

A Neutron Diffraction Study of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

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(Received 29 January 1974; accepted 13 November 1974)

The hydrogen atoms in crystals of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ have been located using 612 non-equivalent neutron diffraction intensities. They lie between the hydrogen positions postulated by Dickens, Mauer & Brown [*J. Res. Natl. Bur. Stand.* (1970). 74A, 319–324] and those predicted by Baur [*Acta Cryst.* (1972). B28, 1456–1465]. Bond valence calculations show that the Na–O and $\text{H} \cdots \text{O}$ bonds are equivalent as regards their strength and that, taking this equivalence into account, all three O atoms of the carbonate group have identical trigonal bipyramidal environments.

Introduction

The crystal structure of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ was first determined by Harper (1936) and later refined by Dickens, Mauer & Brown (1970) using X-ray diffraction. Dickens *et al.* (1970) reported three sets of hydrogen atom positions, one derived from the weighted difference Fourier synthesis, another derived from the least-squares refinements and a third derived from a consideration of the probable hydrogen-bonding scheme. Baur (1972) has pointed out that the third set of positions, that preferred by Dickens *et al.*, gives an H(1)–Na(2) distance of 2.42 Å and an H(1)–O(4)–Na(2) angle of 63°. This implies that H(1) lies within the edge of the oxygen coordination polyhedron around Na(2) [the average Na(2)–O distance is 2.53 Å]. He suggested a new set of hydrogen positions which satisfied the criteria that he outlined in the same paper. The present work was undertaken to resolve the discrepancy.

Structure determination

A single crystal approximately $7 \times 4 \times 2$ mm (long axis [100], short axis [001]) was prepared by evaporation of an aqueous solution at 60°C. Precession photographs were used to align the *a* axis of the crystal along the goniometer head axis. The cell dimensions reported by Dickens *et al.* (1970) together with the nuclear scattering length used in this study are given in Table 1. A four-circle neutron diffractometer (Anderson, 1973) at the McMaster University nuclear reactor was used to measure the intensities. The incident beam, monochromated by reflexion from the (111) face of a copper crystal ($\lambda = 1.091$ Å), had a flux of approximately 10^6 n cm^{-2} s^{-1} . For each reflexion, counts were recorded with an ω step scan (step interval = $\frac{1}{18}^\circ$). The scan range was $1\frac{1}{2}^\circ$ for 2θ less than 40° , 2° for 2θ between 40 and 60° and $2\frac{1}{2}^\circ$ for 2θ between 60 and 105° . These scans were large enough to allow the background to be determined on each side of the peak. The counting time at each step was determined by a monitor count of 10^4 which corresponded to a maximum step count of 3980 for the strongest reflexion. A standard reflexion was

measured at regular intervals and showed no significant variation during the course of the experiment (3 months). The 674 intensity measurements were reduced to 612 non-equivalent reflexions with $2\theta \leq 105^\circ$. Of these, 52 had intensities less than three times the standard error based on counting statistics and were given zero weight if $F_c < F_o$ in the least-squares refinement.

Table 1. *Crystal data for $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$*

Orthorhombic*	$D_m = 2.255$ g cm^{-3}
$a = 6.472$ (2)† Å	$D_x = 2.256$ g cm^{-3} (Pabst, 1930)
$b = 10.724$ (3)	
$c = 5.259$ (2)	$Z = 4$
$V = 365.1$ Å ³	
Space group $P2_1ab$ (No. 29)	
Systematic absences: $h0l$, $h = 2n + 1$; $hk0$, $k = 2n + 1$	
λ (neutron) = 1.091 Å	μ ($\lambda = 1.091$ Å) = 0.001 mm^{-1}
Nuclear scattering lengths: H: -0.372×10^{-12} cm; Na: 0.351×10^{-12} cm; C: 0.665×10^{-12} cm; O: 0.577×10^{-12} cm	
(Bacon, 1969)	

* Data reported by Dickens, Mauer & Brown (1970).

† Throughout this paper the figures in parentheses are standard errors in the last digits quoted.

