

Neutron Diffraction Study of the Hydrogen Bond in Trisodium Hydrogenbissulphate and a Survey of Very Short O—H...O Bonds

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Abstract

$\text{Na}_3\text{H}(\text{SO}_4)_2$, monoclinic, $P2_1/c$, $a = 8.648$ (1), $b = 9.648$ (1), $c = 9.143$ (1) Å, $\beta = 108.77$ (1)°, $Z = 4$. The structure was refined from 2055 neutron diffraction data to $R(F) = 0.049$. Good agreement was found with a previous X-ray measurement except for the H position. A very short hydrogen bond with $\text{O}\cdots\text{O} = 2.432$ (2) Å links the two parts of the $(\text{SO}_4\text{HSO}_4)^{3-}$ dimer. This bond is asymmetrical with $\text{O}-\text{H} = 1.156$ (3) and $\text{H}\cdots\text{O} = 1.276$ (3) Å and $\text{O}-\text{H}\cdots\text{O} = 179.1$ (2)°. The largest thermal vibration of H is practically normal to the bond in contrast to findings in other short $\text{O}-\text{H}\cdots\text{O}$ bonds. The result is compared with other neutron diffraction studies of the H bonds with $\text{O}\cdots\text{O}$ distances shorter than 2.50 Å. The $\text{O}-\text{H}$ vs $\text{O}\cdots\text{O}$ correlation is discussed with reference to the spread of values and the abrupt change of slope at about 2.50 Å.

Introduction

Crystals were grown as previously described (Catti, Ferraris & Ivaldi, 1979). A specimen with approximate dimensions $4 \times 4 \times 5.5$ mm and irregular shape was selected for the neutron experiment. Intensities were collected on the P32 automatic four-circle diffractometer at the FR2 reactor at the KFK, Karlsruhe. The wavelength used was $\lambda = 1.021$ Å. About 3000 reflections were registered at room temperature by an $\omega/2\theta$ scan up to $\sin \theta/\lambda = 0.73$ Å⁻¹. Two reference reflections were measured after every 50 reflections. The maximum variation about the mean value was $\pm 3\%$. A unique data set of 2193 reflections was obtained after averaging of equivalent values. 138 reflections with $F < 2\sigma(F)$ were treated as 'less-thans' and excluded from the following calculations, leaving

2055 observations for the structure refinement.* All calculations were carried out by the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38014 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates (X-ray first line, neutron second line) and equivalent isotropic thermal parameters (neutron), with standard deviations in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq} (Å ²)
S(1)	0.13929 (8)	0.30906 (7)	0.85771 (7)	
	0.1391 (2)	0.3087 (2)	0.8574 (2)	0.0114 (7)
S(2)	0.63436 (8)	0.31874 (7)	0.40524 (8)	
	0.6340 (2)	0.3187 (2)	0.4054 (2)	0.0098 (1)
Na(1)	0	0	0	0.0219 (9)
Na(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.0344 (11)
Na(3)	0.7453 (2)	-0.0060 (1)	0.2774 (1)	
	0.7450 (2)	-0.0060 (2)	0.2767 (2)	0.0187 (6)
Na(4)	0.3869 (1)	0.1559 (1)	0.1279 (1)	
	0.3869 (2)	0.1558 (2)	0.1278 (2)	0.0226 (7)
O(1)	0.1547 (3)	0.1578 (2)	0.8752 (2)	
	0.1546 (1)	0.1581 (1)	0.8750 (1)	0.0174 (4)
O(2)	0.2554 (3)	0.3765 (2)	0.9916 (2)	
	0.2554 (1)	0.3755 (1)	0.9920 (1)	0.0220 (4)
O(3)	-0.0324 (3)	0.3496 (2)	0.8547 (3)	
	-0.0321 (1)	0.3489 (1)	0.8544 (2)	0.0237 (4)
O(4)	0.1596 (3)	0.3568 (3)	0.7146 (3)	
	0.1594 (1)	0.3563 (1)	0.7144 (1)	0.0240 (4)
O(5)	0.6162 (3)	0.3648 (3)	0.5503 (3)	
	0.6162 (1)	0.3644 (1)	0.5504 (1)	0.0255 (4)
O(6)	0.8095 (3)	0.3375 (2)	0.4152 (3)	
	0.8092 (1)	0.3375 (1)	0.4149 (2)	0.0293 (5)
O(7)	0.5926 (3)	0.1718 (2)	0.3752 (2)	
	0.5930 (1)	0.1720 (1)	0.3751 (1)	0.0175 (3)
O(8)	0.5334 (3)	0.4044 (2)	0.2778 (3)	
	0.5333 (1)	0.4039 (1)	0.2779 (1)	0.0245 (4)
H(1)	-0.102 (7)	0.270 (6)	0.877 (6)	
	-0.1083 (3)	0.2603 (2)	0.8821 (3)	0.0372 (8)

