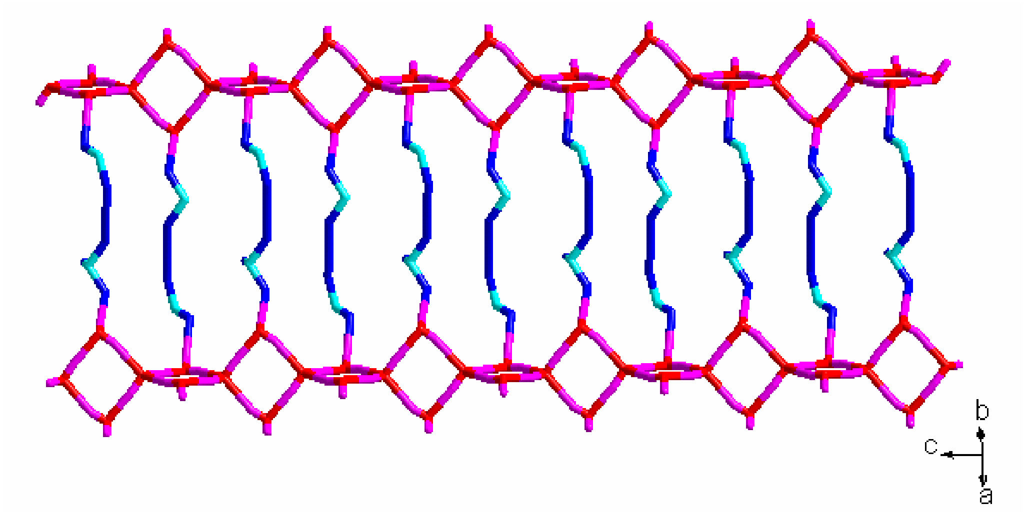


ESI-Fig. 6 Top: The hydrogen bonding interaction of the flip-fop water chain with sulphate anions. Color code: S, cyan; sulphate O, blue. Bottom: the hydrogen bonding interaction of a sulphate helix with the surrounding water tetramer of respective water chains. Colour code: S, yellow / cyan; O, red / blue; H, purple.

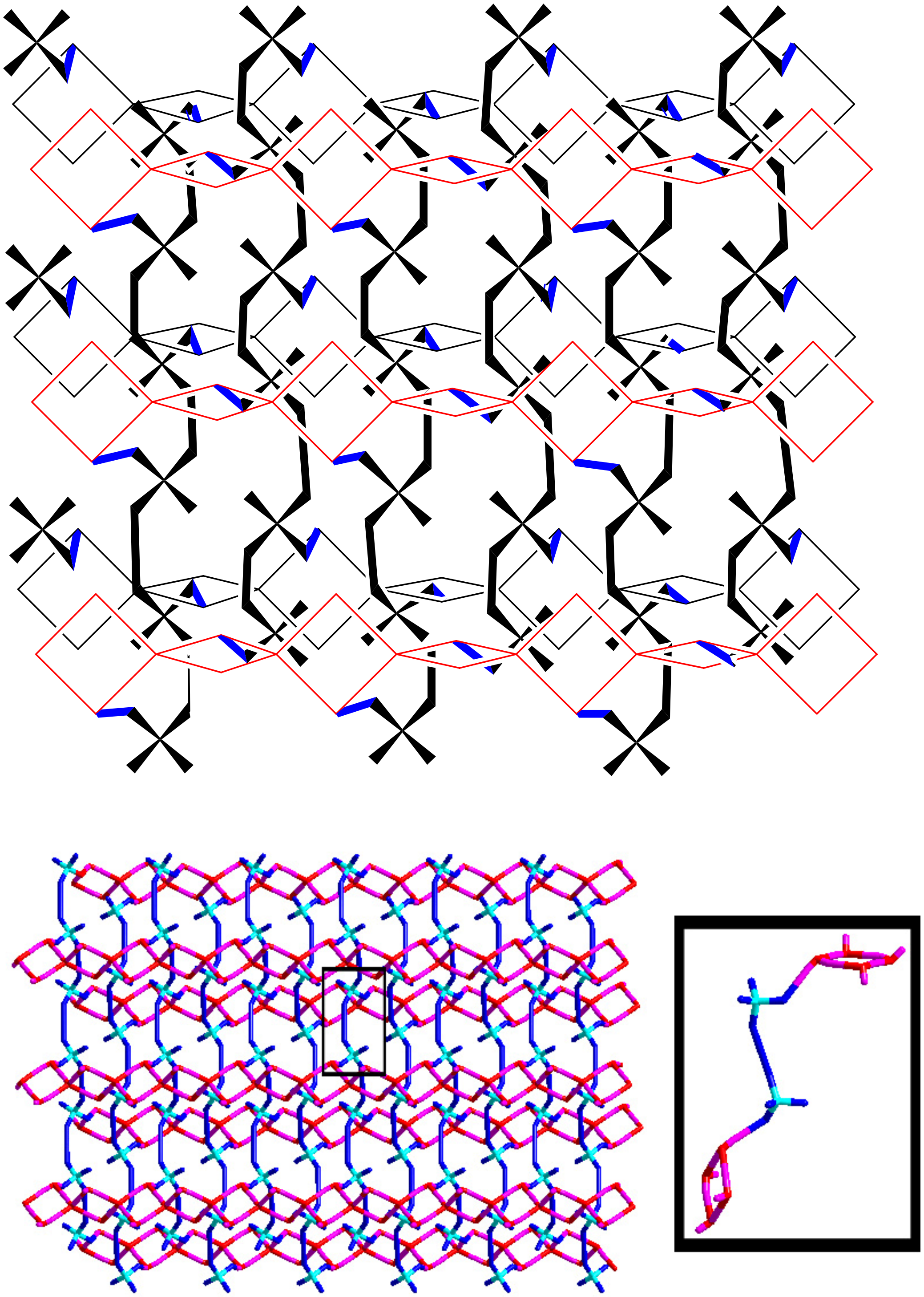
Two water molecules (which are not corner shared) of each water tetramer of the flip-flop water chain are hydrogen bonded to two different sulphate anions. These are indeed strong hydrogen bonds: O(11)–H(11A)···O(2) and O(10)–H(10B)···O(5) (see ESI-

