

Crystal structure of oxonium *o*-toluidinium sulfate at 100K, (C₇H₁₀N)(H₃O)SO₄

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Abstract: A simple oxonium *o*-toluidinium sulfate, (C₇H₁₀N)(H₃O)SO₄, crystallized from water at ambient temperature was found to be monoclinic (space group P2₁/c) at 100K. In the crystal, the H₃O⁺ ions and the SO₄²⁻ anions are linked by O-H...O hydrogen bonds, generating infinite layers lying parallel to the bc plane at x = 1/2. These layers are interconnected by the organic cations, which establish N-H...O hydrogen bonds with the SO₄²⁻ anions. Weak π-π stacking interactions between the benzene rings of neighboring molecules further to stabilize the structure [centroid- centroid distance = 3.648 Å].

Keywords: Hybrid compound, oxonium cation, X-ray diffraction.

Introduction

The coordination chemistry of tetrahedral oxyanions (sulfates, phosphates, selenites, etc...) has constantly been the subject of many research studies. These anions, which are Lewis bases, are used as ligands to elaborate interesting metal complexes. The reaction of sulfuric acid with organic molecules having one or more lone pairs, leads to the formation of salt type hybrid compounds whose anions have the formula [HSO₄]⁻ or [SO₄]²⁻.

The literature reports several SO₄²⁻ salts of organic cations¹⁻⁴. They may be related to the structure of some sulfuric acid hydrates^{5,6} and sulfuric acid anhydride⁷. But the association of the oxonium cation to this kind of material is very rare. On the other hand, there is only one cyclohexaphosphate of mixed cation (*o*-toluidinium /oxonium)⁸.

The present report the structure at 100 K of a new aromatic amine organic sulfate; namely, oxonium *o*-toluidinium sulfate, (2-CH₃C₆H₄NH₃)(H₃O)SO₄, denoted (OOTS).

Experimental Section

Chemical Preparation

The single crystal of (2-CH₃C₆H₄NH₃)(H₃O)SO₄ was obtained by slow evaporation of aqueous solution containing a 1:1 stoichiometric mixture of *O*-CH₃C₆H₄NH₂ and sulfuric acid. The resulting solution was allowed to evaporate slowly at room temperature.

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After several days, colorless transparent parallelepipedic single crystal of (2-CH₃C₆H₄NH₃)(H₃O)SO₄ were obtained.

Structure determination

Single-crystal X-ray diffraction intensity data were obtained on a Bruker Smart APEX-CCD area detector diffractometer using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected at 100 K. Lorentz and polarizing effect corrections were performed before proceeding to the refinement of the structure. Absorption corrections were performed using the multi-scan technique. 4828 reflections were measured, 1245 of which had an intensity of $I > 2\sigma(I)$. The structure was successfully developed in the centrosymmetric space group $P 2_1/c$.

The sulfur atoms were fixed using the direct methods with SHELXS-97⁹ programs. The oxygen atoms and the organic moieties were found from successive Fourier calculations using SHELXL-97¹⁰.

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C–H = 0.98 \AA (methyl) or 0.91 \AA (aromatic) and N–H = 0.91 \AA with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (aromatic) or $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ (methyl, N).

For the oxonium group, H atoms were located in a difference map and refined with O–H distance restraints of 0.88(2) \AA and H–H restraints of 1.5 (2) \AA so that the H–O–H angle fitted to the ideal value of a tetrahedra angle.

Supplementary crystallographic data for this article, in CIF format, are available as an electronic supplementary publication from Cambridge crystallographic data center (CCDC 981066).

Results and Discussion

The final atomic coordinates obtained from the single crystal refinement with U_{eq} are given in Tables 1 and 2. Hydrogen bonds and Interatomic distances, bond angles are listed in Tables 3 and 4, respectively.

Table 1. Crystal data and experimental parameters used for the intensity data collection strategy and final results of the structure determination.