The following neutron scattering lengths were used: $b_{\text{Na}} = 3.63$, $b_{\text{S}} = 2.845$, $b_{\text{H}} = -3.74$, $b_{\text{O}} = 5.803$ fm (Koester, 1977). The refinement was carried out with anisotropic temperature factors for all atoms. An isotropic-extinction parameter (Larson, 1970) was included during the last cycles of refinement and a value of $g = 0.45 (1) \times 10^{-3}$ was obtained. The atomic parameters for a final $R(F) = 0.049$ are listed in Table 1.

Discussion

The positional parameters (Table 1) and the interatomic distances and angles (Tables 2 and 3) from the X-ray and neutron study agree well except for the H position and distances related to this atom. The general build-up of the structure has been described by Catti, Ferraris & Ivaldi (1979) and the same labelling of the atoms is used here.* The hydrogen bond which links

* A single figure in parentheses denotes an atom of the asymmetric unit; a second figure, ranging from 2 to 4, is included for atoms in the positions $-x$, $-y$, $-z$ and $\pm(-x, \frac{1}{2} + y, \frac{1}{2} - z)$. Roman numerals represent the following translations: (i) $-c$; (ii) c ; (iii) $-b$; (iv) $a - b$; (v) $-a - c$; (vi) $a + c$; (vii) $a - b + c$; (viii) $a - c$; (ix) $-a$.

Table 2. *Interatomic distances* (Å) *in the Na polyhedra*

Standard deviations for X-ray bond lengths are 0.002 Å.

	X-ray	Neutron
Na(1)—O(1) ⁱ } Na(1)—O(1,2) ⁱⁱ } Na(1)—O(4,3) ⁱⁱⁱ } Na(1)—O(4,4) ⁱ } Na(1)—O(6,3) ^{iv} } Na(1)—O(6,4) ^v }	2.528	2.530 (1)
Average	2.395	2.398
Na(2)—O(2,3) ^{vi} } Na(2)—O(2,4) ⁱ } Na(2)—O(7) } Na(2)—O(7,2) ^{vi} } Na(2)—O(8,3) ^{iv} } Na(2)—O(8,4) }	2.408	2.413 (1)
Average	2.445	2.448
Na(3)—O(1,2) ^{vi} } Na(3)—O(2,3) ^{vii} } Na(3)—O(3,4) ^{viii} } Na(3)—O(5,4) ⁱ } Na(3)—O(7) } Na(3)—O(8,3) ^{iv} }	2.370	2.368 (2)
Average	2.420	2.422
Na(4)—O(1) ⁱ } Na(4)—O(2) ⁱ } Na(4)—O(4,4) ⁱ } Na(4)—O(5,4) ⁱ } Na(4)—O(7) } Na(4)—O(8) } Na(4)—O(8,3) ^{iv} }	2.527	2.528 (2)
Average	2.510	2.509

Table 3. *Interatomic distances* (Å) *and O—S—O angles* (°) *in the S tetrahedra*

Standard deviations for the X-ray values are 0.002 and 0.003 Å for S—O and O—O distances, respectively, and 0.1° for angles.

