

Hydrogen Bond Studies. XIX.* The Crystal Structure of the 1:1 Addition Compound of Acetic Acid with Sulphuric Acid, $\text{CH}_3\text{C}(\text{OH})_2^+\text{HSO}_4^-$

BY PER-GUNNAR JÖNSSON AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

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The crystal structure of $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{SO}_4$ has been determined from three-dimensional single-crystal X-ray data obtained at -42°C . The crystals are monoclinic, space group $P2_1/c$, with four formula units in a unit cell of dimensions $a=4.529$, $b=9.306$, $c=14.299$ Å and $\beta=95.75^\circ$. The assignment of the hydrogen atoms indicates that the structure contains $\text{CH}_3\text{C}(\text{OH})_2^+$ and HSO_4^- ions. The HSO_4^- ions are linked by hydrogen bonds (length 2.567 Å) to form infinite chains. The $\text{CH}_3\text{C}(\text{OH})_2^+$ ions form links between two such chains with hydrogen bond lengths 2.521 and 2.522 Å. The S–O distances within an HSO_4^- ion are: 1.436, 1.444, 1.450 and 1.546 Å. In the $\text{CH}_3\text{C}(\text{OH})_2^+$ ion the C–C distance is 1.480 Å and the C–O distances are 1.265 and 1.272 Å. The O–C–O angle is 118.4° and the C–C–O angles are 123.5° and 118.2° .

Introduction

Acetic acid forms addition compounds with several strong acids, for example phosphoric, nitric, perchloric, sulphuric and fluorosulphuric acids. It seems probable that hydrogen bonds play a major part in the structures of these compounds. Systematic investigations have now been started as part of the general hydrogen bond studies at this Institute.

From studies of the melting point diagram of the system acetic acid – sulphuric acid, the existence of the 1:1 addition compound $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{SO}_4$ with a melting point of -2.5°C has been concluded (Kendall & Brakeley, 1921).

The present work concerns the determination of the crystal structure of $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{SO}_4$ from single-crystal X-ray data. As will be shown below, the compound can be formulated as acetate acidium hydrogen-sulphate, $\text{CH}_3\text{C}(\text{OH})_2^+\text{HSO}_4^-$.

Experimental

Absolute sulphuric acid was prepared from reagent grade sulphuric acid by the addition of oleum until the maximum freezing point was observed (Kunzler, 1953). Equimolar quantities of water-free acetic acid and absolute sulphuric acid were mixed and sealed into glass capillaries. It was extremely difficult to induce crystallization of this very viscous mixture. Pouring liquid nitrogen over the capillary normally resulted in supercooling, but after many attempts a crystal seed was obtained from which single crystals could be grown. The crystals were grown with the capillary mounted on the goniometer in the low-temperature Weissenberg camera. The details of this camera have been described by Olovsson (1960).

The crystals grew exclusively with their a axes closely parallel to the capillary axis. In order to obtain a crystal with a different orientation a capillary with a short part bent almost to a right angle was used. When the temperature was kept a few degrees below the melting point it was possible to maintain the orientation of a single crystal, initially formed in the short part of the capillary, while it was growing around the bend. With this new orientation with respect to the longer axis of the capillary the growing rate was much slower than earlier. Occasionally, the orientation reverted to the normal one, and it was then necessary to remelt that part of the crystal. After about two weeks a satisfactory single crystal had been obtained with the b axis approximately parallel to the capillary axis. As this single crystal was grown at a time when the structure determination was nearing completion, it was used only for accurate determination of the cell dimensions, no intensity data being taken with this crystal.

Equi-inclination Weissenberg photographs were taken using the multiple-film technique (five films) with Cu K radiation at $-42 \pm 2^\circ\text{C}$ about $[100]$ for the layers $h=0, 1, \dots, 4$. The relative intensities were estimated visually by comparison with an intensity scale. The intensity range was 1 to 5000. Out of a total of 1163 recorded reflexions 260 were too weak to be measured. About 85% of the reflexions within the Cu reflexion sphere were thus recorded.

The data were corrected for absorption, Lorentz and polarization effects on an IBM 7090 computer using the program ERLPA (Van den Hende, 1962). The radius of the cylindrical crystal was 0.010 cm and the absorption coefficient for Cu $K\alpha$ radiation, $\mu=45.2$ cm^{-1} .

In addition, Weissenberg photographs were taken at -190°C , but no changes in structure were indicated in these photographs. The X-ray reflexions were in this case much more diffuse than those previously obtained

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at -42°C . The structure determination was thus based only on the latter data.