Fig. 3 and ESI-Table 4). On the other hand, each sulphate anion of the sulphate helix is hydrogen bonded to a water molecule of the water chain as shown in ESI-Fig. 6.

The careful inspection on the surrounding of a sulphate anion helix reveals two unique features: (i) the supramolecular planes of two water tetramers (from the upper and lower layer water chains) that connect two successive sulphate anions in a helix are perpendicular to each other and (ii) displacement / disposition of the same water tetramers (that connect two successive sulphate anions) with respect to each other (see ESI-Figs. 7 and 8). These two factors should be responsible for twisting the node connecting two sulphate anions in the sulphate helix. This twisting was measured (as S–O···O–S dihedral angle that resulted from two interconnecting sulphate anions) to be 68^{o} and is accountable to induce the helicity among sulphate anions.

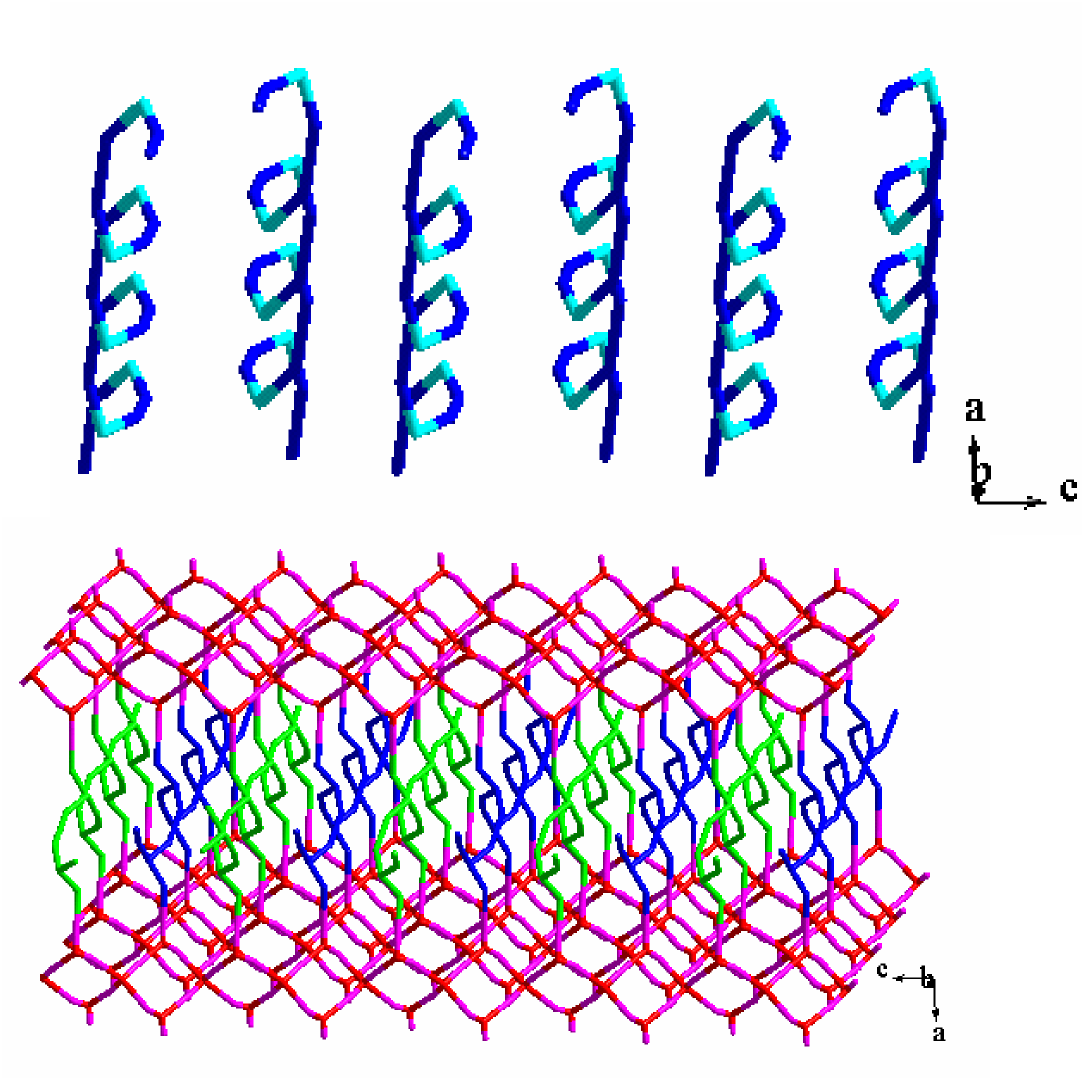


ESI-Fig. 7 Sulphate dimers (the parts of the sulphte helices) are hydrogen bonded to two different water chain in such a way that the connecting water tetramers are perpendicular to each other and these are slightly displaced to each other. Colour code: S, cyan; water O, red; sulphate O, blue.



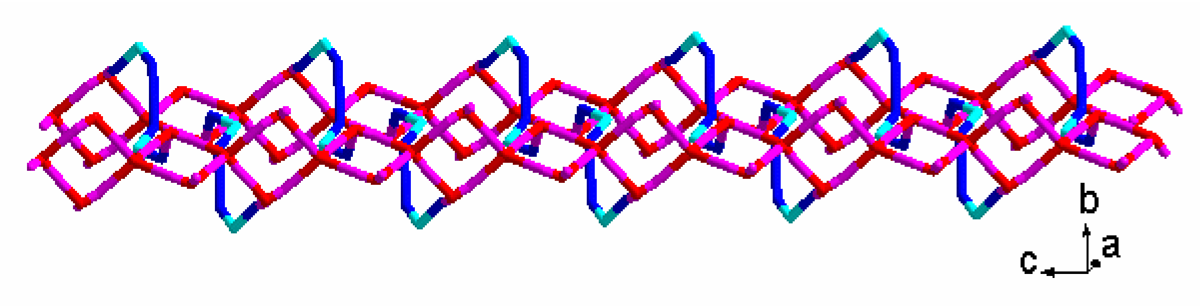
ESI-Fig. 8 Top: Schematic representation showing, how the flip-flip water chains induce helicity in supramolecular aggregation of sulphate anions; bottom: same situation from actual crystal structure. One non-covalent O···O bond connecting two sulphate anions (that are hydrogen bonded to water tetramers from two different water chains) is highlighted separately.

Both left handed and right handed sulphate helices can be generated as shown in ESI-Fig. 9.



