

Structure and Hydrogen Bonding of α -NaHSO₄

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Abstract

α -NaHSO₄ is triclinic, space group $P\bar{1}$, with $a = 7.005$ (1), $b = 7.125$ (1), $c = 6.712$ (1) Å, $\alpha = 95.94$ (2), $\beta = 87.69$ (2), $\gamma = 104.48$ (2)°, $V = 322.5$ (1) Å³, $Z = 4$. The final $R = 0.059$ for 514 counter reflections. Disorder of one of the H atoms was deduced from S–O bond lengths and O...O distances. The disorder causes a peculiar hydrogen-bonding scheme, with one of the hydrogen bonds across a centre of symmetry.

1. Introduction

Recently, a new modification of NaHSO₄ was found and its crystal structure, which is monoclinic, space group $P2_1/n$, determined by powder work (Sonneveld & Visser, 1978).

The purpose of the present determination of the triclinic form of NaHSO₄ was to compare it with the structure of the monoclinic modification. The triclinic phase was called α -NaHSO₄, the monoclinic form β -NaHSO₄.

2. Experimental

Cell constants were determined from Guinier–de Wolff powder photographs, calibrated with corundum as an internal standard. The powder pattern of α -NaHSO₄ could be indexed from the isomorphism with CaHPO₄ (Langmuir, 1919). The procedure for growing crystals was derived from a phase diagram (Landolt–Börnstein, 1962): they were grown from a saturated solution of NaHSO₄ in concentrated H₂SO₄ at 353 K. This solution contained equal molar amounts of NaHSO₄ and H₂SO₄ and just enough water to dissolve all NaHSO₄ at this temperature. By cooling the solution slowly from 353 to 343 K, well developed plate-like crystals were formed. Since anhydrous NaHSO₄ is hygroscopic, the crystals were stored under paraffin oil. A crystal 0.7 × 0.5 × 0.3 mm was mounted in a glass capillary, which was filled on both sides of the crystal with paraffin oil. The capillary was closed at both ends by melting. To confirm the identity of the crystal and to

make sure that it was a single crystal, precession photographs were taken. The cell constants determined in this way agreed well with the values resulting from the powder work.

In the subsequent measurements on a CAD-3 diffractometer at room temperature with Mo $K\alpha$ radiation, the intensities of 2860 independent reflections were determined. For economic reasons we used only the 514 reflections with $h^2 + k^2 + l^2 < 40$ for the structure determination (49 parameters).

3. Structure determination

α -NaHSO₄ is isomorphous with CaHPO₄ (Langmuir, 1919). As starting values for the positional parameters we took the positional values of CaHPO₄ (Jones & Cruickshank, 1961).

Least-squares refinement was carried out with the XRAY system (1972). The refinement included individual isotropic temperature factors and weights $w = 1/\sigma^2(F)$.

An absorption correction was applied, but no correction for extinction was made. The contribution of H atoms was neglected. The final R was 0.059 for 514 reflections.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34456 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters of α -NaHSO₄

	x	y	z	B (Å ²)
Na(1)	2980 (5)	2783 (5)	4529 (5)	1.8 (1)
Na(2)	1690 (5)	6678 (5)	8431 (5)	2.4 (1)
S(1)	2059 (3)	7213 (3)	3854 (3)	0.8 (1)
S(2)	3013 (3)	2100 (3)	9574 (3)	0.9 (1)
O(1)	3181 (8)	9363 (8)	3454 (7)	1.5 (2)
O(2)	3428 (8)	6422 (7)	4887 (7)	1.6 (2)
O(3)	1519 (8)	6160 (8)	1932 (8)	1.7 (2)
O(4)	418 (8)	7472 (8)	5099 (7)	1.6 (2)
O(5)	3337 (8)	363 (8)	8483 (8)	1.8 (2)
O(6)	4454 (8)	2902 (8)	1129 (8)	1.9 (2)
O(7)	1025 (8)	1657 (8)	565 (8)	2.0 (2)
O(8)	3032 (8)	3573 (8)	8155 (8)	2.1 (2)

4. Discussion

4.1. General

The final positions are given in Table 1, distances and angles in Table 2. A projection of the structure is given in Fig. 1. The distances in the S(1)O₄ tetrahedron are in good agreement with those found in other structures which contain HSO₄⁻ ions (Ashmore & Petch,

1975; Cruickshank, 1964; Grimvall, 1971; Pringle & Broadbent, 1965; Sonneveld & Visser, 1978). S(1)—O(1), which is longer than the remaining S(1)—O distances, shows the presence of the H atom bonded to O(1). As can be seen from Table 2, Na(1) is coordinated by seven O atoms with Na(1)—O distances varying from 2.347 to 2.983 Å, while Na(2) is coordinated by eight O atoms with Na(2)—O distances in the range 2.410 to 2.667 Å.

