

Crystal Structure and Physicochemical Properties of 2-Diisopropylammonium Ethylammonium Sulfate Dihydrate

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ABSTRACT

A new organic sulfate ($C_8H_{22}N_2$) $SO_4 \cdot 2H_2O$ denoted DPAES is obtained by interaction of H_2SO_4 with the organic molecule 2-[Diisopropylamino] ethylamine. We describe its crystallographic and structural features. DPAES is triclinic, $P\bar{1}$, with the lattice parameters $a = 6.8841(2)\text{\AA}$, $b = 8.4966(2)\text{\AA}$, $c = 12.0804(3)\text{\AA}$, $\alpha = 81.824(1)^\circ$, $\beta = 88.007(1)^\circ$, $\gamma = 78.649(1)^\circ$, $V = 685.72(3)\text{\AA}^3$, and $Z = 2$. Its atomic arrangement is described as inorganic chains of SO_4^{2-} units and water molecules, these chains are interconnected by organic groups so as to build layers parallel to the (001) planes. The IR data of DPAES are reported and discussed according to the theoretical group analysis and by comparison with IR results of similar compounds. The coupled TG-DTA thermal study shows the departure of two water molecule, confirming the hydrated character of this compound.

Keywords: Chemical Preparation; Crystal Structure; Thermal Behavior; Organic Sulfate; Infrared and Raman Spectroscopy; NMR Spectroscopy

1. Introduction

Studies of charged species have become an active research area in organic chemistry, biology and in crystal engineering. Their role as structural agents is important in molecular association processes of proteins, nucleic acids and in creation of non centrosymmetric crystals for quadratic non-linear optics [1-4]. In this type of materials, the non-linear optical response can be explained primarily by an anharmonic distortion of the electron density distribution inside the molecules due to the intense electric field of an applied optical pulse [5]. The herringbone motif of cations in such non centrosymmetric structures depends upon the ability of host anions to aggregate [6]. The family of compounds which combine the cohesion of sulfate anions with enhanced polarizability of organic molecules was clearly illustrated. The most striking result is the high number of hydrogen bonds to these anions, which results in the sulfate being surrounded by a cloud of hydrogen donors [7]. The present work continues a series of investigations into the factors influencing the dimensions of sulfate anion—organic cation interaction. We report here the chemical preparation, crystallographic features, thermal behavior, and IR analysis of a new

new organic sulfate, ($C_8H_{22}N_2$) $SO_4 \cdot 2H_2O$.

2. Experiment

2.1. Chemical Preparation

Single crystals of DPAES were prepared by slow evaporation, at room temperature, of an aqueous solution of ($C_8H_{20}N_2$) and sulfuric acid (H_2SO_4) in the stoichiometric ratio. Schematically the reaction is (**Figure 1**):

When the most of solution is evaporated, large colorless and prismatic crystals appear deep down the vessel.

2.2. Investigation

The title compound has been studied by various physico-

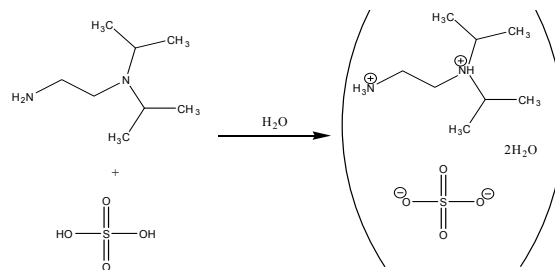


Figure 1. Chemical synthesis of ($C_8H_{22}N_2$) $SO_4 \cdot 2H_2O$.

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chemical methods: NMR and Infrared spectroscopy, X-ray diffraction and thermal analysis.

2.2.1. NMR

The ^{13}C NMR spectrum was recorded with a Bruker ASX-300 solid-state high resolution spectrometer operating at 81 MHz with a 8 kHz spinning speed. Sample was packed in a 4 mm zirconia rotor. Pulses of 3 μs duration were employed with a recycle delay of 5 s between pulses. Spectrum was recorded at room temperature.

2.2.2. Thermal Analysis

Setaram thermoanalyser, TG-DTA92, was used to perform thermal treatment on samples of the DPAES. TG-DTA thermograms were obtained with 19.47 mg sample in an open platinum crucible, heated in air with 5°C min^{-1} heating rate, from room temperature to 300°C , an empty crucible was used as reference.