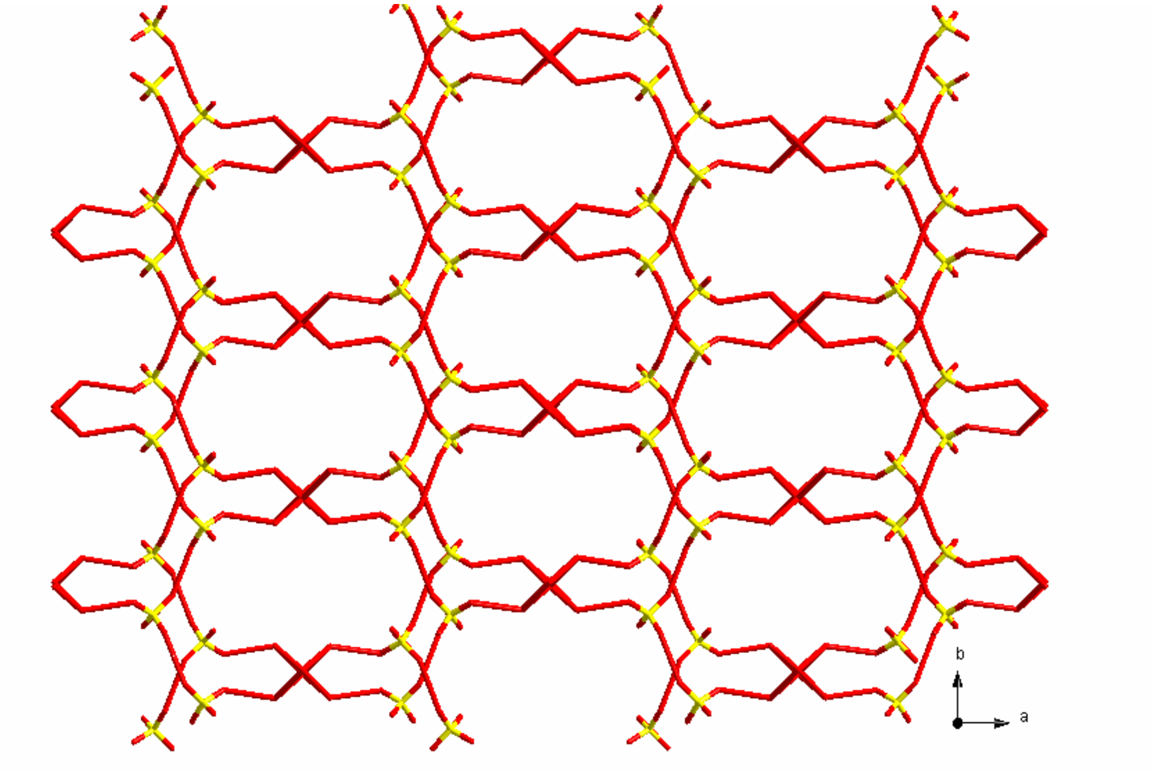
ESI-Fig. 9 Top: Left- and right-handed sulphate helices. Colour code: S, cyan; O, blue. Bottom: both left- and right-handed sulphate helices in two different colours (green and blue) with water chains.

Different handedness (left and right) of the sulphate helices can also be shown to be controlled by the water chains. For example the following figure (ESI-Fig.10) shows two different helices with two different turns (shown in upper and lower sides), which are definitely influenced by the surrounding hydrogen bonded water chains, which are alternatively displaced to each other.



ESI-Fig. 10 Dispositions of two water chains and parts of left- and right-handed sulphate helices. Colour code: S, cyan; water O, red; sulphate O, blue.