Table 2. Selected distances (Å) and angles (°)

Na(1)—O(1')	2.505 (7)	Na(2)—O(2)	2.638 (6)
Na(1)—O(2')	2.520 (6)	Na(2)—O(3)	2.410 (6)
Na(1)—O(2)	2.475 (7)	Na(2)—O(3')	2.621 (7)
Na(1)—O(4)	2.347 (7)	Na(2)—O(4)	2.606 (6)
Na(1)—O(6)	2.467 (7)	Na(2)—O(5')	2.587 (7)
Na(1)—O(7)	2.983 (7)	Na(2)—O(6)	2.667 (7)
Na(1)—O(8)	2.440 (7)	Na(2)—O(7)	2.518 (7)
		Na(2)—O(8')	2.599 (7)
S(1)—O(1)	1.582 (6)	S(2)—O(5)	1.435 (6)
S(1)—O(2)	1.457 (6)	S(2)—O(6)	1.452 (6)
S(1)—O(3)	1.438 (6)	S(2)—O(7)	1.493 (6)
S(1)—O(4)	1.432 (6)	S(2)—O(8)	1.486 (6)
O(1)—O(5)	2.690 (8)	O(4)—O(7)	3.095 (8)
O(1)—O(6')	3.027 (8)	O(5)—O(6')	3.135 (8)
O(2)—O(6)	3.046 (8)	O(5)—O(7')	3.106 (8)
O(2)—O(8')	3.098 (8)	O(6)—O(8')	2.692 (8)
O(2)—O(8)	3.148 (8)	O(7)—O(7')	2.497 (11)
O(3)—O(7')	3.181 (8)		
O(1)—S(1)—O(2)	106.8 (4)	O(5)—S(2)—O(6)	112.8 (4)
O(1)—S(1)—O(3)	106.9 (4)	O(5)—S(2)—O(7)	109.6 (4)
O(1)—S(1)—O(4)	103.5 (4)	O(5)—S(2)—O(8)	109.3 (4)
O(2)—S(1)—O(3)	112.1 (4)	O(6)—S(2)—O(7)	107.5 (4)
O(2)—S(1)—O(4)	112.5 (4)	O(6)—S(2)—O(8)	110.1 (4)
O(3)—S(1)—O(4)	114.2 (4)	O(7)—S(2)—O(8)	107.5 (4)

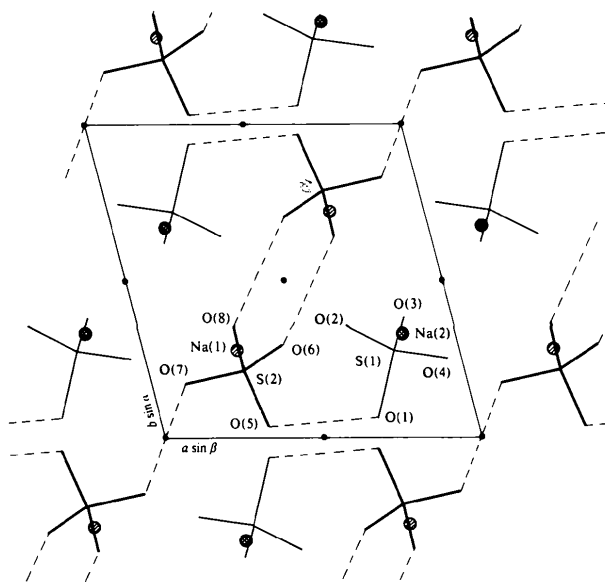


Fig. 1. A projection down *c* of the structure of α -NaHSO₄. Hydrogen bonds are indicated by broken lines.

4.2. Hydrogen and hydrogen bonding

From the S—O distances in the S(2)O₄ tetrahedron, it is not clear which O atom is bonded to H.

Both S(2)—O(5) and S(2)—O(6) are close to the values expected for S—O distances in the HSO₄⁻ ion. Though both S(2)—O(7) and S(2)—O(8) are significantly longer, they are not as long as expected for S—OH. The short distance O(6)—O(8') seems to point to hydrogen bonding of these O atoms, which suggests that the H atom is bonded to O(8).

