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Synthesis, structural study, IR spectroscopic investigation and thermal behaviour of bis(3-ammoniopropyl) ammonium sulfate monohydrate

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ABSTRACT

Crystals of bis(3-ammoniopropyl)ammonium sulfate monohydrate: ($C_6H_{20}N_3$)$SO_4HSO_4.H_2O$ were prepared and grown at room temperature by slow evaporation method. Crystal structure, IR spectroscopy and thermal behaviour were investigated. The structure of this new organic sulfate was determined by single crystal X-ray diffraction technique. The title compound crystallizes in the orthorhombic space group Pbcn. It is composed of dimers resulting from the association of SO_4^{2-} and HSO_4^-anions with water molecules. The inorganic arrangement shows cavities where the organic molecules are located to create a three-dimensional framework.

Keywords: Organic sulfate; Crystal structure; Thermal analysis; IR investigation.

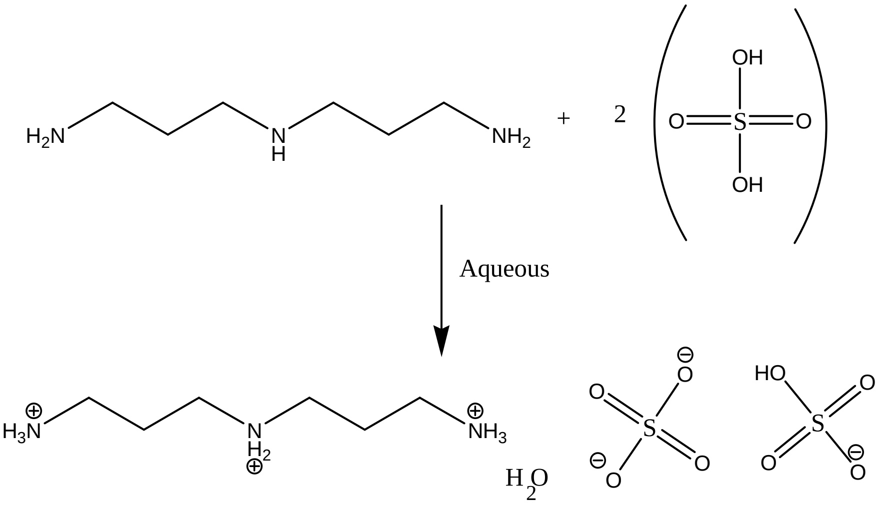
INTRODUCTION

The structural study of several atomic arrangements of organic sulfates has shown the important role of the sulfate anion in the construction of hydrogen bonds networks. In HSO_4^- or SO_4^{2-} anions, the oxygen atoms, as acceptors, provide a strong contribution to the construction of channels or layers which capable to encapsulating polarisable organic molecules.Such a crystal engineering route combines the cohesion and flexibility of anionic inorganic lattices with the enhanced polarizability of organic entities [1]. Beside non-linear optical properties [2], some sulfates exhibit phase transitions, like ($C_6H_{18}N_2$)$SO_4.H_2O$ [3] and ($C_4H_{12}N$)$_2SO_4$[4]. The present study is part of a systematic investigation of the interaction of various amines with sulphuric acid[5-9]. This study allowed the finding of a new organic sulfate, ($C_6H_{20}N_3$) $SO_4.HSO_4.H_2O$.Chemical preparation; crystal structure, thermal behaviour and IR spectrum of this new compound are discussed.

EXPERIMENTAL SECTION

Synthesis

The synthesis of bis(3-ammonio-propyl)ammonium sulfate monohydrate is made in two steps: First, 400 mLof an aqueous solution of sulfuric acid (10^{-1}M) is prepared from the dilution of 2.24mL H_2SO_4(96 %, d = 1.84g/cm^3). The obtained solution is then neutralized by adding drop wise the bis(3-amino-propyl)amine, under magnetic stirring. Second, the resulting solution is then evaporated at room temperature for several weeks. Other syntheses were made by changing the volumes, the pH, the concentration and the rate of evaporation. In all cases, the evaporation of the solutions led, to prismatic and transparent single crystals suitable for a structural study. The preparation of this compound is reproducible and made according to the reaction:



