# Sulfate anion helices formed by the assistance of a flip-flop water chain†

**Pallepogu Raghavaiah,[b] Sabbani Supriya[a] and Samar K. Das*[a]**

*Received (in Cambridge, UK) 24th April 2006, Accepted 9th May 2006*
*First published as an Advance Article on the web 31st May 2006*
**DOI: 10.1039/b605899j**

**A flip-flop extended water structure assists the formation of sulfate anion helices (both left- and right-handed) in a crystalline hydrate of a simple organic–inorganic compound $[C_6H_{10}N_2]SO_4{\cdot}1.5H_2O$ (1).**

Natural occurrence of self assembled organized structures (*e.g.*, molecular helices) in biological macromolecules has motivated chemists to investigate similar arrangements in synthetic systems.[1] In synthetic analogues, the complementary interactions among the chemical entities provide an interesting supramolecular correlation leading to an organized molecular framework.[2] Water, a simple chemical entity present in many crystalline systems, plays a vital role in numerous biological and chemical processes.[3] The hydrogen bonding interactions among water molecules result in the formation of water clusters that are stabilized in diverse organic and inorganic crystalline hosts. These small water clusters have been investigated for better understanding the structure of water in bulk.[4] Many of these systems demonstrate the stabilization of water cluster and the host by a cooperative effect (inter-dependent to each other): one may have profound influence on the supramolecular organization of the other in the same crystal. We describe here the creation of helical structures from sulfate anions, formed by non-covalent O···O contacts and stress the role of a flip-flop water chain in determining the helical arrangement of sulfate anions in the solid state of a simple organic–inorganic compound $[C_6H_{10}N_2]SO_4{\cdot}1.5H_2O$ (**1**). The non-covalent O···O interactions are well-established in the literature including their theoretical aspects.[5] There are reports on O···O contacts that are a consequence of the N···O contacts in aromatic nitro derivatives.[5a] However, any helical construction formed by short O···O contacts was not surveyed prior to this work.

Colourless plate-shaped crystals of **1** were synthesized from an aqueous solution dissolving *o*-phenylenediamine and ferric sulfate.‡ Compound **1** was characterized by routine analysis,§ TGA studies and unambiguously by single-crystal X-ray structure determination.¶

The X-ray crystal structure of **1** shows two crystallographically independent *o*-phenylenediammonium cations, two crystallographically independent sulfate anions and three crystal water molecules in its asymmetric unit (Fig. 1). All three solvent water molecules interact with each other forming an extended water structure, which can be described as a chain of corner-shared water tetramers, alternatively having same conformations as shown in Fig. 2. This can be called a flip-flop water chain in the sense that the supramolecular plane of each water tetramer, along the chain, is perpendicular to the planes of its adjacent water tetramers. The hydrogen bonding parameters for this water chain is described in Table 1. Similar water chain has recently been reported in other molecular crystalline hydrates.[6] In the present system, this water chain plays a significant role in stabilizing sulfate anion helices that are formed through O···O contacts of distance 2.9413(16) Å in the case of S(1)-sulfate helices (Fig. 3).

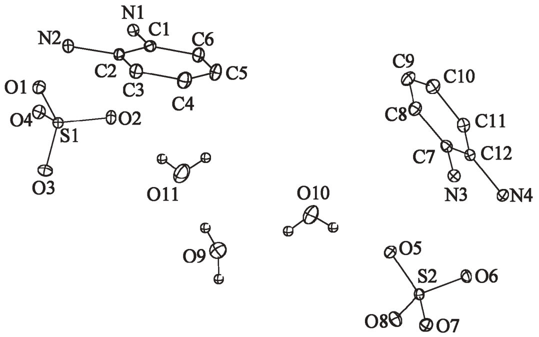

**Fig. 1** ORTEP drawing of compound **1** with atom-labeling scheme showing 50% probability. Asymmetric unit in the crystal structure of **1** is shown. Carbon and amino hydrogens are not shown for clarity.