	X-ray	Neutron	X-ray	Neutron
S(1)—O(1)	1.470	1.463 (2)		
S(1)—O(2)	1.462	1.465 (2)		
S(1)—O(3)	1.527	1.523 (2)		
S(1)—O(4)	1.450	1.450 (2)		
Average	1.477	1.475		
O(1)—O(2)	2.397	2.389 (1)	109.7	109.3 (1)
O(1)—O(3)	2.425	2.415 (1)	108.1	108.0 (1)
O(1)—O(4)	2.426	2.418 (1)	112.4	112.4 (1)
O(2)—O(3)	2.413	2.412 (1)	107.6	107.7 (1)
O(2)—O(4)	2.406	2.409 (2)	111.4	111.6 (1)
O(3)—O(4)	2.402	2.397 (2)	107.5	107.6 (1)
Average	2.412	2.407	109.5	109.8
S(2)—O(5)	1.455	1.452 (2)		
S(2)—O(6)	1.498	1.500 (2)		
S(2)—O(7)	1.467	1.464 (2)		
S(2)—O(8)	1.466	1.463 (2)		
Average	1.472	1.470		
O(5)—O(6)	2.391	2.391 (2)	108.1	108.2 (1)
O(5)—O(7)	2.421	2.418 (2)	111.9	112.1 (1)
O(5)—O(8)	2.392	2.391 (2)	110.0	110.3 (1)
O(6)—O(7)	2.401	2.396 (1)	108.1	107.9 (1)
O(6)—O(8)	2.401	2.397 (1)	108.2	108.0 (1)
O(7)—O(8)	2.408	2.402 (1)	110.4	110.3 (1)
Average	2.402	2.399	109.5	109.4

Table 4. *Hydrogen-bonding scheme* (X-ray first row, neutron second row)

	O...O (Å)	O—H (Å)	H...O (Å)	O—H...O (°)
O(3)—H...O(6,4) ^x	2.434 (4)	1.03 (6)	1.40 (6)	177 (4)
	2.432 (2)	1.156 (3)	1.276 (3)	179.1 (2)

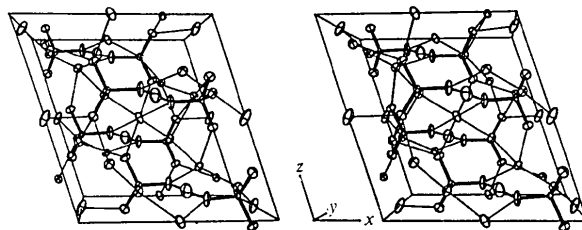


Fig. 1. A stereoscopic view of the structure of $\text{Na}_3\text{H}(\text{SO}_4)_2$. Thermal ellipsoids are at the 50% probability level.

two SO_4 tetrahedra is fairly short with an $\text{O}\cdots\text{O}$ distance of 2.432 (2) Å. The $\text{O—H}\cdots\text{O}$ angle [179.1 (2)°] is almost linear and the H atom is clearly in an asymmetric position with distances of 1.156 (3) and 1.276 (3) Å from donor and acceptor, respectively (Table 4). Fig. 1 gives a stereoscopic view of the structure.

In most cases with very short hydrogen bonds it has been noted that the direction of largest thermal motion of the proton is along the hydrogen bond, instead of being normal as in ordinary bonds (Speakman, 1975; Speakman, Lehmann, Allibon & Semmingsen, 1981). Speakman (1975) attributes this anomaly to the presence of a broad and flat potential-energy well for the proton in very short hydrogen bonds. In $\text{Na}_3\text{H}(\text{SO}_4)_2$ the vibrational ellipsoid has intermediate (0.20 Å) and longest (0.22 Å) axes which are quite similar in length; therefore, to a first approximation, the ellipsoid has infinite symmetry around the shortest axis (0.14 Å, rotation axis). In other words, the section perpendicular to the shortest axis is roughly circular. The intermediate axis (0.20 Å) is found parallel to the bond within 8° ; in such a way the largest direction of vibration (0.22 Å) is practically normal (83°) to the bond, as usual. The r.m.s. displacements of 0.22 and 0.20 Å are relatively large (Speakman, 1975). The form of the potential-energy well for the proton should therefore be broad, perpendicular and parallel to the bond.