2.2.3. Infrared and Raman Spectroscopy

IR and Raman spectra were recorded at room temperature with a Biorad FTS 6000 FTIR spectrometer and a multichannel X-Y Dilor spectrometer instrument using the 514.5 nm radiation from Spectra-Physics model 2000 argon ion laser, respectively over the wavenumbers $4000 - 400 \text{ cm}^{-1}$ and $4000 - 70 \text{ cm}^{-1}$. Thin transparent pellet made by compacting an intimate mixture obtained by shaking 2 mg of the sample in 100 mg of KBr, and polycrystalline sample, sealed in glass tube served to prepare the IR and Raman spectra. The resolution is about 4 cm^{-1} in IR and 2 cm^{-1} in Raman.

2.2.4. X-Ray Diffraction

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 $k\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters were calculated and refined using indexation of collected intensities. The total number of measured reflections was 10,247 among which 5559 were independent and 4818 had an intensity $I > 2\sigma$ (I). The structure of the DPAES compound was developed in the centrosymmetric space group P-1. Sulfur and oxygen atom positions, were located using SHELXS-97 [8]. The carbon (C), nitrogen (N), and hydrogen (H) atom positions, were deduced from difference fourier maps during the refinement with SHELXL-97 program [8]. The final discrepancy factors R and Rw were found to be 0.0404 and 0.1199 respectively. The residual electron density ranged between -0.931 and $0.573 \text{ e} \cdot \text{A}^{-3}$. The crystallographic data and some details of the structural refinement are summarized in **Table 1**.

Table 1. Summary of crystal data, intensity measurements and final results for DPAES.

Compound	($\text{C}_8\text{H}_{22}\text{N}_2$) $\text{SO}_4 \cdot 2\text{H}_2\text{O}$
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	
a = 6.8841(2) \AA	$\alpha = 81.824(1)^\circ$
b = 8.4966(2) \AA	$\beta = 88.007(1)^\circ$
c = 12.0804(3) \AA	$\gamma = 78.649(1)^\circ$
V/Z	685.72(3) \AA^3
ρ_c/ρ_m	1.348/1.367 $\text{g} \cdot \text{cm}^{-3}$
Absorption coefficient, mm^{-1}	0.255
F(000)	304
Color/shape	Colorless/prismatic
Crystal dimensions (mm)	$0.22 \times 0.29 \times 0.35$
Temperature	293(2) K
Diffractometer	Kappa CCD
Monochromator	graphite
Wavelength	$\lambda K\alpha(\text{Mo}) = 0.71073 \text{ \AA}$
Theta range	$1.70^\circ - 35.87^\circ$
h, k, l range	$-10/11, -13/12, 18/19$
Number of scanned reflections	10,247
Number of independent reflections	5559
Number of observed reflections	4818 ($I > 2\sigma$)
Structure determination	SHELXS-97 [8]
Structure refinement	SHELXL-97 [8]
Number of refined parameters	231
R/Rw	0.0404/0.1199
S	1.189
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$ ($\text{e} \cdot \text{\AA}^{-3}$)	$-0.931/0.573$

3. Results and Discussion

3.1. ^{13}C NMR Study

The ^{13}C NMR spectrum of the compound contains seven peaks (**Figure 2**). Peaks at 14.17 and 18.86 ppm correspond to two non-isochronous methyl groups. However the signal at 18.38 ppm corresponds to two isochronous methyl groups. Structural analysis of this compound shows that among the four methyl groups, only two carbon atoms have the same environment. The two CH groups appear as two weak signals at 36.83 and 18.36 ppm. Finally the two ethyl groups appear in the ^{13}C NMR spectrum at 55.25 and 59.17 ppm.