In the crystal, the sulfate helices and the water chains seem to exist by a cooperative effect, both interacting with each other. The sulfate helices (running parallel to the crystallographic *b* axis) remain perpendicular to the water chains that run parallel to the crystallographic *c* axis as shown in Fig. 4. Along the helix, each sulfate anion is hydrogen bonded to a water tetramer of the water chain (Fig. 5(a)). Two different arrangements (*e.g.*, front and back

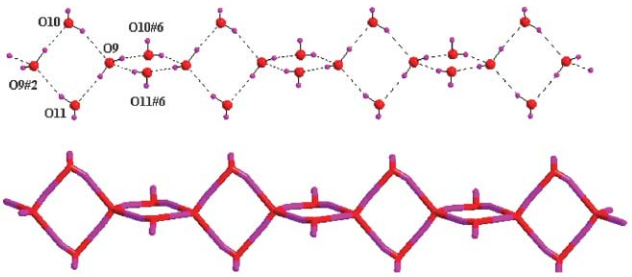

**Fig. 2** Representation of the flip-flop water chain running parallel to the crystallographic *c* axis: (a) ball-and-stick representation, (b) wire-frame representation. Colour code: O, red; H, purple. Atoms with additional labels are related by symmetry transformation to generate equivalent atoms #2: *x*, 1.5 − *y*, 0.5 + *z*; #6: *x*, 1.5 − *y*, −0.5 + *z*.

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[a] *School of Chemistry, University of Hyderabad, Hyderabad 500046, India. E-mail: skdsc@uohyd.ernet.in; Fax: +91 40 2301 2460; Tel: +91 40 2301 1007*
[b] *Department of Chemistry, Goa University, Goa 403206, India*

† Electronic supplementary information (ESI) available: Crystallographic details including Tables and relevant Figures and TGA plot. See DOI: 10.1039/b605899j

**Table 1** 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) |

[a] #2: $x$, $1.5 - y$, $0.5 + z$. [b] #6: $x$, $1.5 - y$, $-0.5 + z$.

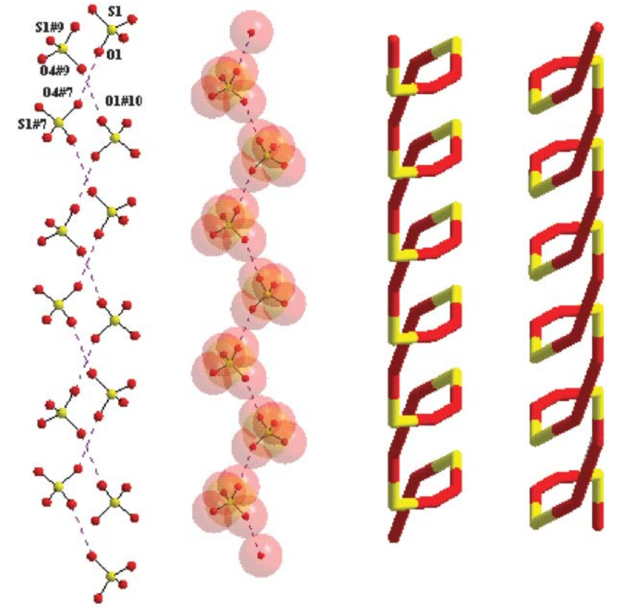

**Fig. 3** Sulfate helices: left, ball-and-stick representation of left and right handed helices; middle, superimpose space-filling model of a left-handed sulfate helix; right: wire-frame representation of helical back bones of left- and right-handed sulfate helices. Colour code: S, yellow; O, red. Atoms with additional labels are related by symmetry transformation to generate equivalent atoms #7: $1 - x$, $0.5 + y$, $0.5 - z$; #9: $1 - x$, $2 - y$, $-z$; #10: $x$, $2.5 - y$, $-0.5 + z$.

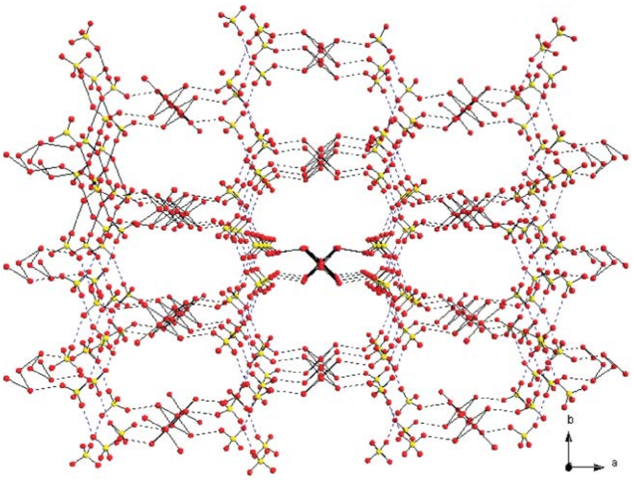

**Fig. 4** A perspective view of left- and right-handed sulfate helices interacting with water chains that are perpendicular to sulfate helices. Colour code: S, yellow; O, red.