Scheme 1: Synthesis of $(C_6H_{20}N_3)SO_4HSO_4.H_2O$ compound

Crystal structure analysis

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 CAD4 diffractometer which uses graphite monochromatized Mo kα radiation ($\lambda = 0.71073$Å). The unit cell parameters were calculated and refined using indexation of collected intensities. The total number of measured reflections was 1962 among which 1688 were independent and 1336 had an intensity $I>2\sigma(I)$. The structure of the$(C_6H_{20}N_3)SO_4.HSO_4.H_2O$ compound was developed in the P*bcn* space group. Sulfate and oxygen atom positions were located by using SHELXS-97 [10]. The carbon (C), nitrogen (N), and hydrogen (H) atom positions, were deduced from difference fourier maps during the refinement With SHELXL-97 program [10]. All hydrogen atoms were located in a difference Fourier map. Anisotropic displacement parameters for all the other atoms were allowed to vary. The anisotropies were found to be moderate. The average density, measured at room temperature using toluene as pycnometric liquid, is in agreement with the calculated density. The final discrepancy factorsR and Rw were found to be 0.0424 and 0.1151 respectively.Crystal data and the results of the final structure refinement are summarized in table 1.

Infrared spectroscopic measurement

IR spectrum was recorded at room temperature with a Bio-Red FTS 6000 FTIR spectrometer, from 4000 to 400 cm^{-1} with a resolution of about 3 cm^{-1}. A thin transparent pellet made by compacting an intimate mixture obtained by shaking 1 mg of the sample in 200 mg of KBr.

Thermal behavior

Setaramthermoanalyser, TG-DTA92, was used to perform thermal treatment on sample of $(C_6H_{20}N_3)SO_4HSO_4.H_2O$. TG-DTA thermograms obtained with 20.56 mg sample in an open platinum crucible. In this technique, sample was heated in air with 5°C/min heating rate; an empty crucible was used as reference.

RESULTS AND DISCUSSION

Structure description

The structure of the bis(3-ammonio-propyl)ammonium sulfate monohydrate can be described by a three-dimensional framework. The anions SO_4^{2-} and HSO_4^- are associated with water molecules to form dimer.The projection of the inorganic entities along the c-axis, shows that these dimers are arranged to form cavities with 6.8068 Å edge(Fig.1).The organic molecules are located in these cavities to form the three-dimensional arrangement (Fig. 2).

The S-O distances vary between 1.444(2) and1.502(1) Å with an average of 1.466Å. Slight differences between the S-O distances are due to the different environments of the oxygen atoms insulfate anions. Indeed, The atom O(1), not engaged in an hydrogen bonding, has the shortest S-O distance. The atoms O(3) and O(2) committed each in a single hydrogen bond have longer distances, while the longest one corresponds to S-O(4) coordinated with an H atom. The length of the S-O bonds depends on the number and the strength of hydrogen bonds in which the oxygen atom is engaged. This has been noted in other structures containing the sulfate or phosphate anions[11, 12].Table2gives the geometric parameters of the sulfate anion.Each SO_4 tetrahedron is surrounded by three organic groups issuing four hydrogen bonds. In general case, the sulfate anions involved with organic molecules, containing nitrogen or (and) oxygen atoms, are surrounded by eight to ten hydrogen bonds [13]. The calculated average distortion indices [14], corresponding to bond distances and angles in the SO_4 tetrahedron (Table 2), shows that the distortion of S-O is more pronounced than the O-O distances and the O-S-O angles. So, the sulfate group has a regular tetrahedral arrangement of oxygen atoms with a slight displacement of the sulfur atom from the gravity center. Each sulfate anion is linked, by hydrogen bonds, to three organic molecules, one sulfate anion and one water molecule (Fig.3).