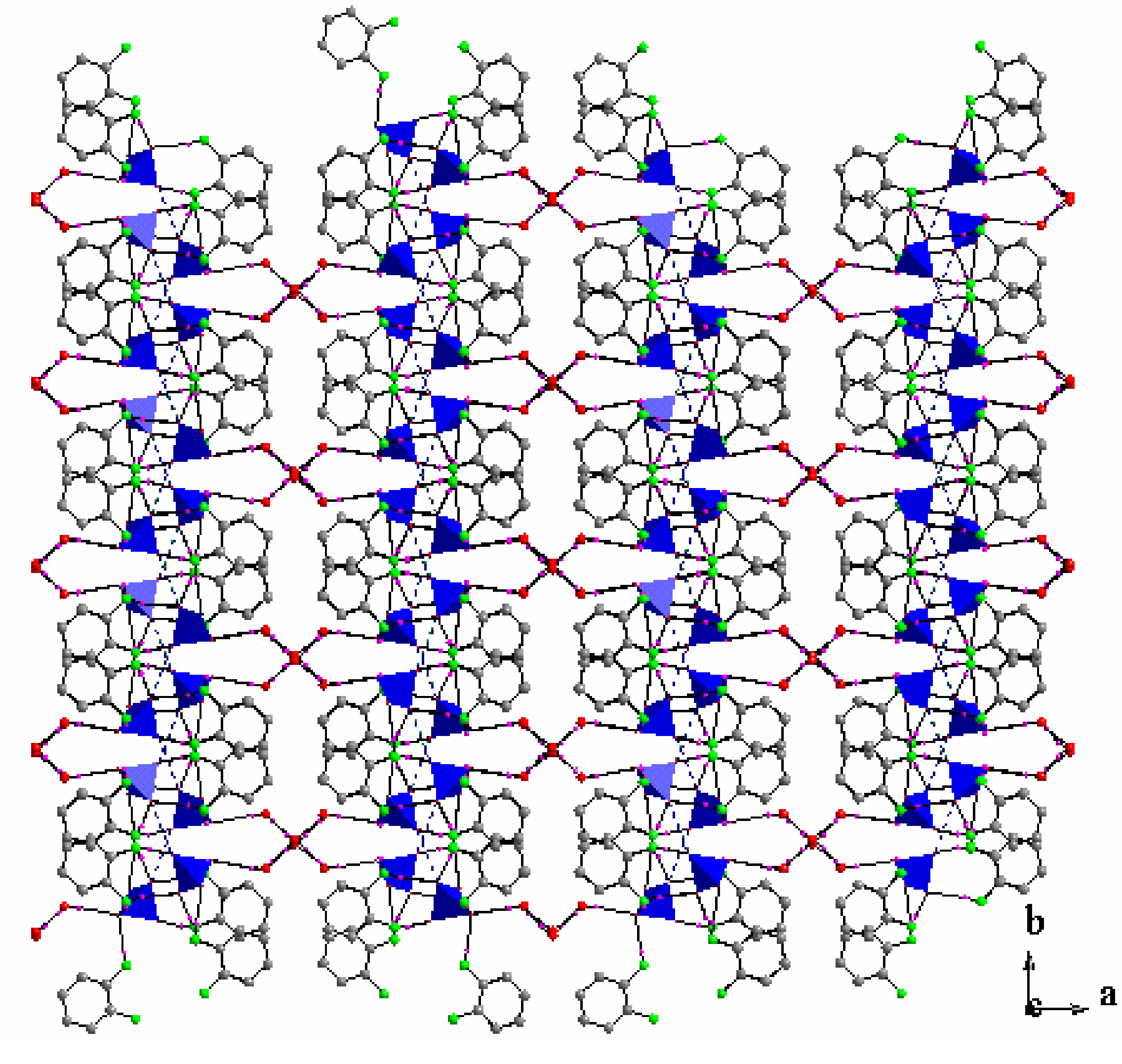
In the crystal of $[C_6H_{10}N_2]\ SO_4 \cdot 1.5\ H_2O$ (**1**), sulphate anion helices (running parallel to the crystallographic *b* axis) and water chains (running parallel to the crystallographic *c* axis) remain perpendicular to each other as shown in ESI-Fig. 11. We believe that, both exist by a cooperative effect.



ESI-Fig. 11 The existence of sulphate helices (running parallel to the crystallographic *b* axis) and waters chains (running parallel to the crystallographic *c* axis) in the crystal of **1**.