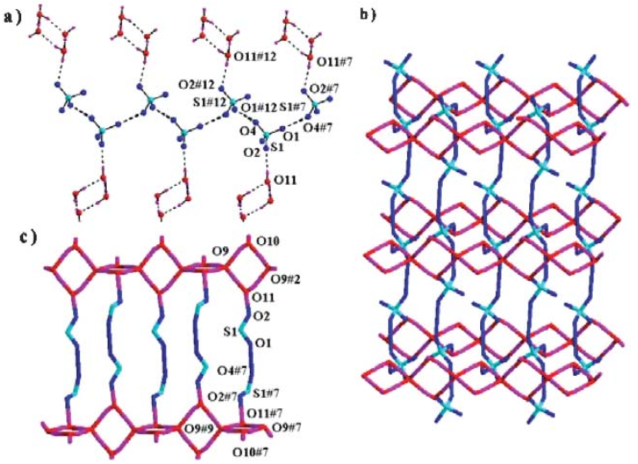

**Fig. 5** (a) A sulfate helix showing that each sulfate anion is hydrogen bonded to a water tetramer (part of the flip-flop water chain). (b) Water chain and sulfate helices showing, how the flip-flip water chains induce helicity in supramolecular aggregation of sulfate anions. (c) Sulfate–sulfate interaction between two water chains. Colour code: S, cyan; Water O, red; sulfate O, blue; H, purple. Atoms with additional labels are related by symmetry transformation to generate equivalent atoms: #2: $x$, $1.5 - y$, $0.5 + z$; #7: $1 - x$, $0.5 + y$, $0.5 - z$; #9: $1 - x$, $2 - y$, $-z$; #10: $x$, $2.5 - y$, $-0.5 + z$; 12: $1 - x$, $-0.5 + y$, $0.5 - z$.

of the helix) of the chain of the water tetramers (Fig. 5) are involved in constructing a sulfate helix. A sulfate anion, hydrogen bonded to a water tetramer of the front chain, undergoes O···O interaction to a sulfate anion that is hydrogen bonded to a water tetramer of the back chain and so on (Fig. 5(b)); thus each sulfate helix touches both front and back water chains alternatively while it proceeds. The careful inspection on the surrounding of a sulfate helix reveals two unique features: (i) the supramolecular planes of two water tetramers that connect two successive sulfate anions in a helix are perpendicular to each other (see Fig. 5) and (ii) there is a slight displacement of the same water tetramers (that connect two successive sulfate anions) with respect to each other. These two factors might be responsible for twisting the node connecting two sulfate anions in the sulfate helix. This twisting was measured (as S–O···O–S dihedral angle that resulted from two interconnecting sulfate anions) to be 68° and is accountable to induce the helicity among sulfate anions. Along the sulfate helix, the O···O separation between two sulfate anions is 2.9413(16) Å, which is shorter than the sum of their van der Waals radii ($r_{\mathrm{vdW}}$: O, 1.52 Å) indicating a strong non-covalent O···O interaction.

All three hydrogen atoms around each of the protonated (tertiary) nitrogen atoms (of *o*-phenylenediammonium cation) are nicely located from difference Fourier maps and their positions are isotropically refined. These located hydrogens remained stable during successive refinement stages. Interestingly, all three hydrogens of each protonated nitrogen atom are exclusively hydrogen bonded with its surrounding sulfate anion oxygen atoms (not with water oxygens) as shown in Fig. 6.

More specifically, the ortho-phenylenediammonium cation with its two $-NH_3^+$ groups is involved in hydrogen bonding interactions with both left- and right-handed sulfate anion helices: from each $-NH_3^+$ group, two hydrogens interact with one handed helix and the third hydrogen with other handed helix (see Fig. 6). Same