3.2. Thermal Behavior

From the TGA weight loss curve (**Figure 3**) we deduce two molecules of water per formula unit (weight loss calculated 12.93%, observed 12.33%). The removal of

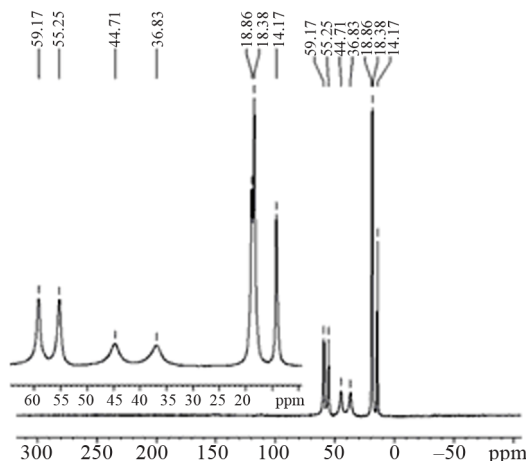


Figure 2. ^{13}C NMR spectrum of DPAES.

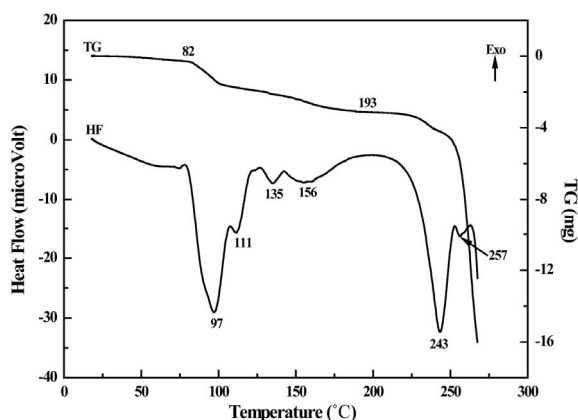


Figure 3. TG-DTA thermograms of DPAES.

the water molecule, observed in the temperature range 82°C - 193°C , is related to four endothermic peaks on the DTA curve. The stability of the compound is not very high since it decomposes in the range 193°C - 275°C . Within this temperature range, a rather bad smell escapes from the resulting black compound. The decomposition occurring with melting is confirmed by an additional thermal treatment in a separate carbolite furnace with run heating of $5^\circ\text{C}/\text{min}$ from room temperature to 300°C , the resulting compound being a black liquid.

3.3. IR and Raman Absorption Spectroscopy

A free SO_4^{2-} ion under T_d symmetry has four fundamental vibrations, the non degenerate symmetric stretching mode $\nu_1(A_1)$, the doubly degenerate bending mode $\nu_2(E)$, the triply asymmetric stretching mode $\nu_3(F_2)$, and triply degenerate asymmetric bending mode $\nu_4(F_2)$. All the modes are Raman active, whereas only ν_3 and ν_4 are active in the IR. The average frequencies observed for these modes are: 981 , 451 , 1104 and 614 cm^{-1} , respectively [9].

In the crystal, the SO_4^{2-} ion occupies lower site sym-

metry C_1 , as a result the IR inactive ν_1 and ν_2 modes may become active and the degeneracies of ν_2 , ν_3 and ν_4 modes may be removed. The degenerate ν_2 mode of the ion is found to be split into two components around 432 and 447 cm^{-1} . Appearance of this IR inactive mode can be due to the lowering of the sulfate ion from T_d to C_1 . The stretching mode ν_1 appears as one band at 982 cm^{-1} . The ν_3 mode appears as one intense band at 1097 with two shoulders at 1152 cm^{-1} and 1191 cm^{-1} . The ν_4 mode is observed as three bands at 618 , 624 and 667 cm^{-1} . The low frequency bands below 150 cm^{-1} are assigned to translational vibrations and to the lattice vibrations of SO_4^{2-} anions. The very weak lines between 80 and 150 cm^{-1} in the Raman spectrum (Figure 4), are probably due to the motion of $\text{O-H}\cdots\text{O}$ hydrogen stretching ($\nu_{\text{O-O}}$) and bending ($\delta_{\text{O-O}}$) of the infinite chains $(\text{SO}_4^{2-}, 2\text{H}_2\text{O})_n$. The shoulder and the intense Raman bands near 790 and 800 cm^{-1} are easily assigned to the $\nu_3(\text{SO}_4)$ symmetrical vibration. The $\nu_1(\text{SO}_4)$ mode is assigned to the broad peak at 874 cm^{-1} in Raman spectrum.