Table 1: Crystal data and structure refinement of $(C_6H_{20}N_3)SO_4HSO_4.H_2O$

Chemical Formula	$(C_6H_{20}N_3)SO_4\ HSO_4.H_2O$
Molar Mass	345.39 g/mol
Temperature	293 (2) K
Crystal system	Orthorhombic
Space Group	Pbcn
Unit cellparameters	*a = 8.9689(3) Å* *b = 10.2423(3) Å* *c = 16.5600(4) Å*
Volume/Z	1521.24(8) $Å^3$/4
$\rho_{calculated}$ /$\rho_{measured}$	1.568 $g.cm^{-3}$ / 1,543 $g.cm^{-3}$
Absorption Coefficient	0.394 mm^{-1}
F(000)	736
Crystal dimensions	0.38×0.29×0.23 mm^3
Color/Shape	Colorless/Prismatic
Diffractometer	CAD4
Radiation, monochromator (graphite)	Mo (□$_{K□}$ = 0.71073 Å)
Scan Mode	□ω□□□
Theta range (θ)	2.46–24.96°
h, k, l range	$0 \leq h \leq 10$, $0 \leq k \leq 12$, $-2 \leq l \leq 18$
Program data reduction	XCAD4
Number of reflectionsmeasured	1688
Number of reflectionsobserved	1336
Absorption correction	None
Structure resolution	Direct Method: SHELXS [6]
Structure refinement	Based on F^2: SHELXL [6]
Constraints/independentparameters	0/136
Extinction coefficient = 0.064(5)	S = 1.08
Final R_1 indices [$I>2\sigma(I)$]	0.0424
wR_2	0.1241
$\Delta\rho_{max} =$ 0.332 e/$Å^3$	$\Delta\rho_{min}$ = -0.344 e/$Å^3$

The protonation of the symmetric molecule, bis(3-amino-propyl) amine, according to the experimental protocol described previously, led to thebis(3-ammonio-propyl) ammonium cation with protonation of the three nitrogen atoms.The nitrogen atom N(2) of this cation is located in special position.

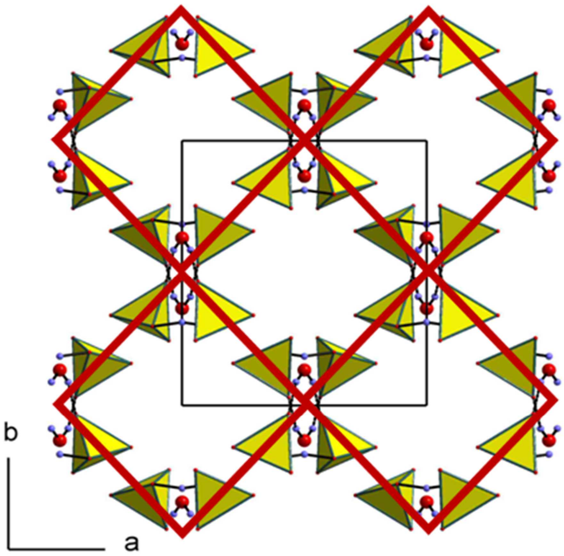


Figure 2: Projection along the *c*axis of the anionic arrangement

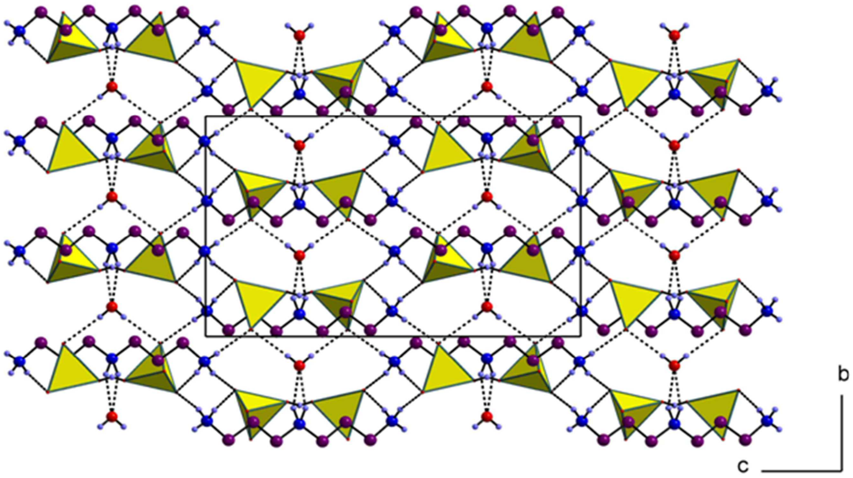


Figure 2: Projection along the *aaxis* of the atomic arrangement (for clarity, the H atoms of carbon are omitted; H-bonds are represented by *dashed lines*)

