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# Synthesis and characterizations of a new organic cation sulfate: $[2,6-(C_2H_5)_2C_6H_3NH_3]_2$ (HSO<sub>4</sub>)<sub>2</sub>.3H<sub>2</sub>O

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# ABSTRACT

In the crystal structure of  $[2,6-(C_2H_5)_2C_6H_3NH_3]_2(HSO_4)_2.3H_2O$ , inorganic entities form corrugated layers parallel to ab plane between which organic groups are located. This structure is characterised by the existence of two groups  $HSO_4^-$  crystallographically independent which form dimmers  $(H_2S_2O_8)^{2^-}$ . These dimers are interconnected by water molecules via strong H-bonds  $(d_{O...O} < 2.73 \text{ Å})$ .

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#### Keywords

Chemical synthesis, X-ray diffraction, Thermogravimetric analysis (TGA), Infrared spectroscopy.

#### Introduction

Organic sulfates resulting from interaction between sulfuric acid and organic molecules, such as amines, amino alcohols, and amino acids, have been studied by several laboratories. The attention paid to these materials increased when it was established that these compounds could present particular physicochemical properties. In fact, it has been demonstrated that some organic sulfates have good protonic conduction and, thus, are interesting as solid electrolytes [1]. Besides structural considerations resulting from crystallographic studies, some organic sulfates exhibit non-linear optical properties like  $C_5H_6N_3O_2HSO_4$  [2], or phase transitions like  $(C_4H_{12}NO_2)HSO_4$  [3]. In this paper, we report single-crystal X-ray study of 2,6-diethylanilinium bis (hydrogensulfate) trihydrate (I).

## **Experimental:**

## **Chemical preparation**

An ethalonic 2,6-diethylaniline solution (5 mmol, in 5 mL) was added dropwise to an aqueous solution of sulfuric acid (0.5 M, 10 mL)with stirring for a few minutes at 293 K to avoid overheating. The obtained solution remained clear, without any precipitant. This solution was left at 293 K for 24 h during which time a colourless prismatic crystals were formed.

## Investigation techniques

The crystal structure was carried out with direct methods from the SHELXS-97 [4], in the WinGX package [5] and refined by full-matrix least-squares method with the program SHELXL-97. All nonhydrogen atoms were refined isotropically and then anisotropically by full matrix least-square method. An ORTEP [6] drawing of the molecular structure is shown in Fig. 1. The main bond distances and bond angles for the title compound are provided in Table 1 and the main geometrical features of the hydrogen-bond scheme in Table 2. The parameters used for the X-ray diffraction data collection as well as the strategy used for the crystal structure determination and its final results are reported in Table 3.



## Fig. 1 ORTEP drawing of the title compound, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 35% probability level

Setaram thermoanalyzers, TG-DTA92 was used to perform thermal treatment on samples of bis (2,6-diethylanilinium hydrogen sulfate) trihydrate.

TG-DTA thermograms were registered with 10.4 mg samples in an open platinum crucible. Sample was heated in air at a  $3^{\circ}$ C/min heating rate; an empty crucible was used as reference.

IR spectra were recorded at room temperature with a "Perkin-Elmer Spectrum 1000" spectrophotometer over the wavenumber  $4000-400 \text{ cm}^{-1}$ .

A thin, transparent pellet was made by compact an intimate mixture obtained by shaking 2 mg of the sample in 100 mg of KBr.

<sup>13</sup>C MAS - NMR spectrum was obtained with a solid state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz.