Ishikawa (1978) has given a smooth curve for the O—H vs O...O correlation. A survey of 25 recent neutron diffraction determinations of very short hydrogen bonds (O...O \leq 2.50 Å) (Table 5) not yet included in this curve shows (Fig. 2) that most of the O—H distances are on the lower side of the curve and that, in general, the dispersion of points is too large to justify the elaborate course of Ishikawa's curve. The

spread means that for short O...O distances a variety of O—H lengths is possible for the same O...O distance, as already suspected by Küppers, Kwick & Olovsson (1981). For O...O 2.39–2.40 Å nine observations are reported with O—H ranging from 1.108 to 1.198 Å. The very few symmetry-restricted (SR; Catti & Ferraris, 1974) hydrogen bonds without disorder which have been reported recently are not included in our up-dating of Ishikawa's plot, because they should necessarily lie on the dotted straight line. On the other hand, the spread of O—H values now pointed out and the several recent findings of disorder or asymmetry for bonds previously considered symmetric no longer justify a special interpolation curve reserved for the SR bonds, as already suspected by Catti & Ferraris (1976).

As far as only the general trend is considered, the influence of O...O distance on the O—H bond is definite also for short bonds, in spite of the spread of values. In particular, the abrupt change of slope for O...O about 2.50–2.55 Å shows that for shorter distances the acceptor becomes more efficacious in attracting the proton. This higher power of attraction is present, however, only on average and the O—H length is definitely a function not only of O...O but also of other causes which become more important with the weakening of O—H. These causes presumably include the crystal environment and the other bonds involving donor and acceptor, but not linearity of the hydrogen bond (*cf.* Table 5). The abrupt change of slope for the

Table 5. Short and asymmetric O—H...O bonds recently studied by neutron diffraction and not included in Ishikawa's (1978) paper (room-temperature data if not stated otherwise)