Table 2: Bond lengths (Å) and angles (°) in sulfate anion

SO_4^{2-} tetrahedron				
S	O(1)	O(2)	O(3)	O(4)
O(1)	**1,444(2)**	2,384(2)	2,414(3)	2,366(3)
O(2)	110,7(1)	**1,453(2)**	2,379(3)	2,420(2)
O(3)	111,9(1)	109,1(1)	**1,468(2)**	2,409(3)
O(4)	106,8(1)	109,9(1)	108,4(1)	**1,502(2)**
DI(S–O) = 0,0335	*DI(O–O) = 0,00793*		*DI(O–S–O) = 0,0124*	

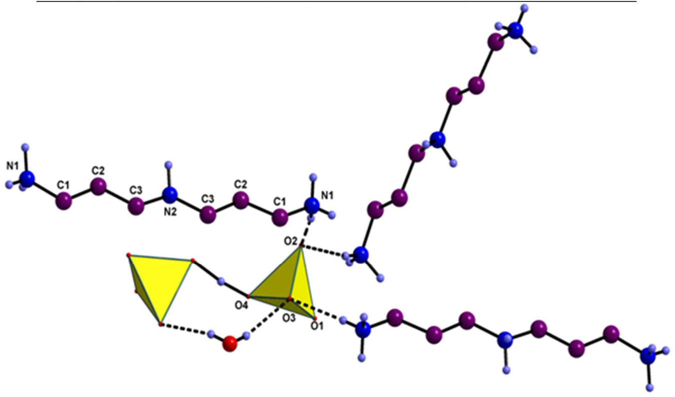


Figure 3: Each sulfate anion is linked, by hydrogen bonds, to three organic cations, one sulfate anion and one water molecule (for clarity, the H atoms of carbon are omitted; H-bonds are represented by *dashed lines*)

Nitrogen atoms of NH_3groups, share through their three protons, three hydrogen bondsN-H···Owith oxygen atoms of sulfate anions(Fig.4). The nitrogen atom of the NH_2 groupment, share through its two protons, two hydrogen bondsN-H···O with oxygen atoms of water molecule. Each organic cation is surrounded by six sulfate anions and one water molecule. The cation's distances and angles are given in table 3. C–C and C–N distances vary between 1.481(3) and1.511(3) Å with an average distance: 1.496 Å. The angles vary from 110.1(2) to 114.6(3)° with an average value of 111.45°. All these values are comparable with those found in known structures[15, 16].

Previous works shows the important role of hydrogen bonds in the stability of the three dimensional arrangement. The geometric characteristics of these bonds are reported in table 4. N-H···O bonds connect the different sulfate anions to organic cations. The six N-H···O hydrogen bonds are considered strong referring to the H···O and N···O distances [17, 18]. In fact, H···O and NΛO distances vary respectively between1.96 (3) – 2.08(3) Å and 2.716 (3) – 2.943(3) Å. The O···H–N angles, ranging from 123.7(1) to 174(3)°, show a strong linearity character of the hydrogen bonding. The cohesion and stability of the crystalline building are maintained by the three-dimensional network of hydrogen bonds.