Unit cell and space group

The diffraction symmetry and systematic absences indicated the space group $P2_1/c$ (no. 14).

The unit-cell parameters were determined from zero-layer oscillation photographs taken about [100] and [010] at -42°C with unfiltered Cu K radiation (Cu $K\alpha_1\lambda=1.54051$ Å, Cu $K\alpha_2\lambda=1.54433$ Å). Reflexions from a quartz single crystal were superimposed on the photographs for calibration ($a=4.913$ Å for α quartz at 20°C). The cell dimensions together with their estimated standard deviations are:

$$a=4.529 \pm 0.004, b=9.306 \pm 0.005, c=14.299 \pm 0.006 \text{ \AA}, \\ \beta=95.75^\circ \pm 0.04^\circ.$$

The density was estimated from the volume and weight of a homogeneous crystalline sample contained in a glass tube of uniform diameter. The observed density was 1.7 g.cm^{-3} . With four formula units per unit cell, the calculated density at -42°C is 1.75 g.cm^{-3} .

Determination of the atomic coordinates

The coordinates of the sulphur atom and of the four oxygen atoms belonging to the sulphate group were determined from a three-dimensional Patterson synthesis. From a three-dimensional F_o synthesis based on these atomic positions, the coordinates of the remaining oxygen and carbon atoms were then determined. All these atoms are in the general fourfold positions of the space group $P2_1/c$.

The preliminary atomic coordinates were first improved in a series of three-dimensional electron density calculations, after which the atomic coordinates, individual isotropic thermal parameters and inter-layer scale factors were refined by the method of least squares.

The first series of least-squares calculations was performed on FACIT EDB with a program (SFLS) written by Åsbrink & Brändén. The main features of this

program have been reported earlier (Brändén & Lindqvist, 1963). A block-diagonal approximation is used in this program to minimize the function $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used was $w=1/(a+|F_o| + c|F_o|^2)$ with $a=4.0$ and $c=0.03$. Reflexions too weak to be observed were given zero weight.

Finally some cycles of least-squares calculations were performed on the CD 3600 computer in Uppsala with a modified version of the full-matrix least-squares program by Gantzel, Sparks & Trueblood (1962). In these calculations all the observed data were used, except five reflexions which were suspected to be affected by secondary extinction. The function minimized and the weighting scheme used were the same as above. After two cycles of isotropic refinement the agreement index, $R=\sum ||F_o| - |F_c||/\sum |F_o|$ was 0.110.

Anisotropic thermal parameters of the form

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$$

were now introduced for S, O and C. In these refinements the inter-layer scale factors were fixed to the values obtained in the last cycle of isotropic refinement and only an overall scale factor was varied. The total number of parameters refined was 82. After three cycles of anisotropic refinement the R value was 0.082.

A three-dimensional difference synthesis was now computed using only reflexions with $\sin \theta/\lambda$ less than 0.35 \AA^{-1} . Five of the hydrogen atoms appeared in reasonable positions with peak heights between 0.31 e.\AA^{-3} and 0.38 e.\AA^{-3} . At the expected position of the remaining hydrogen atom H(1), there was a smeared-out peak with a height of only 0.14 e.\AA^{-3} . The five hydrogen atoms with well-defined peaks, H(2)–H(6), were included in two further cycles of anisotropic refinement with fixed parameters. Their coordinates were taken as the peak positions in the difference maps and an isotropic thermal parameter of 4.0 \AA^2 was applied to each hydrogen atom. The average shift in the atomic coordinates for S, O and C was 0.5σ and the largest 1.4σ . The R value decreased to 0.076.

A final difference synthesis was now computed; the new hydrogen positions are given in Table 3. They did not differ significantly from the earlier set, however.

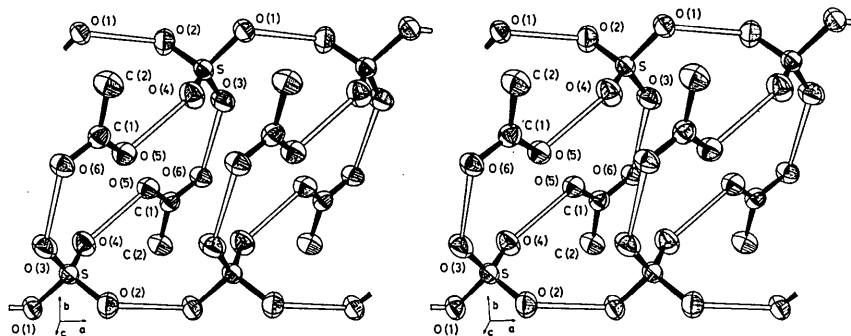


Fig. 1. Stereoscopic illustration of the structure showing the hydrogen bonding pattern. The origin is indicated in the bottom left corner. The thermal ellipsoids are scaled to include 50% probability.