Temperature	100 K
Empirical Formula	C ₇ H ₁₄ NO ₅ S
Formula Weight (g.mol ⁻¹)	223.24
Crystal system	Monoclinic
Space group	$P 2_1/c$
a	9.3964 (15) \AA
b	10.2826 (17) \AA
c	9.9936 (15) \AA
α	90°
β	90.451 (3)°
γ	90°
Z	4
V	965.5 (9) \AA^3
ρ_{cal}	1.536 Mg m ⁻³
F(000)	472

Table 1. To be continued

μ (Mo $K\alpha$)	0.33 mm ⁻¹
Index ranges	-11 ≤ h ≤ 11.-12 ≤ k ≤ 6.-11 ≤ l ≤ 11
Reflexionscollected	4828
Independent reflexions	1686
reflections with $I > 2\sigma(I)$	1245
Rint	0.055
Refinedparameters	141
R[F ² > 2σ(F ²)]	0.045
wR(F ²)	0.1
Goodness of fit	1.034
θ_{\min}	2.2°

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for (C₇H₁₀N)(H₃O)SO₄

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.48543 (7)	0.14087 (7)	0.2961 (7)	0.0134 (2)
O1	0.42440 (19)	0.16020 (19)	0.36496 (18)	0.0158 (5)
O2	0.3903 (2)	0.05173 (19)	0.15359 (18)	0.0175 (5)
O3	0.4963 (2)	0.26533 (19)	0.16129 (18)	0.0173 (5)
O4	0.62592 (19)	0.07692 (19)	0.24619 (18)	0.0176 (5)
N1	-0.3124 (2)	0.4267 (2)	0.0332 (2)	0.0138 (6)
H1A	-0.3189	0.4225	-0.0576	0.021*
H1B	-0.3349	0.5084	0.0610	0.021*
H1C	-0.3739	0.3686	0.0699	0.021*
C1	-0.1665 (3)	0.3953 (3)	0.0758 (3)	0.0142 (7)
C2	-0.1099 (3)	0.2770 (3)	0.0364 (3)	0.0158 (7)
C3	0.0289 (3)	0.2497 (3)	0.0784 (3)	0.0198 (7)
H3	0.0713	0.1696	0.0533	0.024*
C4	0.1063 (3)	0.3366 (3)	0.1556 (3)	0.0212 (7)
H4	0.2009	0.3162	0.1822	0.025*
C5	0.0456 (3)	0.4537 (3)	0.1942 (3)	0.0196 (7)
H5	0.0982	0.5130	0.2481	0.023*
C6	-0.0920 (3)	0.4837 (3)	0.1538 (3)	0.0153 (7)
H6	-0.1345	0.5638	0.1793	0.018*
C7	-0.1917 (3)	0.1843 (3)	-0.0513 (3)	0.0217 (7)
H7A	-0.2873	0.1719	-0.0150	0.032*
H7B	-0.1421	0.1005	-0.0540	0.032*
H7C	-0.1989	0.2200	-0.1420	0.032*
OW	0.6721 (2)	0.8871 (2)	0.0787 (2)	0.0170 (5)
HW2	0.648 (4)	0.908 (3)	-0.0071 (18)	0.054 (12)*
HW1	0.644 (4)	0.8093 (19)	0.104 (3)	0.063 (14)*
HW3	0.655 (4)	0.952 (2)	0.134 (3)	0.061 (14)*

Table 3. Hydrogen-bond geometry (Å).

D—H···A	D—H	H···A	D···A	
OW—HW2···O2 ⁱ	0.91 (2)	1.56 (2)	2.471 (3)	178 (3)
OW—HW3···O4 ⁱⁱ	0.88 (2)	1.73 (2)	2.610 (3)	178 (3)
OW—HW1···O1 ⁱⁱⁱ	0.88 (2)	1.69 (2)	2.567 (3)	173 (3)
N1—H1A···O4 ^{iv}	0.91	2.02	2.922 (3)	169
N1—H1B···O1 ^v	0.91	1.92	2.815 (3)	166
N1—H1C···O3 ^{vi}	0.91	1.86	2.767 (3)	173

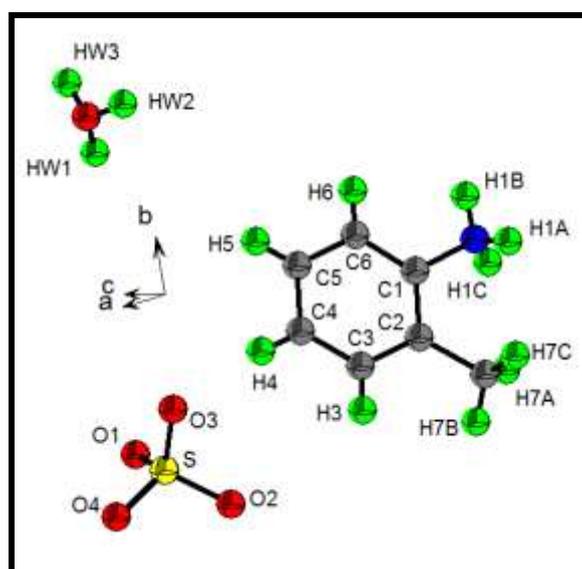
Note: OW; oxygen of the oxonium cation, HW; hydrogen of oxonium cation.

