

Structural and vibrational study of a new organic hydrogen sulfate

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Abstract

This paper presents a structural and vibrational study of a new compound, namely, monohydrate 1,5-pentanediammonium hydrogen sulfate ($\text{NH}_3(\text{CH}_2)_5\text{NH}_3(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$). The X-ray crystal structure shows that this compound crystallizes in the monoclinic system, space group $P2_1/c$, with the lattice parameters $a = 9.2250(2) \text{ \AA}$, $b = 7.7540(4) \text{ \AA}$, $c = 20.8520(1) \text{ \AA}$, $\beta = 116.23(3)^\circ$, $V = 1337.97(10) \text{ \AA}^3$, and $Z = 4$. From the structural investigations, it is found that the studied compound is built by infinite anionic ribbons parallel to the “ a ” axis. These ribbons form tunnels in which organic cations are inserted. Infrared (IR) spectrum of the compound in the $300\text{--}4000 \text{ cm}^{-1}$ spectral region is reported. A tentative assignment of the observed bands, supported by a molecular orbital semi-empirical calculation, is given.

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1. 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 groups. 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 of interest as solid electrolytes [1]. Few studies realized on the organic sulfate have been concerned with organic diamine chains [2,3]. Yet, to our knowledge, no one has been interested in long linear chain diammonium organic sulfate.

In the present paper, we are interested in the structural and vibrational study of a new long linear chain diamine organic sulfate; namely, monohydrate 1,5-pentanediammonium hydrogen sulfate ($\text{NH}_3(\text{CH}_2)_5\text{NH}_3(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$) (DAP-HS) $\text{NH}_3(\text{CH}_2)_5\text{NH}_3(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$. The structural part of this study, deals with the experimental work which includes the chemical preparation, the structural determination and the related results. In the vibrational part, we present the in-

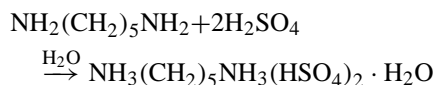
frared (IR) spectrum of the studied DAP-HS compound in the $300\text{--}4000 \text{ cm}^{-1}$ spectral region. To differentiate the observed bands related to the vibrational modes of the organic chain skeleton from those of $[\text{HSO}_4]^-$ and H_2O entities and to give a tentative assignment of the observed bands, we have performed a semi-empirical SCF calculation of the vibrational frequencies of a molecular cluster modeling the organic chain in its crystalline environment.

2. Structural study

2.1. Experimental

2.1.1. Chemical preparation and characterization

Single crystals of DAP-HS were grown by slow evaporation of aqueous solution containing a 1:2 stoichiometric mixture of 1,5-diaminopentane and sulfuric acid with the following reaction:



The resulting solution was allowed to evaporate slowly at room temperature. After several days, colorless transparent

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parallel epipedic single crystals of DAP-HS were obtained. The elemental contents were checked by chemical analysis. Measured by floatation in toluene, the average value of the DAP-HS density was found to be about 1.62 g cm^{-3} which is in agreement with the calculated one 1.57 g cm^{-3} .

2.1.2. Structural determination

A suitable single crystal was carefully selected under a polarizing microscope and mounted at the end of a thin glass fiber. Crystal structure determination was performed using a Kappa CCD diffractometer which uses graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters, optimized by least-squares refinement, were calculated and refined using indexation of collected intensities. The total number of measured reflections was 3533 among which 996 were independent and 832 had an intensity $I > 2\sigma(I)$. The structure of the DAP-HS compound was developed in the centro-symmetric space group $P2_1/c$. Sulfur atom positions were located using SHELXS-97 [4]. The oxygen (O), carbon (C), and nitrogen (N) atom positions, were deduced from difference Fourier maps during the refinement with an adopted version of SHELXL-97 program [5]. The hydrogen atoms were fixed geometrically. The final discrepancy factors R_1 and wR_2 were found to be 0.0484 and 0.0959, respectively. The residual electron density ranged between -0.195 and 0.170 e\AA^{-3} . The crystallographic data and some details of the structural refinement are summarized in Table 1.