When they were used with fixed parameters in another cycle of least-squares refinement, the average positional parameter shift in this final cycle was about 0.05σ and the largest 0.2σ . The final R value was 0.076 for 898 observed reflexions.

Tables 1 and 2 list values for the atomic coordinates and thermal parameters with their standard deviations, obtained from the final least-squares refinement. The observed and calculated structure factors at this stage are compared in Table 4.

Table 1. Atomic coordinates with standard deviations ($\times 10^4$)

	x	y	z
S	1173 (3)	2445 (1)	1090 (1)
O(1)	-1239 (8)	1264 (4)	1028 (3)
O(2)	3740 (8)	1840 (5)	1630 (3)
O(3)	-46 (9)	3655 (4)	1542 (3)
O(4)	1697 (9)	2738 (5)	124 (3)
O(5)	4486 (8)	6002 (4)	749 (3)
O(6)	1258 (8)	6275 (4)	1767 (3)
C(1)	3201 (11)	6818 (6)	1288 (4)
C(2)	3837 (14)	8372 (6)	1393 (4)

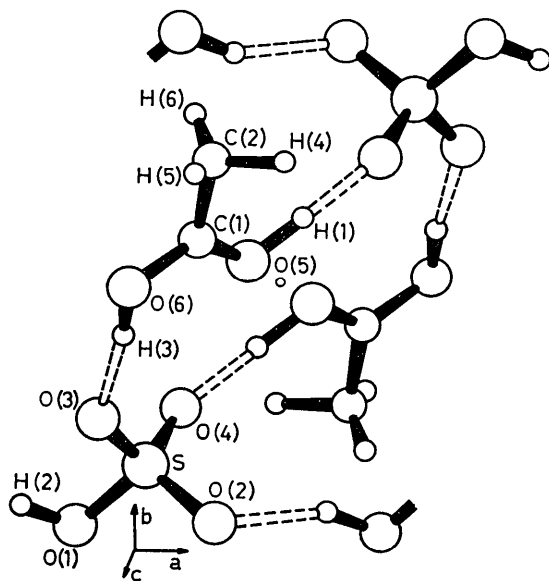


Fig. 2. The hydrogen positions. H(1) has been placed on the bond axis O(4)–O(5) at a distance of 1.05 \AA from O(5). The other hydrogens are located at their positions as determined from the difference maps (see Table 3). A centre of symmetry is indicated close to O(5).

Table 3. Hydrogen atom parameters

	x	y	z	B
H(2)	-0.288	0.174	0.118	4.0 \AA^2
H(3)	0.092	0.524	0.159	4.0
H(4)	0.658	0.857	0.164	4.0
H(5)	0.363	0.855	0.193	4.0
H(6)	0.290	0.871	0.077	4.0

The atomic scattering factors used in the above calculations were those given for neutral S, O, C and H in *International Tables for X-ray Crystallography* (1962).

Description and discussion of the structure

The structure is shown in Figs. 1 and 2. These figures were prepared on a computer-controlled plotter using the program *ORTEP* (Johnson, 1965). The bond distances and angles are given in Table 5 and are illustrated in Fig. 3. Distances corrected for anisotropic thermal motion are not given, since no experimental scaling has been done, and thus part of the anisotropy has been accounted for by refinement of individual scale factors for the separate layers.

The assignment of hydrogen to the bonds (see below) indicates that the structure can be considered to be built up of $\text{CH}_3\text{C}(\text{OH})_2^+$ (acetate acidium) ions and HSO_4^- ions. If the positions of the hydrogen atoms are ignored, the structure can be described in terms of an acetic acid part and a sulphuric acid (or sulphate) part.