Symmetry codes : (i) $-x+1, -y+1, -z$; (ii) $x, y+1, z$; (iii) $-x+1, y+1/2, -z+1/2$; (iv) $x-1, -y+1/2, z-1/2$; (v) $-x, y+1/2, -z+1/2$; (vi) $x-1, y, z$.

Table 4. Main distances (Å) and angles (°) for (C₇H₁₀N)(H₃O)SO₄ atomic arrangement.

Bond lengths (Å)		Angles (°)	
S-O1	1.486(2)	O1-S-O2	106.63(11)
S-O2	1.485(2)	O1-S-O3	107.08(12)
S-O3	1.455(2)	O1-S-O4	106.52(11)
S-O4	1.483(2)	O2-S-O3	113.34(11)
		O2-S-O3	110.97(10)
		O3-S-O4	109.00(11)

The asymmetric unit of the title compound, (C₇H₁₀N)(H₃O)SO₄, (Fig.1) consists of protonated o-toluidinium, oxonium cations, and SO₄²⁻ anions, the o-toluidinium cation is essentially planar.

**Figure 1:** Asymmetric unit of the title structure.

The atomic arrangement of the title compound is characterized by the existence of inorganic layers, built by isolated SO_4^{2-} anions and oxonium cations. Each oxonium ions is connected to three adjacent neighboring sulfate anions through strong $\text{O(W)}-\text{H}\cdots\text{O(T)}$ hydrogen bonds (Fig. 2).

The organic and inorganic species establish between them two types of hydrogen bonds. The first one is $\text{O(W)}-\text{H}\cdots\text{O(T)}$, involving short contacts with $\text{H}\cdots\text{O}$ lengths ranging between 1.56 (2) – 1.73 (3) Å^{11, 12}, connects the H_3O^+ and SO_4^{2-} entities to develop the inorganic layer parallel to bc plane at $x = 1/2$. The second type is $\text{N}-\text{H}\cdots\text{O(T)}$, with $\text{H}\cdots\text{O}$ distances ranging from 2.768 (3) to 2.922 (3) Å, links the organic cations to the $[\text{SO}_4.\text{H}_3\text{O}]_n^{n-}$ layer (Fig. 2).

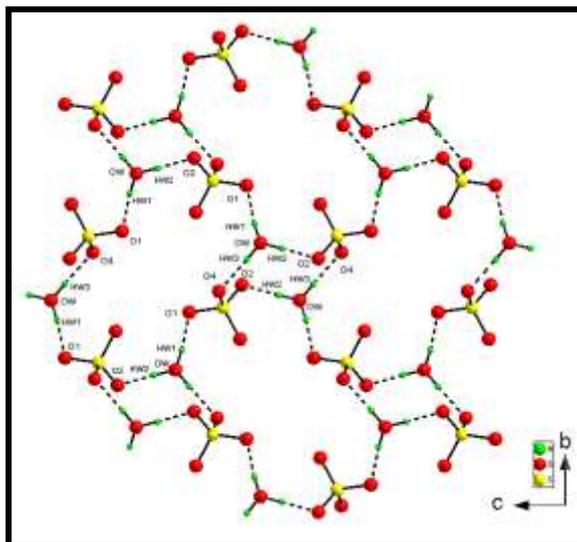


Figure 2. Hydrogen bonding scheme of the inorganic entities in the crystal structure of $(\text{C}_7\text{H}_{10}\text{N})(\text{H}_3\text{O})\text{SO}_4$ in projection along the a -axis (This figure is in connection with Table 2).