2.2. Results and discussion

The final atomic positional and thermal parameters of the DAP-HS are listed in Table 2. In Fig. 1, a projection of the crystal structure in the (b and c) plane is presented. This projection shows that organic cations are inserted in anionic tunnels built of infinite ribbons parallel to the (100) direction. The $[\text{HSO}_4]^-$ anions are associated together in pairs through one $\text{O-H}\cdots\text{O}$ hydrogen bond and form $[\text{H}_2\text{S}_2\text{O}_8]^{2-}$ dimers. These dimers are themselves connected via water molecules giving $[\text{H}_4\text{S}_4\text{O}_{16}\cdot 2\text{H}_2\text{O}]^{4-}$ clusters. These clusters are interconnected through two hydrogen bonds building the infinite ribbons (Fig. 2). Each organic chain is implicated in six $\text{N-H}\cdots\text{O}$ hydrogen bonds with six $[\text{HSO}_4]^-$ entities. The geometrical parameters of the various entities involved in the DAP-HS structure are shown in Table 3. The existence of two distinct S atoms, S(1) and S(2), having tetrahedral coordination can be observed in this table. The S–O bond lengths range from 1.429(2) to 1.537(3) \AA in $[\text{HS}(1)\text{O}_4]^-$ and from 1.421(2) to 1.553(2) \AA in $[\text{HS}(2)\text{O}_4]^-$. The corresponding O–S–O angle values vary, respectively, from 104.4(1) to 114.3(1) $^\circ$ and from 102.5(1) to 112.8(1) $^\circ$. Distortion indices of various distances and angles in the $[\text{HSO}_4]^-$ anion, calculated using the Baur's method [6], are $\text{ID}(\text{S}(1)\text{--O}) = 0.0194$, $\text{ID}(\text{O--S}(1)\text{--O}) = 0.0290$, $\text{ID}(\text{O--O}) = 0.0058$, $\text{ID}(\text{S}(2)\text{--O}) = 0.0307$, $\text{ID}(\text{O--S}(2)\text{--O}) = 0.0300$,

Table 1

Summary of crystal data, intensity measurement, and final results for the DAP-HS compound

Crystal data	
Formula:	$\text{NH}_3(\text{CH}_2)_5\text{NH}_3 (\text{HSO}_4)_2\cdot\text{H}_2\text{O}$
F_w	316.35
Crystal system:	monoclinic
Space group:	$P2_1/c$
a	$9.2250(2) \text{ \AA}$
b	$7.7540(4) \text{ \AA}$
c	$20.8520(10) \text{ \AA}$
β	$116.230(3)^\circ$
V	$1337.97(10) \text{ \AA}^3$
Z	4
$F(000)$	672
$\rho_{\text{cal}}/\rho_{\text{meas}}$	$1.57/1.62 \text{ g cm}^{-3}$
Linear absorption factor:	$\mu(\text{Mo K}\alpha) = 0.438 \text{ mm}^{-1}$
Morphology:	parallelepipedic
Intensity measurement	
Temperature:	293(2) K
Diffractometer:	Kappa CCD
Monochromator:	graphite plate
Wavelength:	Mo K $\alpha = 0.71069 \text{ \AA}$
Scan mode:	ω/θ
θ range:	$6.11\text{--}21.47^\circ$
Measurement area:	$-9 \leq h \leq 9; -7 \leq k \leq 7; -21 \leq l \leq 21$
Number of scanned reflections:	3533
Number of independent reflections:	996
Number of observed reflections ($I > 2\sigma(I)$):	832
Structure determination	
Structure determination:	SHELXS-97 [4]
Structure refinement:	SHELXL-97 [5]
wR_2/R_1 :	0.0959/0.0484
Goodness-of-fit, S , on F^2 :	1.017
$w = 1/[\sigma^2(F_o)^2 + (0.0629P)^2]$; $P = F_o^2 + 2F_c^2/3$	
Final Fourier residual:	min (-0.195 e\AA^{-3}), max (0.170 e\AA^{-3})

and $\text{ID}(\text{O--O}) = 0.0076$. These values show a strong distortion of the S–O distances compared to O–O ones. The pentanediammonium cation is found to be in the fully all-*trans* conformation and no mixture of *cis*–*trans* conformational is observed as in the same chain containing

Table 2

Atomic coordinates and U_{eq} (\AA^2) of the DAP-HS compound

Atoms	x	y	z	U_{eq}
S(1)	0.1666(1)	0.9205(9)	0.3594(4)	0.0383(5)
S(2)	0.7453(1)	1.3763(9)	0.3836(4)	0.0377(5)
O(11)	0.3377(3)	0.8345(2)	0.3890(1)	0.0527(8)
O(12)	0.0548(3)	0.7813(2)	0.3287(1)	0.0458(8)
O(13)	0.1600(3)	1.0498(2)	0.3093(1)	0.0493(8)
O(14)	0.1529(3)	0.9952(3)	0.4202(1)	0.0480(8)
O(21)	0.5996(3)	1.3226(3)	0.8277(1)	0.0487(7)
O(22)	0.8547(3)	1.4358(3)	0.9013(1)	0.0547(8)
O(23)	0.7199(3)	1.5209(2)	0.7780(1)	0.0520(8)
O(24)	0.8254(3)	1.2370(2)	0.8073(1)	0.0522(8)
O(W)	0.5600(3)	1.0597(3)	0.4443(1)	0.0605(9)
N(1)	0.2957(4)	1.3898(3)	0.7026(2)	0.0468(9)
N(2)	0.1332(4)	1.4297(3)	0.3185(1)	0.0404(9)
C(1)	0.3611(5)	1.3814(4)	0.6492(2)	0.0477(9)
C(2)	0.2324(5)	1.4105(4)	0.5737(2)	0.0464(9)
C(3)	0.3011(5)	1.4158(4)	0.5204(1)	0.0469(9)
C(4)	0.1792(4)	1.4341(4)	0.4448(2)	0.0438(9)
C(5)	0.2539(4)	1.4194(4)	0.3933(2)	0.0375(9)

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

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