Two oxygen atoms, O(1) and O(2), in each sulphate group are involved in hydrogen bonding with neighbouring sulphate groups ($\text{O}\cdots\text{O}$ distance 2.57 \AA), forming infinite chains of sulphate groups along [100]. The other two oxygen atoms in the sulphate group, O(3) and O(4), are joined by hydrogen bonds ($\text{O}\cdots\text{O}$ distance 2.52 \AA in both cases) to oxygen atoms in two different acetic acid groups. In this way two sulphate chains are joined to a 'double-chain' by links formed by hydrogen bonds and acetic acid groups. The hydrogen bonding pattern is thus essentially one-dimensional; there are infinite double-chains of sulphate groups running through the structure along [100], but there are no hydrogen bonds between different double-chains.

There are four short $\text{C}\cdots\text{O}$ distances involving the methyl carbon which are less than about 3.3 \AA ; these are listed in Table 6. Evidence for the existence of

Table 2. Thermal parameters with standard deviations ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	326 (8)	66 (1)	36 (1)	-22 (4)	59 (3)	2 (1)
O(1)	340 (19)	81 (4)	51 (2)	-59 (13)	74 (10)	-16 (5)
O(2)	349 (22)	133 (6)	46 (2)	7 (17)	22 (10)	21 (6)
O(3)	530 (25)	75 (5)	68 (3)	-51 (16)	156 (13)	-9 (5)
O(4)	479 (24)	135 (6)	41 (2)	-77 (18)	68 (11)	27 (6)
O(5)	470 (22)	75 (4)	44 (2)	13 (15)	105 (11)	-13 (5)
O(6)	466 (22)	81 (4)	36 (2)	-35 (14)	101 (10)	-6 (4)
C(1)	355 (27)	83 (6)	34 (3)	14 (19)	8 (13)	7 (6)
C(2)	599 (37)	87 (7)	38 (3)	-83 (23)	67 (16)	-18 (6)

C-H...O hydrogen bonds in crystals with C...O lengths up to 3.3 Å have been given by Sutor (1963). However, no such bond seems to exist in the present structure as the closest methyl-hydrogen approach to

O is about 2.7 Å, and the C-H...O angles are not very favourable for hydrogen bonding.

The hydrogensulphate ion

The S-O bond lengths and O-S-O bond angles of the sulphate group strongly indicate that a hydrogen atom is attached only to O(1), and the structure thus contains HSO₄⁻ ions (*cf.* Cruickshank, 1961). The distances and angles are in good agreement with those found earlier for these types of bonds. Table 7 compares bond lengths in some related structures.

The acetate acidium ion

The atoms C(1), C(2), O(5) and O(6) are coplanar; none of the atoms deviates from the least-squares plane by more than 0.001 Å. The oxygen atoms O(3) and O(4) which are connected by hydrogen bonds to the acetate acidium ion deviate from this plane by 0.115 and -0.030 Å, respectively. The least-squares calculation was performed by the method suggested by Blow (1960).

There seem to be no previous diffraction studies on structures containing protonated carboxylic acids. The structure of crystalline acetic acid has been determined by Jones & Templeton (1958). A comparison of the

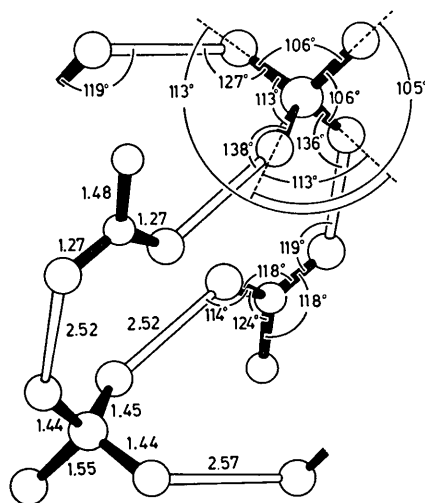


Fig. 3. Bond distances and angles. The orientation is the same as in Fig. 2.

Table 5. Bond distances and angles with standard deviations

Standard deviations of distances are multiplied by 10³.

Covalent bonds			
S-O(1)	1.546 (4) Å	O(1)-S-O(2)	106.3 (0.2)°
S-O(2)	1.444 (4)	O(1)-S-O(3)	106.4 (0.2)
S-O(3)	1.436 (4)	O(1)-S-O(4)	105.1 (0.3)
S-O(4)	1.450 (4)	O(2)-S-O(3)	113.0 (0.3)
		O(2)-S-O(4)	112.5 (0.3)
		O(3)-S-O(4)	112.8 (0.3)
C(1)-O(5)	1.265 (6) Å	O(5)-C(1)-O(6)	118.4 (0.5)°
C(1)-O(6)	1.272 (6)	O(5)-C(1)-C(2)	123.5 (0.5)
C(1)-C(2)	1.480 (8)	O(6)-C(1)-C(2)	118.2 (0.5)
Hydrogen bonds			
O(1)...O(2)	2.567 (6) Å	S—O(1)...O(2)	118.5 (0.2)°
O(5)...O(4)	2.521 (6)	S—O(2)...O(1)	126.5 (0.3)
O(6)...O(3)	2.522 (6)	C(1)-O(5)...O(4)	113.8 (0.3)
		S—O(4)...O(5)	138.2 (0.3)
		C(1)-O(6)...O(3)	118.7 (0.3)
		S—O(3)...O(6)	136.1 (0.3)