The S-O distances range from 1.455(2) to 1.486(2) Å with an average of 1.477(2) Å. Slight differences in the S-O bond lengths together with the slight deformation of the anions indicate a different manner of connection of the oxygen atoms in the hydrogen bond system in the $(\text{C}_7\text{H}_{10}\text{N})(\text{H}_3\text{O})\text{SO}_4$ crystal structure. Each sulfate anion is surrounded by six hydrogen bonds: three from three NH_3 groups and three from three H_3O cations. 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 structures¹³. O (1) and O (4), with S-O bond distances of 1.486(2) and 1.483(2) Å, respectively, participates in two hydrogen bonds, contrary to O (3), with participates in one hydrogen bond, has the shortest S-O distance of 1.455 (2) Å. Except for the O(2) atom, with participates in one hydrogen bond, has the S-O distance of 1.485 (2) Å similar to S-O(1)/(4) bond distances. This short distance indicates a strong hydrogen bond $\text{Ow}\cdots\text{O(2)}$ [$\text{Ow}-\text{Hw(2)} \cdots \text{O(2)} = 2.471(3)$ Å, $\text{Hw(2)} \cdots \text{O(2)} = 1.56(2)$ Å]

The calculated average values of the distortion index¹⁴ corresponding to the different angles and distances in the SO_4 tetrahedra [DI (OSO) = 0.012; DI (SO) = 0.01; and DI(OO) = 0.004], show a pronounced distortion of the SO distances and OSO angles if compared to OO distances. So, the SO_4 group can be considered as a rigid regular arrangement of oxygen atoms, with the sulfur atom slightly displaced from the gravity centre.

An examination of the organic moiety geometrical features shows that the C1, C2, C3, C4, C5 and C6 atoms of the phenyl ring of the title compound have a good coplanarity and form a conjugated plane with an average deviation of 0.004 Å. The mean value of the C–C bond length is [1.387 Å], complies with that in 3-Hydroxyanilinium hydrogensulfate [1.386 Å]¹⁵ and 2,3-Dimethylanilinium dihydrogenophosphate [1.388 Å]¹⁶. The centrosymmetric arrangement of the amines with an average distance of 3.648 Å between two centroids of the two adjacent aromatic rings suggests weak interactions like $\pi \dots \pi$ in this compound¹⁷. Although these interactions are weak, they play a very important role in the crystal structure because they connect two cations (Fig. 3).

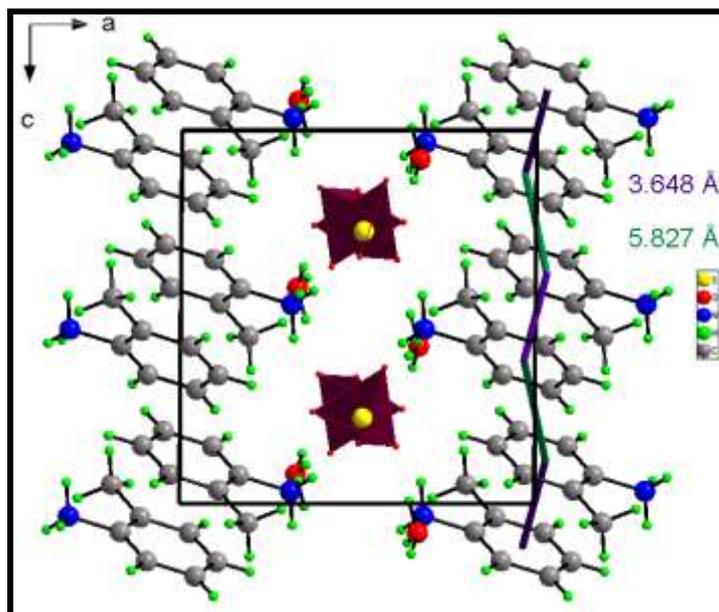


Figure 3: The atomic arrangement of $(C_7H_{10}N)(H_3O)SO_4$ in projection along the b-axis. Offset-face-to-face interactions motifs ($\pi - \pi$ stacking) in the cation-cation layer.

The NH_3^+ group of the cation forms weaker hydrogen bonds which are in the typical range for related sulfates¹⁸.

Conclusion

Crystal structure of this compound was found to be built by infinite layers of $(H_3O.SO_4)^+$ parallel to the bc planes around $x = 1/2$. Between these layers, the toluidinium cations are located. Both inorganic and organic components perform different interactions (H-bonds and $\pi \dots \pi$ interactions) to stabilize the three-dimensional network.

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