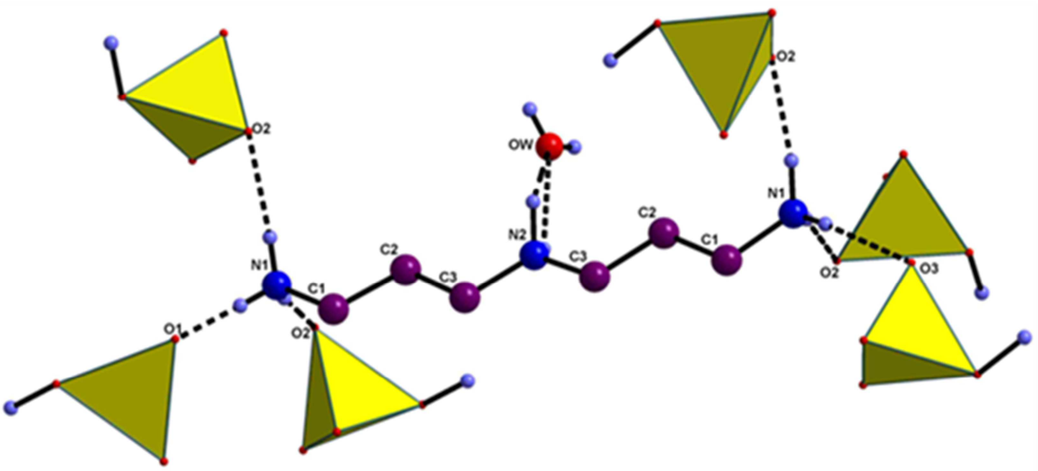


Figure 4:Each nitrogen atoms of NH_3 groups, share through their three protons, three Hydrogen bonds N–H···O, with oxygen atoms of sulfate anions (for clarity, the H atoms of carbon are omitted; H-bonds are represented by *dashed lines*)

Table 3: Geometric parameters of the organic cation

Bond lengths (Å)		**Bond angles (°)**	
		C(3)—N(2)—C(3)#1	114,6(3)
N(2)—C(3)	1,481(3)	C(3)—N(2)—H(2C2)	120,31(10)
N(2)—C(3)#1	1,481(3)	C(3)#1—N(2)—HN2	109,49(10)
N(2)—H(N2)	0,960(2)	N(1)—C(1)—C(2)	110,1(2)
C(1)—N(1)	1,485(3)	N(1)—C(1)—H(1C1)	107,5(16)
C(1)—C(2)	1,511(3)	C(2)—C(1)—H(1C1)	108,9(17)
C(1)—H(1C1)	0,94(3)	N(1)—C(1)—H(2C1)	108,1(16)
C(1)—H(2C1)	0,97(3)	C(2)—C(1)—H(2C1)	111,4(16)
		H(1C1)—C(1)—H(2C1)	111(2)
		C(1)—N(1)—H(2N1)	118,2(16)
N(1)—H(2N1)	0,99(3)	C(1)—N(1)—H(3N1)	113(2)
N(1)—H(3N1)	0,76(4)	H(2N1)—N(1)—H(3N1)	97(3)
N(1)—H(1N1)	0,88(3)	C(1)—N(1)—H(1N1)	108(2)
		H(2N1)—N(1)—H(1N1)	111(2)
		H(3N1)—N(1)—H(1N1)	110(3)
		C(3)—C(2)—C(1)	110,3(2)
C(2)—C(3)	1,507(3)	C(3)—C(2)—H(1C2)	107,6(19)
C(2)—H(1C2)	0,88(3)	C(1)—C(2)—H(1C2)	114,4(19)
C(2)—H(2C2)	0,95(3)	C(3)—C(2)—H(2C2)	111,9(18)
		C(1)—C(2)—H(2C2)	110,1(18)
		H(1C2)—C(2)—H(2C2)	102(2)
		N(2)—C(3)—C(2)	110,9(2)
C(3)—H(1C3)	0,95(3)	N(2)—C(3)—H(1C3)	105,9(17)
C(3)—H(2C3)	0,90(3)	C(2)—C(3)—H(1C3)	114,2(17)
OW—H(10)	0,76(4)	N(2)—C(3)—H(2C3)	107(2)
		C(2)—C(3)—H(2C3)	111,7(19)
		H(1C3)—C(3)—H(2C3)	107(3)

Table 4: Bond lengths (Å) and angles (°) in the Hydrogen-bonding scheme [a]