The remaining observed bands in the spectrum can be assigned to CH_3 , CH_2 , NH_3^+ , H_2O and skeletal symmetric and asymmetric stretching and deformation modes. The domain of high frequencies in the spectrum is characterized by $\text{N}(\text{C}, \text{O})\text{-H}$ stretching, combination bands and harmonics, while the lower one corresponds to the bending and to the external modes [10]. The IR spectrum of DPAES is depicted in Figure 5.

Frequencies in the range 1644 - 1512 cm^{-1} are attributed to $\text{N}(\text{O})\text{-H}$ bending mode. The shifting of the stretching and bending vibrations of the NH_3 and H_2O groups from the free state value confirms the formation of hydrogen bonds of varying strengths in the crystal. CH_2 and CH_3 bending, wagging and rocking may occur in the range 1474 - 1299 cm^{-1} . Frequencies in the range 944 - 728 cm^{-1} are attributed to C-C bending, NH_3 rocking and NH_3 torsion. Skeletal vibrations may occur in the ranges 1067 - 990 cm^{-1} and 531 - 492 cm^{-1} . The frequencies of the observed bands are shown in Table 2 with our proposal for their assignments.

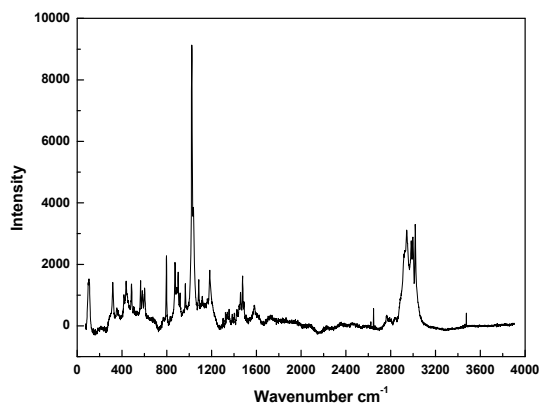


Figure 4. Raman spectrum of DPAES.

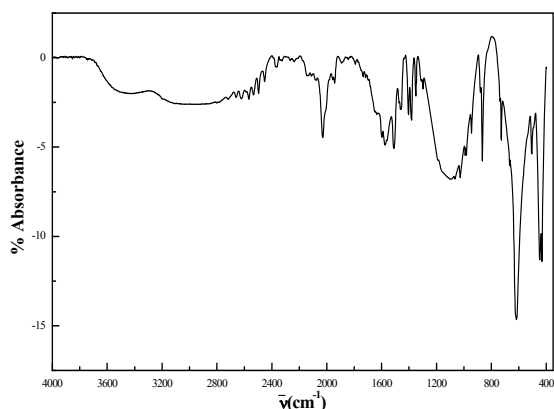


Figure 5. IR spectrum of DPAES.

Table 2. Assignment of the observed IR bands.

Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)	Assignment
3534 m		1474 w	
3253 m		1460 w	
3194 m		1404 w	
2776 m	$\nu(\text{CH})$	1382 w	$\delta(\text{CH}) + \rho(\text{CH}) + \omega(\text{CH})$
2718 w	$\nu(\text{CH}_2)$	1351 vw	$\delta(\text{CH}_2) + \rho(\text{CH}_2) + \omega(\text{CH}_2)$
2660 w	$\nu(\text{OH}_2)$	1311 vw	$\delta(\text{CH}_3) + \rho(\text{CH}_3) + \omega(\text{CH}_3)$
2622 w	$\nu(\text{NH}_3) + \nu(\text{NH})$	1299 vw	
2586 w	$\nu(\text{CH}_3)$	1191 sh	
2533 w		1152 sh	$\nu_{\text{as}}(\text{SO}_4)$
2496 w		1097 s	
2452 w		1067 s	
2367 vw		1026 s	Skeletal vibrations
2338 vw		990 m	
2326 vw	Bands of	982 m	$\nu_s(\text{SO}_4)$
2266 vw	Combination	944 m	
2237 vw	And harmonics	880 w	$\delta(\text{C}-\text{C})$
2139 vw		867 m	$\rho(\text{NH}_3)$
2110 vw		737 w	$\tau(\text{NH}_3)$
2081 w		728 m	
2029 m		667 m	
2009 m	$\delta(\text{OH}_2)$	624 sh	$\delta_{\text{as}}(\text{SO}_4)$
1957 w		618 vs	
1942 w		531 m	
1892 vw		506 m	Skeletal vibrations
1844 vw		492 w	
1792 vw	Bands of	447 vs	$\delta_s(\text{SO}_4)$
1748 vw	Combination	432 vs	
1734 vw	And harmonics		
1717 vw			
1696 vw			
1644 w			
1599 m			
1574 m	$\delta(\text{NH}_3) + \delta(\text{NH})$		
1560 m			
1512 m			

s: strong; vs: very strong; m: medium; vw: very weak; w: weak; sh: shoulder.