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Fig. 2 Projection of the structure along the a axis Results and discussion:

## **Crystal structure**

The asymmetric unit, built of two sulfate anions, two organic cations and three water molecules, has the geometrical configuration shown in the Fig. 1. Both groups HSO4- are crystallographically independent and held together by strong O-H...O hydrogen bonds (d O...O = 2.50Å) to form  $(H_2S_2O_8)^2$ dimers. Interconnected by the water molecules, via H-bonds Ow-H...O, these dimmers develop inorganic layers parallel to ab plane around  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$  (Fig. 2). Plane direction of these layers, link mode of dimmers and the orientation of organic entities are different from that observed from that of other organic hydrogen sulphates[7]. Geometrical characteristics of all components of title compound are calculated. Each HSO<sup>4-</sup> group exhibits a compact assembly of oxygen atoms in which the sulphur atom shows a slight displacement from the gravity center of the tetrahedron SO<sub>4</sub>. In these tetrahedral, the distances S - O are significantly longer than the S = O distances because of the multiplicity of SO bonds and their electronic mesomerism. Both diethylanilinium cations, which are located between the inorganic layers, establish hydrogen bonds (not shown for the figure clarity) of type N-H...O and C-H...O with the sulfate anions and the water molecules. Meanwhile, they develop strong  $\pi$  -  $\pi$  stacking interactions between their aromatic rings separated by a distance of 3.763 Å. less than 3.8, maximum value accepted for  $\pi$  -  $\pi$  interactions [8]. The phenyl rings of these cations are planar with a maximum atomic deviation of 0.0003 Å. The coplanarity can be seen from the torsion angle values of C1-C2-C9-C10 ( $t_1 = 73.5^\circ$ ) and C1-C6–C7–C8 ( $t_2 = 103.5^\circ$ ) in the first diethylanilinium cation and  $(C12-C13-C19-C20 (t_2 = -74.3^\circ) \text{ and } C12-C11-C17-C18 (t_1)$  $= 179.0^{\circ}$ ) in the second one.



#### $(HSO_4)_2.3H_2O$

## Infrared spectroscopy

Studies of the  $SO_4^{2-}$  tetrahedra have located its fundamental frequencies at 981 [v<sub>1</sub>(A1)], 451 [v<sub>2</sub> (E)], 1104 [v<sub>3</sub> (T2)], and 614 cm<sup>-1</sup> [v<sub>4</sub> (T2)] [9]. All the modes are Raman active, whereas only v<sub>3</sub> and v<sub>4</sub> are active in the IR. In the crystal, the SO<sub>4</sub><sup>2-</sup> ion occupy a lower site symmetry C1, as a result the IR inactive v<sub>1</sub> and v<sub>2</sub> modes may become active and the degeneracies of v<sub>2</sub>, v<sub>3</sub>

and  $v_4$  modes may be removed. The degenerate  $v_2$  mode of the ion is found to be split into two components around 430 and 453 cm<sup>-1</sup>. Appearance of this IR inactive mode can be due to the lowering of the sulfate ion from Td to C1. The stretching mode v1 appears as one band at 998 cm<sup>-1</sup>. The  $v_3$  mode appears as one intense band at 1073 with two shoulders at 1157 and 1197 cm<sup>-1</sup>. The  $v_4$  mode is observed as three bands at 615, 625, and 666 cm<sup>-1</sup> (Fig. 3).

The infrared absorption spectrum exhibits broad bands between 3600 and 2000 cm<sup>-1</sup> and 1650 and 1400 cm<sup>-1</sup> which are assigned according to literature [10] to the valency vibration of organic cation and water molecules.



Fig. 4 DTA and TGA curves of [2,6-(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>]<sub>2</sub> (HSO<sub>4</sub>)<sub>2</sub>.3H<sub>2</sub>O at rising temperature

## Thermal behaviour

The simultaneous TG-DTA curves of the title compound (Fig. 4) show that the compound loses the coordinated water molecules in two steps. The first step is characterized by the endothermic peak at 100°C (observed loss = 3.18%) corresponding to the removal of one water molecule. The remaining two water molecules are lost at 150°C (observed loss = 6.76%). The observed total loss in these two steps (9.94%) corresponds to the calculated loss of three molecules of lattice water in the composition of the title compound (9.90%). The difference of the hydrogen bonds in the network explains the departure of the water molecules at two temperatures. By heating further, the important weight loss observed in the temperature range of 280-500°C corresponds probably to the degradation of the anhydrous phase. A black deposit of carbon is obtained at the end of the experience.