	N(O)–H	H…O	N(O) …O	N(O)–H…O
N(1)—H(1N1)…O(2^{i})	0,88(3)	2,08(3)	2,943(3)	165(3)
N(1)—H(2N1) …O(2^{ii})	0,99(3)	1,96(3)	2,943(3)	171(2)
N(1)—H(3N1) … (3)	0,76(3)	2,05(4)	2,802(3)	174(3)
N(2)—H(N2) …O(W^{iii})	0,960(2)	2,062(3)	2,716(5)	123,7(1)
OW—HW…O(3^{iv})	0,76(4)	2,07(4)	2,800(3)	163(5)

[a] *Symmetry operators:*
(i) : –x+1/2, y+1/2, z *(ii):* -x+1, -y+2, -z+1 *(iii) :* -x+1/2, -y+5/2, z+1/2
(iv) : -x+1, y, -z+1/2

Thermal behaviour

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the title compound are presented in figure 5.The TG curve reveals no loss of mass in the heating range 22-83ºC. However, it shows a significant loss between 83 and 143°C, corresponds to the departure of one water molecule(% water: calculated 5.09 %, observed 5.01%).This loss of mass is accompanied by two endothermic phenomena on the ATD curve at 103 and 126°C.On the other hand three other endothermic effects are given by the ATD curve. The first one at 168°C probably corresponds to a transition, the second peak at 208ºC, indicates the fusion of the sample. The third one, observed at 279°C, corresponds to the degradation of the compound.