However, this assumption does not explain the large value of S(2)—O(7), nor does it explain the value of O(7)—O(7'), which is even shorter than is expected for hydrogen-bonded O atoms in this kind of compound. A similar anomaly has been encountered in CaHPO₄ (Dickens, Bowen & Brown, 1972; Catti, Ferraris & Filhol, 1977). The P(1)—O distances found in these determinations are as expected, P(1)—O(1) being considerably longer than the other P(1)—O distances. Both P(2)—O(6) and P(2)—O(7) are longer than P(2)—O(5) and P(2)—O(8), while O(7)—O(7'), as in α -NaHSO₄, is very short. (Atom identification is similar in both compounds.)

These phenomena have been explained as disorder of one of the H atoms. In CaHPO₄ (Dickens *et al.*, 1972) the H atom was found to be distributed between O(6) and O(7), which makes it possible that hydrogen bonding exists between O(6) and O(8') as well as between O(7) and O(7'). Since the purpose of our determination was to obtain global structural knowledge of α -NaHSO₄, no attempt was made to determine the H-atom positions. Because of the similarity of the anomaly in the S—O and O...O distances in α -NaHSO₄ and the P—O and O...O distances in the isomorphous CaHPO₄, it is assumed that the H atom of the HS(2)O₄⁻ ion is disordered. However, a remarkable difference with respect to CaHPO₄ is that the H atom is distributed between O(7) and O(8), and not between O(6) and O(7) as in CaHPO₄. An indication that disorder of H atoms is present in more compounds of this structure type is found in α -SrHPO₄ (Boudjada, Masse & Guitel, 1978). Although the authors do not discuss the positions of the H atoms, the P(2)—O distances in that structure may well be explained by disorder of one of the H atoms.

Because of the hydrogen bonding assumed in α -NaHSO₄, between O(6) and O(8') as well as between O(7) and O(7'), HS(2)O₄⁻ ions are coupled to form infinite chains in the [110] direction. HS(1)O₄⁻ ions are linked to these chains by means of the hydrogen bonding between O(1) and O(5).

4.3. Comparison of α - and β -NaHSO₄

As was already mentioned in the discussion of the structure of β -NaHSO₄, one of the differences of β -NaHSO₄ with respect to the structure of α -NaHSO₄ can be understood by looking at the configurations of the cations and anions.

In α -NaHSO₄ this configuration is of the NaCl type, with each Na⁺ ion coordinated by six HSO₄⁻ ions, while in β -NaHSO₄ the structure can be seen as a distorted CsCl type, each Na⁺ ion being surrounded by eight HSO₄⁻ ions.

A further difference is seen by considering the hydrogen-bonding scheme. While in α -NaHSO₄ the hydrogen bonding gives rise to the presence of infinite chains of HSO₄⁻ ions, in β -NaHSO₄ the HSO₄⁻ ions are coupled to form dimers.

Furthermore, in α -NaHSO₄ one of the Na atoms is eight-coordinated by O atoms. In β -NaHSO₄, however, there exists only seven-coordination of Na. There is a remarkable similarity between the seven-coordination of Na in β -NaHSO₄ and the seven-coordination of Na(1) in α -NaHSO₄. In β -NaHSO₄ six of the Na—O distances vary from 2.37–2.56 Å while one Na—O

distance is much longer (2.91 Å). In α -NaHSO₄ six of the Na(1)—O distances are in the range 2.347–2.520 Å, while the seventh has a much larger value (2.983 Å).

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Structure Cristalline du Bis(dihydrogénopyrophosphate) Tripotassique et Monosodique K₃Na(H₂P₂O₇)₂

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Abstract

K₃Na(H₂P₂O₇)₂ is monoclinic, space group C2/c with $a = 16.912$ (8), $b = 7.251$ (5), $c = 11.015$ (6) Å, $\beta = 100.26$ (6)° and $Z = 4$; $V = 1316.8$ Å³, $D_m = 2.465$ (5), $D_x = 2.459$ Mg m⁻³, $\mu = 1.36$ mm⁻¹ for Mo K α . The structure was solved by direct methods and refined by least squares ($R = 0.027$) with 1753 reflexions measured on an automatic three-circle dif-

fractometer (Mo K α radiation). The three independent H atoms were located on difference maps; they are involved in three O...O hydrogen bonds of length 2.609 (3), 2.544 (3) and 2.503 (4) Å. In the two shorter contacts, the proton is required to lie on a crystallographic element of symmetry (centre and twofold axis). The hydrogen bond lying across the twofold axis was found to be anomalous in several structural details, and the electron density difference

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