NMR results

The <sup>13</sup>C CP-MAS-NMR spectrum of the title compound is given in Fig. 5. In this spectrum, the presence of a resonance peak number greater than four (six in the approximately intensity ratio 1:1:2:1:1:2) in the resonance range of the aliphatic carbons, between 10 and 30 ppm, proves the existence of two crystallographically independent organic moieties in the asymmetric unit of the compound structure. This result is also in good agreement with the X-ray data. The other resonance signals at higher chemical shifts, between 120 and 140 ppm, are related to the aromatic carbon atoms.



 $(C_2H_5)_2C_6H_3NH_3]_2$  (HSO<sub>4</sub>)<sub>2</sub>.3H<sub>2</sub>O

#### References

[1] Casciola M, Costantiono U, D'amico S. Solid State Ionics, 1986, 22, 17.

[2] Pecaut J, Le Fur Y, Masse, R. Acta Cryst. B, 1993, 49, 535.

[3] Guerfel T, Jouini A. Journal de la Société Chimique de Tunisie, 2000,4, 723.

[4] Sheldrick G M, SHELX-97, University of Gőttingen., Federal Republic of Germany (1997).

[5] Farrugia LJ, Win GX Program for crystallography Package. J. Appl. Cryst., 1999, 32, 837.

[6] Farrugia LJ. ORTEP-3, program for molecular drawing. J. Appl. Cryst. 1997, 30, 565.

[7] Marouani H, Rzaigui M, Al-Deyab S. Acta Cryst. 2010, E66, 02613.

[8] Janiak J. J Chem. Soc. Dalton Trans., 2000, 3885.

[9] Hertzberg G., Infrared and Raman Spectra of Polyatomic Molecules; Van Nostrand: New York, 1966.

[10] Akriche S, Rzaigui M. Struct. Chem. 2008, 19, 827.

# $Table \ 1 \ Main \ interatomic \ distances \ (\mathring{A}) \ and \ bond \ angles \ (\circ) \ in \ the \ [2,6-(C_2H_5)_2C_6H_3NH_3]_2 \ (HSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O(MSO_4)_2.3H_2O$

S(1)04 tetrahedra	
S1-011474(2)	01-\$1-02 109.46(1)
S1-021460(2)	01-\$1-03 111 22(1)
S1-031463(2)	01-81-04 107 25(1)
S1-04 1 493(2)	02-81-03 110 66(1)
	02_51_04_100.00(1)
	03_\$1_04 109 07(1)
S(2)04 tetrahetra	05-01-04 10007(1)
S2-051436(2)	05-52-06 112 20(3)
S2_061447(2)	05_52_07 113 20(6)
22-001.447(2) 20.071.477(2)	
52-07 1.42/(2) CD 00 1.59/2)	
32-00100(2)	
	07-52-08 105,04(4)
Organac group 1	ac at ac 100 Mat
NI-CI 1.409(3)	C6-C1-C2 123.4(2)
C1-C6 1388(3)	C6-C1-N1 117 9(2)
C1-C2 1393(3)	C2-C1-N1 118.7(2)
C6-C5 1.400(4)	C5-C6-C7 119.2(2)
C6-C7 1.505(3)	C1-C6-C7 123.8(2)
C2-C3 1386(3)	C3-C2-C1 117.1(2)
C2-C9 1.517(3)	C3-C2-C9 120.0(2)
C5-C4 1371(4)	C1-C2-C9 1229(2)
C9-C10 1.522(4)	C4-C5-C6 1209(2)
C3-C4 1367(4)	C2-C9-C10 113.6(2)
C7-C8 1.519(4)	C4-C3-C2 1212(2)
	C6-C7-C8 113.8(2)
	C3-C4-C5 120.4(2)
	C5-C6-C1 117.0(2)
Organic group II	
N2-C12 1471(3)	C12-C11-C16 116.6(3)
C11-C12 1.401(3)	C11-C12-N2 116.8(2)
C11-C16 1395(4)	C13-C12-N2 119 5(2)
C16-C15 1375(5)	C15-C16-C11 120 8(3)
C11-C17 1515(4)	C11-C17-C18 116.6(3)
C12-C13 1381(3)	C13-C12-C11 123 8(2)
	C12-C13-C19 122 9(2)
C13-C19 1.503(4)	C14-C13-C19 120 4(3)
C15-C14 1363(4)	C14-C15-C16 120 7(3)
C13-C14 1 401(4)	C12-C13-C14 116 7(3)
C20. C10 1 515(4)	C15-C14-C13 101 1/2)
C17.C18 1 500/45	C17.C11.C16 123.8(3)
011-010 1009(1)	C12.C11.C17_110.6/2V
	UIS-UI9-UZU IIZ./(Z)