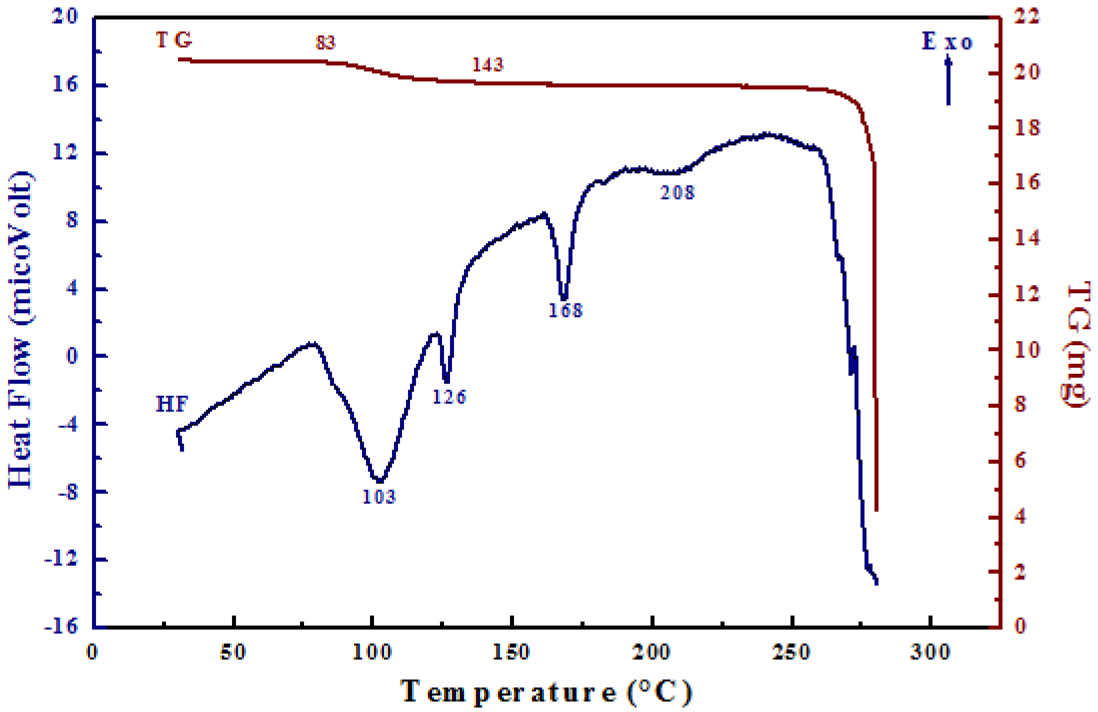


Figure 5: TG-DTA thermograms of $(C_6H_{20}N_3)SO_4HSO_4.H_2O$

Infrared spectroscopic investigation

To make a qualitative assignment of IR peaks to vibrational modes, we examine the modes and frequencies observed for HSO_4^- anion. The ideal, five atom SO_4 tetrahedral group exhibit T_d symmetry. Thus, there are nine vibrational modes. Only four of which are independent: $\nu_1(A_1) = SO_4$ symmetric stretch; $\nu_2(E) =$ O–S–O bend; $\nu_3(F_2) = SO_4$ asymmetric stretch and $\nu_4(F_2) =$ O–S–O bend. The ν_1 and ν_3 stretching modes are observed in 1200-900 cm^{-1}, whereas the ν_2 and ν_4 bending modes are distinguished in the 600-400 cm^{-1} domain.The average frequencies [10], respectively, observed for these modes are: 981, 451, 1104 and 614 cm^{-1}[19, 20].

The influence of the addition of one proton to the anion can be understood through a two-step process. First, in HSO_4, one of the oxygen atoms is replaced with a hydroxyl group with point mass. This reduces the symmetry from T_d to C_{3v}, and eliminates degeneracies such that there are six rather than four independent vibrational modes. Second, the vibrations associated with the hydroxyl group are considered. There should be three such modes: O–H stretching, S–O–H in-plane bending and S–O–H out-of-plane bending (or torsion). With regard to the compound including HSO_4 tetrahedron the two stretching vibrations, asymmetric and symmetric of SO_3 group, are observed respectively at 1087 and 982 cm^{-1}; while that related to S–O(H) occurs at 847 cm^{-1}[21]. Then, we attribute the three intense bands at 1072, 934 and 899 cm^{-1} to those three vibrations in the compound. The splitting of F_2 stretching mode of SO_4, into two intense components at 1072 cm^{-1}(E) and 934 cm^{-1}(A_1) corroborates the symmetry lowering of HSO_4 in the solid state. On the other hand, bending modes of SO_3 groups are observed at lower frequencies. The two bands; medium at 587 cm^{-1} and strong at 544 cm^{-1}, corresponds to the asymmetric $\delta_{as}(SO_3)$ and symmetric deformation $\delta_s(SO_3)$. The δ_sOSO(H) appear as one weak band at 447 cm^{-1}. The shoulder one at 803 cm^{-1} and the medium at 1207 cm^{-1}, corresponds respectively to the out-of-plane bending γ(SOH) and to the in-plane bending δ(SOH) vibrations. It is to be noted that IR spectra doesn't confirm the lowermost local symmetry C_1 deduced from RX study; because vibrations corresponding to E symmetry are not splitted. This suggests a higher symmetry of SO_3 group in the HSO_4 anion. Indeed a study of geometrical characteristic of the SO_3 group showspseudo-symmetry C_{3v} in agreement with the IR spectrometric investigation.

The remaining observed bands in the spectrum can be assigned to CH_2, NH_3^+, NH_2^+, OH and skeletal symmetric and asymmetric stretching and deformation modes [19]. The domain of high frequencies in the spectrum is characterized by N(C, O)–H stretching, combination bands and harmonics, while the lower one corresponds to the bending and to the external modes. The IR spectrum of the compound is depicted in Fig. 6.A broad band extending from 3700 to 2153 cm^{-1} is observed in the IR spectrum. This broad band must be due to the symmetric and asymmetric stretching modes of NH_3, CH_2, NH_2 and OH. The “indicator band” at 2028 cm^{-1} in the IR spectrum is an important indication of the presence of NH_3^+ in the compound. This band is a combination of the asymmetric deformation vibration and torsion vibration of the NH_3^+ group [22, 23].

NH_3 bending, rocking and torsion may occur in the ranges 1689–1598, 959–841 and 551–513 cm^{-1}. The shifting of the stretching and bending vibrations of the NH_3 group from the free state value confirms the formation of hydrogen bonds of varying strengths in the crystal. Skeletal vibrations may occur in the ranges 1567-1477, 1258-1227 and 821–798 cm^{-1}. Frequencies in the range 1453–1297 cm^{-1} are attributed to ω (CH_2), δ (CH_2), ρ (CH_2) and δ (OH).