Table 6. Packing distances less than 3.5 Å involving the methyl carbon

From atom	position	to atom	position	Distance
C(2)	<i>x, y, z</i>	O(2)	<i>x, 1 + y, z</i>	3.245 Å
C(2)	<i>x, y, z</i>	O(2)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	3.258
C(2)	<i>x, y, z</i>	O(4)	$1 - x, 1 - y, \bar{z}$	3.278
C(2)	<i>x, y, z</i>	O(4)	$\bar{x}, 1 - y, \bar{z}$	3.312

Table 7. Some bond lengths (Å) in hydrogen-bonded sulphate structures

	S-O	S-OH	σ (S-O)	O...O*	σ (O...O)	
KHSO ₄	1.47	1.56	0.015	2.62		Cruickshank (1964)
NaHSO ₄ · H ₂ O	1.450	1.613	0.013	2.70	0.02	Pringle & Broadbent (1965)
H ₂ SO ₄	1.426	1.535	0.015	2.63	0.02	Pascard-Billy (1965)
H ₂ SO ₄ · H ₂ O	1.448	1.560	0.004	2.657	0.005	Taesler & Olovsson (1968)
CH ₃ COOH · H ₂ SO ₄	1.443	1.546	0.004	2.567	0.006	Present paper

* Hydrogen bonds between sulphate groups.

C–O bond lengths in acetic acid (1.29 ± 0.02 and 1.24 ± 0.02 Å) with those found in the present structure (1.272 ± 0.006 and 1.265 ± 0.006 Å) indicates that the latter does in fact contain the acetate acidium ion.

A number of studies of protonated carboxylic acids in solution have previously been done by spectroscopic and nuclear magnetic resonance methods. However, there still seems to remain some doubt in the literature as to the site of protonation. Most investigators have favoured a structure involving protonation of the carbonyl oxygen, but others claim support for the hydroxyl protonated structure. A study of the protonated acetic acid in liquid sulphuric acid has recently been done by spectroscopic methods by Hoshino, Hosoya & Nagakura (1966). These authors arrived at the conclusion that the protonation occurs at the carbonyl oxygen, in agreement with the results of the present determination of the structure of the solid 1:1 compound.

The C–C distance in the present structure is 1.480 ± 0.008 Å as compared to 1.54 ± 0.02 Å in acetic acid. Dewar & Schmeising (1960) assumed the value to be 1.515 Å for the C–C sp^2 – sp^3 bond length. The mean value for the acetate ion in three recently determined structures is 1.52 Å (Nahringbauer, 1967). Thus, there seems to be a significant shortening of the C–C bond in the present case. This effect may be caused by transfer of positive charge to the carboxyl carbon.

Hydrogen positions

From the difference maps the positions of the methyl hydrogen atoms and two of the hydrogen atoms participating in hydrogen bonding could be determined. Of the latter, H(2) was found to be attached to the sulphate group and H(3) to the acetic acid group. The difference map gave no definite information as to the position of H(1). According to the description given in the preceding sections, H(1) must be attached to the acetic acid group. However, this assignment is based mainly on indirect evidence supported by the covalent bond lengths.

Relation to physical properties

The melting point of the present compound is -2.5°C as compared with 16.6°C for acetic acid and 10.4°C for sulphuric acid. This may appear unexpectedly low in view of the strong hydrogen bonds present. However, the very high viscosity at temperatures near the melting point indicates that much of the hydrogen

bonding persists in the liquid state. Abnormally low melting points and an anomalous increase in viscosity in the region of the freezing-point are also observed in hydrogensulphates of the alkali metals, as discussed by Rogers & Ubbelohde (1950). Of these, the structure of KHSO_4 has been determined (Cruickshank, 1964); it contains hydrogen bonded HSO_4^- chains similar to those in the present structure.

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