Table 2 Bond lengths (Å) and angles (°) in the hydrogen-bonding scheme

, bond lengths (A) and angles () in the nythogen-bonding					
	D-HA	D-H(Å)	HA(Å)	DA(Å)	D-HA(°)
	O4-H4O8	0.82	2.05	2.550(4)	123
	O8-H8O4	0.82	2.12	2.550(4)	113
	O22-H13O4	0.83(5)	1.86(5)	2.596(5)	148(4)
	O22-H22O21	0.83(2)	2.11(2)	2.475(5)	106 (2)
	O21-H20O7	0.81(5)	1.91(4)	2.697(4)	167(9)
	O21-H21O1	0.82(5)	1.92(5)	2.726(4)	170(6)
	O20-H24O22	0.82(4)	1.78(5)	2.519(7)	149(6)
	O20-H25O6	0.81(3)	2.51(4)	2.901(6)	111(3)
	N1-H1AO3	0.89	2.35	2.897(4)	120
	N1-H1BO1	0.89	1.95	2.830(4)	173
	N1-H1CO5	0.89	1.98	2.851(4)	167
	N2-H2AO6	0.89	2.53	2.935(4)	108
	N2-H2BO2	0.89	2.28	2.800(4)	117
	N2-H2CO3	0.89	2.33	2.900(4)	106
	N2-H2CO6	0.89	2.56	2.935(4)	146
	C9-H9AO2	0.97	2.54	3.485(5)	165
	C10-H10CO4	0.96	2.46	3.301(5)	146
	C17-H17BO6	0.97	2.58	3.474(5)	153
	C20-H20BO22	0.96	2.58	3.277(6)	130

Empirical formula	[2,6-(C <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>3</sub> ] <sub>2</sub> (HSO <sub>4</sub> ) <sub>2</sub> .3H <sub>2</sub> O	
Formula weight	548.66	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /n	
a	11.030(3) Å	
b	11.376(7) Å	
c	21.528(3)Å	
β	97.69(3) <sub>0</sub>	
Z	4	
V	2677.0(18) Å <sup>3</sup>	
рсаl	1.361 g cm <sup>-3</sup>	
E(000)	1176	
u(MoK α)	0.139 mm <sup>-1</sup>	
Measurement area: h, k,1	hmax = 18, $kmax = 19$ , $lmax = 31hmin = -18$ , $kmin = -3$ , $lmin = -5$	
Collected unique reflections 12659 (Rint = 0.03) Unique reflections included [I[2σ(I]]: 4588 with 340 refined parameters		
R[F2>2σ (F2)]	0.073	
Δρmin, Δρmax	-0.41, 0.45 eÅ <sup>-3</sup>	
Goodness-of-fit	0.937	

Table 3 Crystal data and experimental parameters used for the intensity measurements