

SHORT STRUCTURAL PAPERS

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A New Modification of Sodium Hydrogensulphate

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Abstract. A new, probably metastable, phase of NaHSO_4 was found by dehydrating $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. The conditions that control the formation of this new phase are not quite clear. The unit-cell dimensions, $a = 8.759$ (1), $b = 7.500$ (1), $c = 5.147$ (1) Å, $\beta = 99.49$ (2)°, $V = 333.5$ Å³, $Z = 4$, the space group $P2_1/n$ as well as the structure were determined from 113 lines of the powder pattern. The structure can be described as a distorted CsCl-type. Although hydrogen has not been considered in the refinement, S–O bond lengths and O–O distances point to hydrogen-bond coupling of pairs of anions.

Introduction. In an attempt to prepare NaHSO_4 from $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ and to establish the powder pattern of the anhydrous salt, an unknown pattern was incidentally recorded on a Guinier photograph. Later on it became clear that this pattern represented an unknown modification of anhydrous NaHSO_4 , which we named $\beta\text{-NaHSO}_4$ to distinguish it from the known triclinic phase, referred to as $\alpha\text{-NaHSO}_4$.

Although several attempts were made to find the proper preparation conditions, the success of the first experiment was repeated only a few times. However, since a few high-quality Guinier photographs of the nearly pure β -phase were available, the determination of its structure seemed possible.

Anhydrous NaHSO_4 can easily be prepared by dehydration of the monohydrate, which can be carried out by the use of a drying agent (such as P_2O_5), by evacuation or by heating of the specimen (below 186°C, the decomposition temperature).

Depending on the specific drying conditions, two different phases of NaHSO_4 are formed. Between 80 and 186°C dehydration gives the pure α -phase, while below 80°C the dehydration yields at least a small fraction of $\beta\text{-NaHSO}_4$ (together with $\alpha\text{-NaHSO}_4$). It is not quite clear which conditions affect the dehydration to give a smaller or larger fraction of the β -phase. The largest yields of $\beta\text{-NaHSO}_4$ were obtained between 0 and 25°C. The line positions were measured from a powder photograph of $\beta\text{-NaHSO}_4$ made at 25°C with a Guinier–de Wolff focusing camera (with Cu $K\alpha$ radiation). The pattern was calibrated with corundum. The intensities were measured with a microdensitometer from the same photograph, with the program *PEAK* (Sonneveld & Visser, 1975), which enabled us to find the integrated intensities. The intensity data were corrected for absorption and oblique incidence. The unit cell was determined with the help of an indexing program written by Visser (1969).

A comparison of the unit-cell volumes of α and $\beta\text{-NaHSO}_4$ (Table 1) shows that the new phase is not likely to contain water of crystallization. This conclusion is corroborated by the structure determination.

Since only 59 of the observed 113 powder lines of the $\beta\text{-NaHSO}_4$ pattern are singly indexed reflections, a Patterson synthesis seemed rather unpromising. A better approach seemed to be the use of a simplex refinement program (Bassi, 1968; Nelder & Mead, 1965) which was already available. This program does not require the starting values of the parameters to be close to the correct values. Because the asymmetric unit consists of only one formula unit and, moreover, we could assume in the first stage of the refinement the HSO_4^- ion to be a regular tetrahedron with an approximately known S–O distance, we only had to estimate the positions of the Na and S atoms and the orientation of the HSO_4^- tetrahedron. The position of the H atom was ignored throughout the refinement. A very rough NaCl-like model was constructed based on a regular alternation in three orthogonal directions of Na^+ and HSO_4^- ions, and in agreement with the known sym-

Table 1. Comparison of the volumes per unit cell and per formula unit

	Z	V (Å ³)	V/Z (Å ³)
$\alpha\text{-NaHSO}_4$	4	322.5	80.6
$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$	4	432.7	108.2
$\beta\text{-NaHSO}_4$	4	333.5	83.4

metry of the structure. The ensuing starting values of the position and orientation parameters were good enough to enable the program to find the correct structure. The original position of the HSO_4^- ion proved to be almost correct, but the program moved the Na^+ ion over a distance of approximately $\frac{1}{10}$, $\frac{1}{4}$, $\frac{1}{3}$ of the cell edges. The final structure proved to be closer to the CsCl type.