3.4. Structure Description

The action of sulfuric acid on the organic molecule 2-[diisopropylamino] ethylamine, leads to protonation of its two nitrogen atoms and the formation of the cation 2-[diisopropylammonium] ethylammonium. In this structure the organic cation has no local symmetry; each organic cation is surrounded by three SO_4^{2-} anions. The organic groups are grafted to the oxygen atom of the tetrahedral SO_4^{2-} via $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

The nitrogen atom N(2) binds to connect a single SO_4^{2-} group and the terminal N(1) connects one water molecule and two sulfate anions. The main geometric features of the sulfate anion, the organic cations and of the hydrogen bonds are assigned in **Tables 3** and **4**. We note that the distances N-C and C-C range from 1.483(1) to 1.529(1) Å, angles C-C-C and C-N-C vary from 109.5(1) to 113.89(8)°.

The hydrogen bonds which maintain the cohesion of atomic arrangement are characterized by O(N)···O distances ranged between 2712(2) and 2854(2) Å. The hydrogen

Table 3. Principal interatomic distances (Å) and angles (°) in DPAES.

Anion SO_4^{2-}				
S	O(1)	O(2)	O(3)	O(4)
O(1)	1.463(1)	109.84(7)	110.43(7)	108.73(8)
O(2)	2.401(1)	1.471(1)	108.93(6)	109.44(7)
O(3)	2.404(1)	2.388(1)	1.463(1)	109.45(6)
O(4)	2.388(2)	2.405(2)	2.399(1)	1.475(1)
Cation 2-[diisopropylammonium]ethylammonium				
N(1)—C(1)	1.483(1)	C(7)—C(6)—N(2)	110.2(9)	
N(2)—C(2)	1.503(1)	C(2)—N(2)—C(3)	110.69(8)	
N(2)—C(3)	1.528(1)	C(2)—N(2)—C(6)	111.92(8)	
N(2)—C(6)	1.529(1)	C(3)—N(2)—C(6)	113.89(8)	
C(2)—C(1)	1.520(1)	N(2)—C(2)—C(1)	112.97(8)	
C(3)—C(5)	1.516(2)	C(5)—C(3)—C(4)	109.5(12)	
C(3)—C(4)	1.521(2)	C(5)—C(3)—N(2)	111.18(1)	
C(6)—C(8)	1.515(2)	N(1)—C(1)—C(2)	109.7(1)	
C(6)—C(7)	1.519(2)	C(8)—C(6)—C(7)	112.62(1)	
		C(8)—C(6)—N(2)	112.5(1)	
Water molecule				
H(1W2)—OW(2)—H(2W2)			118.7(2)	
H(1W1)—OW(1)—H(2W1)			111.6(2)	

Table 4. Bond lengths (Å) and bond angles (°) in the hydrogen bonding scheme of DPAES.

	N(O)—H	H···O	N(O)—H···O	N(O)···O
OW2—H1W2···O4(i)	0.909	2.000(3)	148.48(3)	2.815(2)
OW2—H2W2···O1(ii)	0.784	1.991(3)	176.30(3)	2.774(2)
OW1—H1W1···O1	0.791	2.097	157.91	2.846(2)
OW1—H2W1···O2(iii)	0.827	2.063	159.81	2.854(2)
N2—HN2···O3(iv)	0.924	1.805(2)	166.18(2)	2.712(1)
N1—H2N1···OW2	0.794	1.973(3)	173.62(3)	2.764(1)
N1—H1N1···O2(v)	0.892	1.921(3)	172.47(3)	2.808(1)
N1—H3N1···O4(vi)	0.845	1.990(3)	167.82(2)	2.822(2)

^aSymmetry codes: (i): $x - 1, y, z + 1$; (ii): $-x - 1, -y + 1, -z + 1$; (iii): $x - 1, y, z$; (iv): $-x, -y, -z + 1$; (v): $-x, -y + 1, -z + 1$; (vi): $x, y, z + 1$.

bonding strength can be interpreted according to the $d_{O(N)\cdots O}$ distances [11]: Among the eight H-bonds, building the structure, four are considered strong, since the four $N\cdots O$ distances are less than 2.984 Å [12].