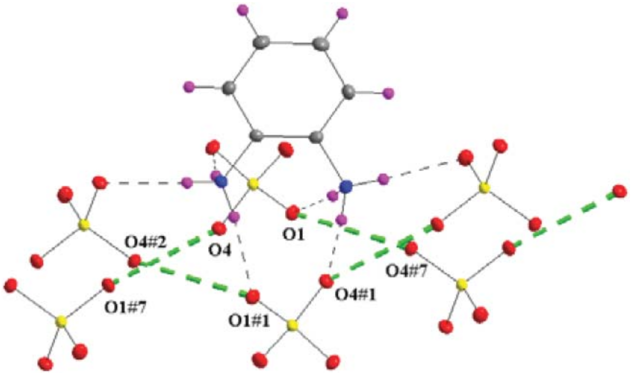

**Fig. 6** Hydrogen bonding situation of $-NH_3^+$ hydrogens with left- and right-handed sulfate anion helices. The green dashed-lines represent O···O non-covalent interactions leading to left- and right-handed helices. Atoms with additional labels are related by symmetry transformation to generate equivalent atoms #1: $1 - x, 2 - y, 1 - z$; #2: $x, 1.5 - y, 0.5 + z$; #7: $1 - x, 0.5 + y, 0.5 - z$.

situation was observed for other crystallographically independent *ortho*-phenylenediammonium sulfate (see ESI†).

In summary, the generation of supramolecular helices requires a reliable non-covalent motif that can provide the desired connectivity of the building blocks in a predictable manner. Hydrogen bonds, metal coordination, and π–π stacking interactions are often utilized in this regard. Simple non-covalent O···O interactions (in less than 3 Å O/O separation, which do not include these H-bond, metal coordination and π–π stacking interactions) involved in a supramolecular helical construction is not yet explored. We succeeded to demonstrate supramolecular organization of water molecules and creation of sulfate anion helices through non-covalent non-hydrogen bonded O···O contacts and various functionalities offered by water chain. We have shown that a simple compound possessing organic cations and inorganic anions can provide novel structural features that may serve in understanding the basic principles of supramolecular chemistry.

We thank Department of Science and Technology, Government of India, for financial support and the National X-ray Diffractometer facility at University of Hyderabad. We are grateful to UGC, New Delhi, for providing infrastructure facility at University of Hyderabad, under UPE grant. We thank Professor T. P. Radhakrishnan, School of Chemistry, University of Hyderabad, for his help. We also thank Professor K. S. Rane and Dr. B. R. Srinivasan, Department of Chemistry, Goa University, for helpful discussions. Special thanks to Professor Edward R. T. Tiekink, Department of Chemistry, University of Texas at San Antonio, for helpful suggestions. S. S. thanks UGC, New Delhi for a fellowship.

## Notes and references

‡ An aqueous solution of ferric sulfate (2.6 g, 6.50 mmol) was added to an aqueous solution of *o*-phenylenediamine (2 g, 18.52 mmol) and the pH of the resulting solution was adjusted to 1.2 by dropwise addition of concentrated sulfuric acid. The red reaction mixture was filtered and the filtrate was left undisturbed at room temperature for 24 h. Colourless plate-shaped crystals of compound **1**, suitable for single-crystal X-ray structure determination, were filtered off and washed with cold water and dried at room temperature Yield: 0.93 g (22% based on *o*-phenylenediamine).

§ Anal. Calc. for $C_6H_{13}N_2O_{5.5}S$: C, 30.89; H, 5.62; N, 12.01; S, 13.75. Found: C, 31.04; H, 5.51; N, 12.19; S, 14.01%. IR (KBr, $cm^{-1}$): 3455, 2920, 2602, 1630, 1579, 1541, 1504, 1375, 1317, 1155, 1068, 966, 756, 607, 528, 449. $^1H$ NMR (400 MHz, $D_6$-DMSO): $\delta$ 6.8–7.0 (4H, m, aromatic protons).

¶ *Crystal data* for **1**: $C_{12}H_{26}N_4O_{11}S_2$, $M = 466.49$, monoclinic, $P2_1/c$, $a = 26.946(2)$, $b = 9.5581(9)$, $c = 7.5203(7)$ Å, $\beta = 93.2080(10)^\circ$, $V = 1933.8(3)$ Å$^{-3}$, $Z = 4$, $D_c = 1.602$ g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 0.342 mm$^{-1}$ , total reflections = 21667, 4646 unique reflections ($R_{int} = 0.0365$), largest difference peak and hole = 0.409 and −0.686 e Å$^{-3}$ Final $R_1$ [$I > 2\sigma(I)$] = 0.0382, $wR_2 = 0.1009$, goodness of fit on $F^2 = 1.131$. CCDC 293163. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605899j

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