After an intermediate stage, in which four S—O distances were added to the parameters, the refinement was continued with three parameters for each of the six atomic positions, together with a scale factor and an overall isotropic temperature factor. This makes 20 parameters, while the number of powder lines was 113. The atomic form factors for S, Na^+ and O^- were those given by Moore (1963). The function minimized was $r = \sum_i w_i (I_o - I_c)^2 / \sum_i w_i I_o^2$ where $w = 1/(1 + I_o/c)$ ($c = I_{\text{max}}/5$). The final value of r was 0.90×10^{-2} . The final value of the conventional residual R index, calculated for 59 singly indexed reflections, was 0.114. The

overall isotropic temperature factor became 2.0 \AA^2 .* Finally, a few cycles of least-squares refinement were carried out with the 59 singly indexed reflections to determine the standard deviations in the atomic positions and in the interatomic distances and angles.

Discussion. The final atomic positions and their standard deviations are given in Table 2, the interatomic distances and angles with their standard deviations in Table 3. A projection of the structure is given in Fig. 1. The H atom, completely ignored so far, can be placed now; it must be attached to O(3) as S—O(3) is significantly longer than the remaining S—O distances. The geometry of the HSO_4^- tetrahedron is in good agreement with the results of other alkali hydrogensulphate structure determinations (Table 4). The Na^+ ion is surrounded by seven O atoms (Table 3), six at a distance varying from 2.37–2.56 Å, and one at a distance which is considerably longer (2.91 Å). This last O atom completes a fairly regular octahedron with five of the six other O atoms. Hydrogen bonding was derived from the O—O distances (Table 3): the O(2'')—O(3) distance is considerably shorter than other O—O distances. Fig. 1 makes clear that the HSO_4^- ions

Table 2. Fractional atomic coordinates ($\times 10^3$) of $\beta\text{-NaHSO}_4$

	<i>x</i>	<i>y</i>	<i>z</i>
Na	201 (2)	490 (2)	219 (3)
S	439 (2)	277 (2)	836 (3)
O(1)	338 (2)	252 (3)	38 (4)
O(2)	596 (3)	325 (3)	967 (4)
O(3)	365 (3)	432 (3)	647 (4)
O(4)	431 (4)	121 (3)	673 (5)

Table 3. Selected distances (Å) and angles (°)

The primes correspond to each of the four HSO_4^- ions in the unit cell, or their translated equivalents.

Na—O(1)	2.42 (3)	S—O(4)	1.44 (2)
Na—O(1')	2.38 (3)	O(1)—O(3')	3.04 (3)
Na—O(2'')	2.91 (3)	O(2)—O(4'')	2.98 (4)
Na—O(2'')	2.56 (3)	O(2'')—O(3)	2.67 (3)
Na—O(3)	2.46 (3)	O(1) S O(2)	109.3 (1.4)
Na—O(4''')	2.48 (4)	O(1)—S—O(3)	107.1 (1.5)
Na—O(4')	2.37 (3)	O(1)—S—O(4)	109.2 (1.7)
S—O(1)	1.48 (2)	O(2)—S—O(3)	110.8 (1.5)
S—O(2)	1.47 (3)	O(2)—S—O(4)	114.7 (1.8)
S—O(3)	1.58 (2)	O(3)—S—O(4)	105.4 (1.4)

* A list of $I_o - I_c$ has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33034 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

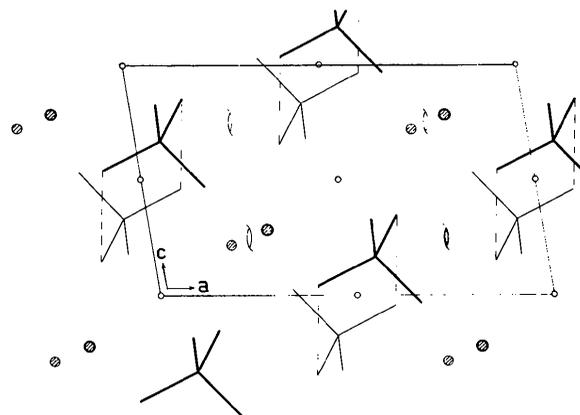


Fig. 1. One unit cell of $\beta\text{-NaHSO}_4$ projected down *b*. *n*-glide planes are at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, the centres of symmetry are at $y = 0$ and $y = \frac{1}{2}$. \circ Na, \times HSO_4^- , --- hydrogen bond.