	O...O	O—H	H...O	O—H...O	$\Delta(\text{O—H, H...O})$	References
$\text{Cu}(\text{HC}_8\text{H}_4\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	2.391 (2) Å	1.108 (4) Å	1.290 (4) Å	172.1 (4) ^a	0.182 Å	Bartl & Küppers (1980)
$\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{CH}_3\text{OH}$	2.393 (4)	1.195 (5)	1.205 (5)	171.3 (5)	0.010	Küppers <i>et al.</i> (1981)
	2.388 (4)	1.172 (5)	1.226 (5)	169.3 (6)	0.054	
$\text{LiHC}_8\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$	2.400 (2)	1.114 (2)	1.296 (2)	168.9 (1)	0.182	Küppers, Takusagawa & Koetzle (1982)
	2.390 (2)	1.181 (2)	1.216 (2)	171.7 (1)	0.035	
$[\text{Ni}(\text{C}_{13}\text{H}_{21}\text{N}_5\text{O}_4)]$	2.390 (8)	1.198 (14)	1.200 (14)	170.8 (8)	0.002	Hussain, Schlemper & Yelon (1981)
D-Quinolinic acid	2.393 (2)	1.138 (2)	1.257 (2)	175.2 (2)	0.119	Takusagawa & Koetzle (1979)
Imidazole H maleate	2.393 (3)	1.196 (5)	1.197 (5)	176.8 (4)	0.001	Hsu & Schlemper (1980)
$\text{H}_3\text{PO}_4 \cdot \text{CO}(\text{NH}_2)_2$	2.400	1.186	1.224	169.5	0.038*	Nozik, Fykin, Bukin & Muradyan (1976)
$\text{Ca}(\text{H maleate})_2$	2.424 (2)	1.121 (3)	1.305 (3)	175.9 (3)	0.184	Hsu & Schlemper (1980)
$\text{Na}_3\text{H}(\text{SO}_4)_2$	2.432 (4)	1.156 (3)	1.276 (3)	179.1 (2)	0.120	This work
$\text{KH}(\text{CHOO})_2$ (120 K)	2.437 (2)	1.165 (3)	1.271 (3)	179.1 (3)	0.106	Hermansson, Lehmann & Tellgren (1982)
$[\text{Ni}(\text{C}_3\text{H}_7\text{N}_2\text{O}_2)_2\text{D}]^+\text{Cl}^- \cdot \text{D}_2\text{O}$	2.439 (8)	1.058 (9)	1.391 (10)	169.7 (7)	0.333	Hsu, Schlemper & Fair (1980)
$\text{NaH maleate} \cdot 3\text{H}_2\text{O}$ (120 K)	2.445 (2)	1.079 (2)	1.367 (2)	176.1 (2)	0.288	Olovsson, Kwick, Lehmann & Olovsson (1982)
KD_2PO_4	2.455 (6)	1.063 (5)	1.397 (5)	172.6 (5)	0.334	Thornley, Nelmes & Rouse (1975)
CaHPO_4	2.461 (2)	1.182 (3)	1.283 (3)	173.5 (3)	0.101	Catti, Ferraris & Filhol (1977)
1,3-Diphenyl-1,3-propanedione	2.463 (4)	1.163 (9)	1.362 (9)	154.7 (5)	0.199	Jones (1976a)
$[\text{Pt}(\text{C}_3\text{H}_7\text{N}_2\text{O}_2)_2\text{H}]^+\text{Cl}^- \cdot 3.5\text{H}_2\text{O}$	2.472 (8)	1.087 (8)	1.389 (7)	173.8 (7)	0.302	Schlemper & Fair (1977)
NaH_2PO_4	2.485 (5)	1.040 (9)	1.459 (8)	167.7 (7)	0.419	Choudhary, Nelmes & Rouse (1981)
$\text{C}_7\text{H}_5\text{O}_4 \cdot 2\text{H}_2\text{O}$ (100 K)	2.487 (1)	1.071 (1)	1.417 (1)	177.5 (1)	0.346	Stevens & Coppens (1980)
KH crotonate	2.488 (2)	1.141 (2)	1.348 (2)	178.0 (3)	0.207	McGregor, Speakman & Lehmann (1977)
1-Phenyl-1,3-butanedione	2.489 (5)	1.238 (11)	1.322 (12)	153.2 (7)	0.084	Jones (1976b)
RbH_2PO_4	2.489 (11)	1.061 (16)	1.430 (15)	175.4 (25)	0.369	Kennedy & Nelmes (1980)
$\text{KH}(\text{CHCl}_2\text{COO})_2$	2.498 (3)	1.107 (4)	1.392 (4)	177.6 (3)	0.285	Hadži, Leban & Orel (1979)
TiH_2PO_4	2.50 (1)	1.15 (2)	1.36 (2)	177 (1)	0.210	Nelmes & Choudhary (1981)

* E.s.d.'s not available.

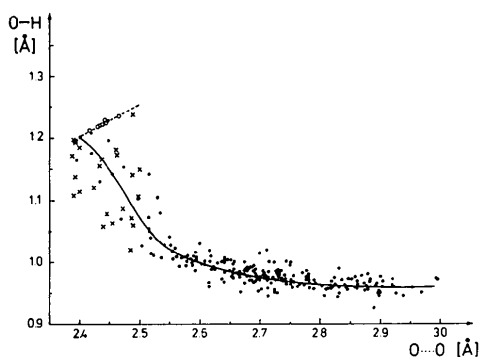


Fig. 2. Correlation between O—H and O...O distances in O—H...O bonds. Curve and dots from Ishikawa (1978); crosses refer to values in Table 5.

curve O—H vs O...O at about 2.50 Å could be related to the evidence of covalency for short H...O pointed out by Stevens & Coppens (1980). Unfortunately, the small sample of hydrogen bonds studied by neutron diffraction which is available does not allow a deeper insight. It should, however, be remembered that part of the curve in Fig. 2 deals only with non-water donors, because no hydrogen bond with O...O < 2.55 Å is donated by a water molecule (Chiari & Ferraris, 1982).

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