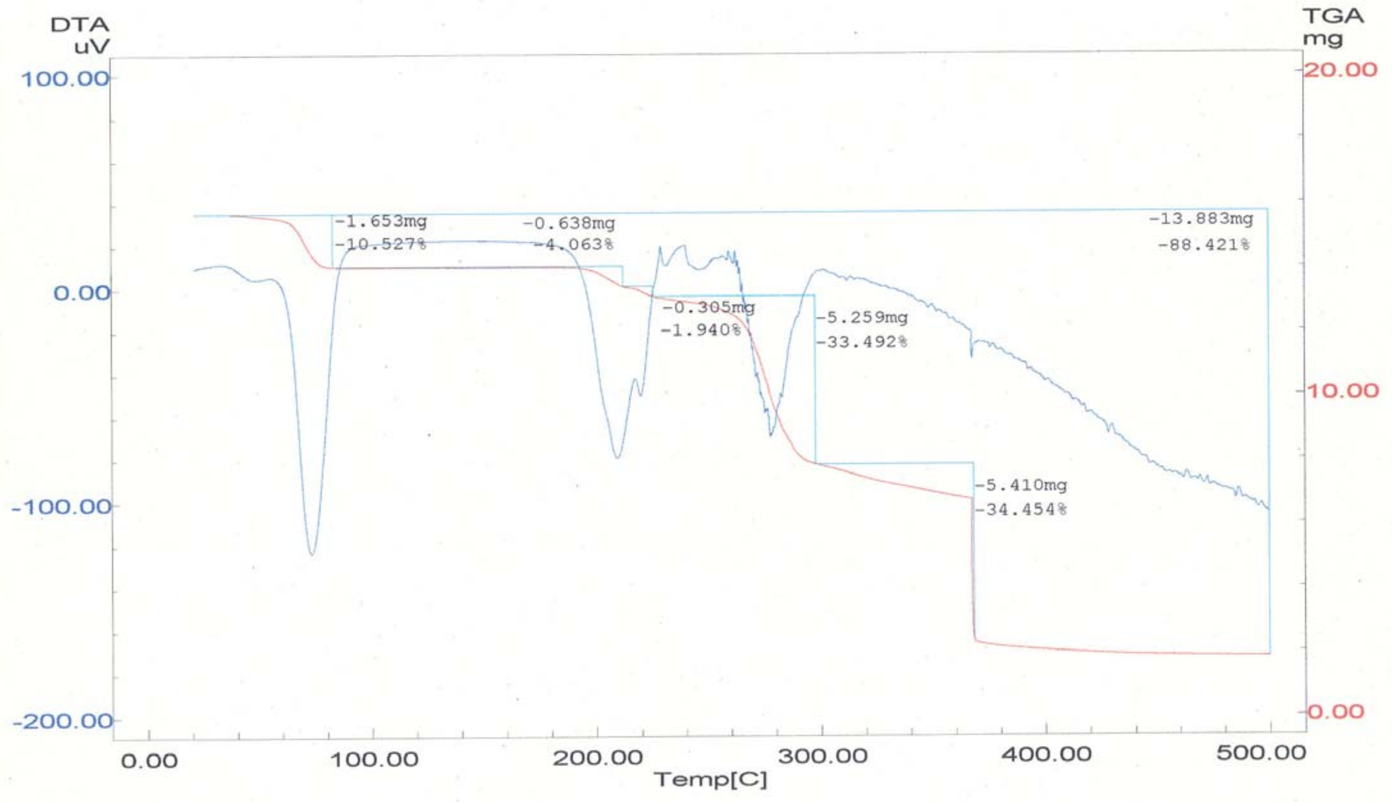
G. The packing diagram of [$C_6H_{10}N_2$] SO_4 · 1.5 H_2O (1)

The packing diagram of [$C_6H_{10}N_2$] SO_4 · 1.5 H_2O (**1**) is shown in ESI-Fig. 12. This shows the overall supramolecular interactions in the crystal of **1**.



ESI-Fig. 12 The packing diagram of [$C_6H_{10}N_2$] SO_4 · 1.5 H_2O (**1**) showing the overall supramolecular interactions that involve (i) non-covalent non-hydrogen bonded O···O (between two interacting sulphate anions), (ii) sulphate anion-water hydrogen bonding (O–H···O) interactions and (iii) sulphate anion-NH_3^+ hydrogen bonding (N–H···O) interactions. The sulphate anions are shown in blue tetrahedrons. Colour code: C, gray; N, green; water O, red; sulphate O, blue.

H. Thermogravimetric Analysis of $[C_6H_{10}N_2]\ SO_4 \cdot 1.5\ H_2O$ (1)



ESI-Fig. 13 TGA plot of $[C_6H_{10}N_2]\ SO_4 \cdot 1.5\ H_2O$ (**1**).

The TGA studies on **1** were performed under nitrogen atmosphere at the heating rate of 1° per minute. It shows the first loss at around 80°C that corresponds to the solvent water molecules (1.5 H_2O) per formula unit. Then the dehydrated solid remains stable upto ~ 200°C.