Table 4. Bond lengths (Å) in the HSO_4^- ion

	$\beta\text{-NaHSO}_4^a$	$\text{NaHSO}_4 \cdot \text{H}_2\text{O}^b$	$\text{NaHSO}_4 \cdot \text{H}_2\text{O}^c$	KHSO_4^d	RbHSO_4^e
S—OH	1.58	1.61	1.60	1.56	1.57
Mean of other three S—O	1.46	1.45	1.45	1.47	1.44

References: (a) This work. (b) Pringle & Broadbent (1965). (c) Grimvall (1971). (d) Cruickshank (1964). (e) Ashmore & Petch (1975).

are coupled to form dimers by means of hydrogen bonding. This kind of coupling was also observed in KHSO_4 (Loopstra & MacGillavry, 1958).

Confirmation of the significant difference of one S—O distance in the HSO_4^- tetrahedron with respect to the remaining S—O distances was obtained from the Hamilton significance test (Hamilton, 1965): the hypothesis that all four S—O distances are equal must be rejected at the significance level $\alpha = 0.01$.

The difference between the structures of the α and β -phases becomes clear, if both structures are described in terms of cations and anions. Then the structure of β - NaHSO_4 can be regarded as a distorted CsCl structure while the structure of α - NaHSO_4 (determination in progress) can be described as a distorted NaCl structure. According to this approach one should expect the β - NaHSO_4 structure to be more loosely packed. This is in accordance with the difference in

unit-cell volume of about 3% (Table 1), and also with the greater stability of the α -phase.

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$\text{Cs}_3\text{Sb}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ with the Hexagonal $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ Structure Type

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Abstract. $\text{Cs}_3\text{Sb}_2\text{I}_9$: FW 1748, hexagonal, $P6_3/mmc$, $a = 8.349$ (2), $c = 20.936$ (9) Å, $Z = 2$, $D_x = 4.68$ g cm^{-3} , $R = 0.062$, $\mu(\text{Mo } K\alpha) = 178$ cm^{-1} , $F(000) = 1488$; $\text{Cs}_3\text{Bi}_2\text{I}_9$: FW 1959, $P6_3/mmc$, $a = 8.404$ (2), $c = 21.183$ (19) Å, $D_x = 5.02$ g cm^{-3} , $R = 0.092$, $\mu(\text{Mo } K\alpha) = 245$ cm^{-1} , $F(000) = 1616$. The investigation involved single-crystal diffractometry, absorption correction and least-squares refinement. The structures are isotypic with $\text{Cs}_3\text{Cr}_2\text{Cl}_9$. The $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ type is compared with six other structure types having the same composition and similar construction principles. It is shown by a unit-cell shift that the $\text{K}_3\text{W}_2\text{Cl}_9$ and $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ structures are lower-symmetry versions of the $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ type.

Introduction. $\text{Cs}_3\text{Sb}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ have been synthesized by Dr F. Lévy using counter diffusion of liquid reagents slowed down by silicate gel (CsI in H_2O and SbCl_3 or BiCl_3 in HCl). Originally the composition of the red crystals formed was unknown. However, the structure determination led us to the chemical formula

given, which also agreed with the results of the chemical analysis. Preliminary diffraction experiments indicated that the two compounds are isotypic and that their Laue symmetry is $6/mmm$. A crystal of $\text{Cs}_3\text{Sb}_2\text{I}_9$ was ground in a compressed-air mill to an ellipsoid ($190 \times 128 \times 128$ μm) while a $\text{Cs}_3\text{Bi}_2\text{I}_9$ crystal was available in the form of a platelet ($23 \times 64 \times 80$ μm). Lattice constants and intensities were measured on an automatic four-circle diffractometer (Philips PW 1100) with Mo $K\alpha$ radiation and a graphite monochromator in the θ - 2θ scan mode. Data collection for $\text{Cs}_3\text{Sb}_2\text{I}_9$ ($\text{Cs}_3\text{Bi}_2\text{I}_9$) was carried out to a limit of 0.7 Å $^{-1}$ in $\sin \theta/\lambda$, yielding 727 (757) independent reflections, of which 707 (588) with $|F|$ greater than $3\sigma_F$ were used for the structure refinement. In both cases, the *CAMEL JOCKEY* experimental method for absorption correction (Flack, 1975, 1977) was used. Examination of the systematic absences indicated that $P6_3mc$, $P6_2c$ and $P6_3/mmc$ were possible space groups. The structure was solved by the Patterson method. Relativistic Hartree-Fock scattering factors (Cromer & Mann,