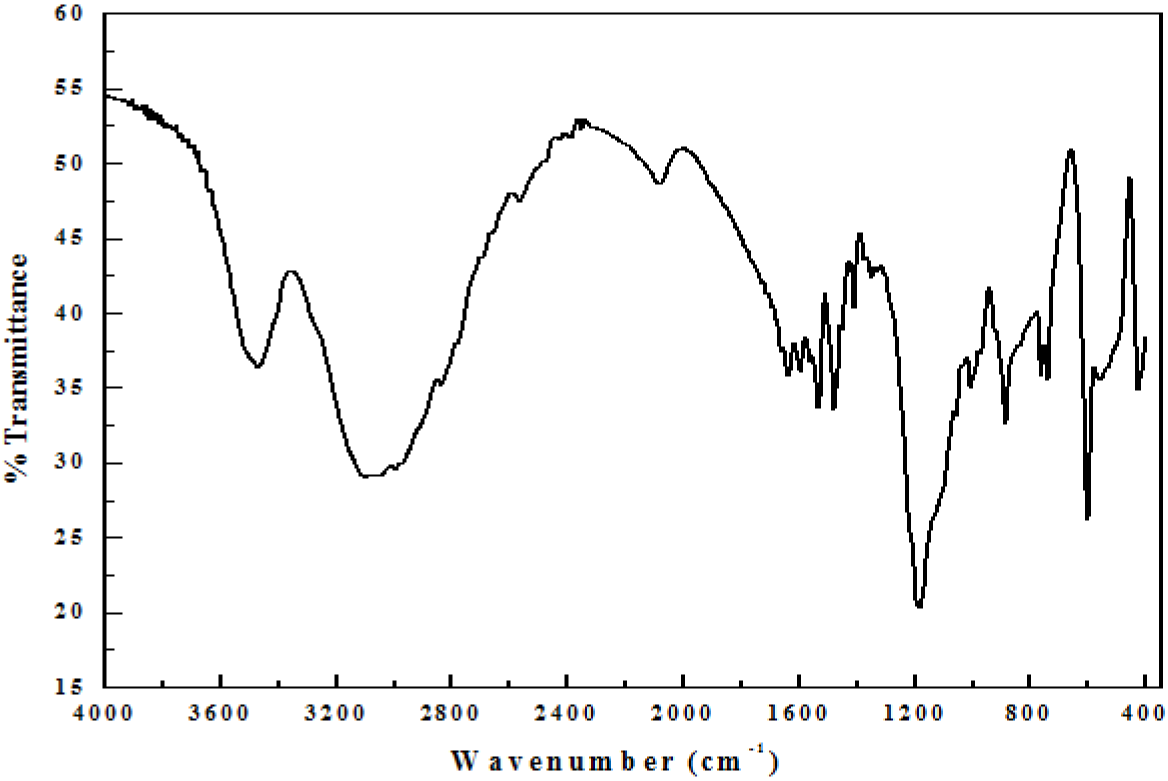


Figure 6:IR spectrum of ($C_6H_{20}N_3$)$SO_4HSO_4.H_2O$.

CONCLUSION

A new organic sulfate, ($C_6H_{20}N_3$) $SO_4HSO_4.H_2O$ was obtained by slow evaporation method. It has been characterizedby X-ray single crystal diffraction, differential thermal analysis, thermogravimetry and infrared spectroscopy. The structure consists of a three dimensional arrangement. Sulfate anions are associated with water molecules via hydrogen bonds, to form dimer. The thermal evolution of the title compound has been followed by TGA–DTA analysis. It shows that the compound crystallizes with one water molecule. The DTA curve shows one endothermic peakat 168°C which may be ascribed to a structural phase transition. Infrared spectroscopy confirms the results given by the structure refinement. In general, it is believed that this work has contributed to new horizons for the development of new organic sulfates.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 1444106.Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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