The coordination of sulfurous atoms is tetrahedral. The S–O distances and O–S–O angles spread within the respective ranges: 1.463 - 1.475 Å and 108.73 - 110.43, slight differences between the S–O distances are due to different environments of oxygen atoms of sulfate anions. The atom O(3), is engaged in a single hydrogen bond, has the shortest S–O distance, while atoms O(2) and O(4) each engaged in two hydrogen bonds have longer distances. The high sensitivity of the S–O bond distances to the strength and the number of the hydrogen bonds which may be formed, has been also noted in other crystal structures [13-15]. The calculated values of the distortion indices corresponding to the different distances and angles in the SO_4^{2-} tetrahedron are: $DI(SO) = 0.0034$; $DI(OO) = 0.0026$; $DI(OSO) = 0.004$ [16].

The structure is described by a stack of two-dimensional arrangement formed by a sulfate anion, an organic cation and two water molecules. The projection of the structure along the b axis (Figure 6), shows that anionic entities and organic cations form layers in the (a, b) plane. The stability between successive layers is performed by van der Waals interactions $C-H\cdots O$ originating from the organic cations.

The inorganic arrangement of this compound consists of SO_4^{2-} anion and two water molecules. The projection of the anionic arrangement along the b direction in Figure 7 shows that the water molecule OW1 connects SO_4^{2-} anionic groups along the a direction via two hydrogen bonds $OW1-H\cdots O1$ and $OW1-H\cdots O2$. While the second OW2 connects two tetrahedral groups, therefore the response of water molecules in the construction the anionic framework leads to the formation of chains parallel to the a direction.

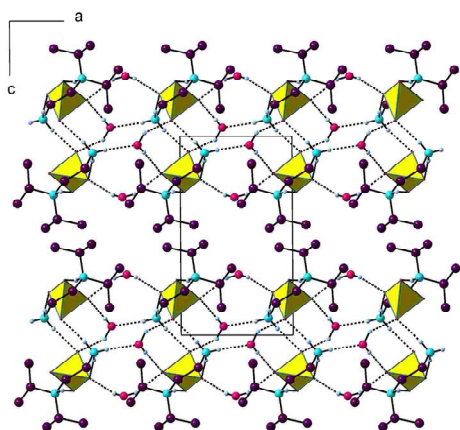


Figure 6. Projection along the b axis of the atomic arrangement. (For clarity, the H atoms of Carbon are omitted; H-bonds are represented by dashed lines).

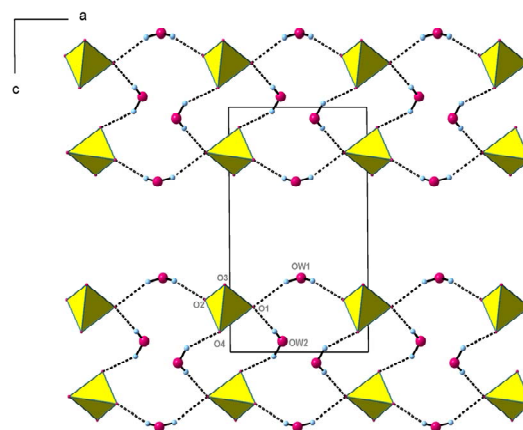


Figure 7. Projection along the b axis of the anionic arrangement of DPAES (H-bonds are represented by dashed lines).

4. Conclusion

Chemical preparation, crystal structure determination, ^{13}C NMR, IR and Raman vibrational study of a new compound were described. Its atomic arrangement is organized as a layers in the (001) plane. The asymmetric unit of the crystal consists of two water molecules, one organic cation and one SO_4 anion. These entities are assembled by two kinds of hydrogen bonds, $O-H\cdots O$ and $N-H\cdots O$. The stability between successive layers is performed by $C-H\cdots O$ van der Waals interactions originating from the organic cations.

5. Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 875591. 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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