Lorentz corrections were applied but an absorption correction ($\mu = 0.08$ cm^{-1}) was not considered necessary as its neglect introduces a maximum error of 4% in the relative values of F_o . The hydrogen atom positions were located from a three-dimensional difference Fourier synthesis which was calculated using the non-hydrogen atom coordinates reported by Dickens *et al.* The structure was refined using the locally written full-matrix least-squares program *CUDLS*. Several strong reflexions showed evidence of extinction and a secondary isotropic extinction correction (Zachariasen, 1963; Larson, 1967) was applied in the final cycle of refinement. The function minimized was $\sum \omega(|F_o| - |F_c|)^2 = \sum \omega \Delta^2$ where $\omega = (0.0833 - 0.0652F_o + 0.0168F_o^2)^{-1}$, the coefficients in the weighting function being chosen to give average values of $\omega \Delta^2$ that were the same in all range of F . In the final round of refinement the shift/error was 0.042 and the agreement indices for all reflexions were $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| =$

Table 2. Atomic parameters of Na₂CO₃·H₂O

Anisotropic thermal parameters (\AA^2) appear in the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Values are $\times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Na(1)	0	1932 (5)	1392 (9)	142 (25)	190 (2)	107 (18)	4 (15)	11 (17)	-1 (14)
Na(2)	643 (12)	12 (5)	-3782 (10)	156 (24)	139 (18)	218 (24)	36 (16)	-15 (20)	-18 (16)
C	-2145 (9)	2546 (2)	6024 (4)	52 (7)	89 (8)	125 (8)	-11 (7)	-6 (9)	-8 (7)
O(1)	-2010 (10)	1389 (3)	5466 (7)	150 (12)	84 (10)	316 (14)	5 (12)	-45 (14)	-46 (10)
O(2)	-2033 (10)	3366 (3)	4266 (5)	186 (13)	179 (11)	144 (10)	-2 (14)	-12 (13)	27 (9)
O(3)	-2398 (9)	2883 (3)	-1650 (6)	164 (16)	267 (13)	122 (11)	-45 (12)	9 (12)	-26 (9)
O(4)	322 (11)	-296 (3)	692 (6)	189 (15)	192 (13)	215 (13)	-9 (14)	-12 (13)	46 (10)
H(1)	1464 (14)	-662 (8)	1611 (15)	253 (28)	383 (31)	396 (33)	62 (27)	-38 (29)	30 (29)
H(2)	-805 (13)	-899 (7)	1000 (13)	268 (26)	280 (29)	262 (24)	25 (23)	38 (22)	-20 (23)

0.059 and $R_2 = [\sum \omega \Delta^2 / \sum \omega F_o^2]^{1/2} = 0.063$ but the strongest reflection, 400, gave very poor agreement ($F_o = 154$, $F_c = 105$). Increasing the weights of this reflexion in the refinement reduced the discrepancy with changes in the atomic parameters of the order of two standard deviations but resulted in poorer overall agreement. The final parameters given in Table 2 are those which give the best overall agreement.*

Discussion

The positions of the non-hydrogen atoms are not significantly different from those of Dickens *et al.* (1970) except for the *y* coordinate of C. As is usual for neutron diffraction studies, the temperature factors are generally smaller than those from the X-ray study. Selected bond lengths and bond angles are given in Table 3. Within the experimental error, the CO₃²⁻ group has *D*_{3h} symmetry. Dickens *et al.* reported a significant difference between C-O(1) [1.299 (3) Å] and C-O(2) [1.274 (2) Å] which they ascribe to the difference in bonding around the oxygen atoms. The significantly different *y* coordinate of C in our study makes C-O(1) and C-O(2) equal and only possibly significantly different from C-O(3).

The structure was checked by calculating the bond valence sums around each atom using the bond strength (valence)-bond length curves of Brown & Shannon (1973). Using the expression $s = (R/1.378)^{-4.065}$ for the C-O bond the standard deviation between sums of the bond valences (shown in Fig. 1) around each atom and the atomic valences is satisfactorily small (0.06 v.u.).

The environments of the carbonate oxygen atoms show a remarkable similarity when considered in terms of the valences rather than the lengths of the bonds, since the Na-O and H-O bonds are seen to have equal valences. Fig. 1 gives the bond valences and Table 3 the bond angles around the carbonate oxygen atoms. Each oxygen atom forms one strong bond to C

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30777 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and four weak bonds to Na or H atoms. The five bonds are arranged at the corners of a trigonal bipyramid and although the distances of the Na-O and H-O bonds differ considerably (Na-O = 2.299 to 2.822 Å and H-O = 1.699 to 1.987 Å) the bond valences are virtually identical. The equatorial bonds have bond valences of 0.20 ± 0.04 v.u. and the axial bonds have bond valences of 0.14 ± 0.03 v.u. in accord with the observation that

Table 3. Interatomic distances (Å) and angles (°) in Na₂CO₃·H₂O

Symmetry code			
i	<i>x</i> , <i>y</i> , 1+ <i>z</i>	v	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, <i>z</i>
ii	$\frac{1}{2}+x$, - <i>y</i> , 1- <i>z</i>	vi	$-\frac{1}{2}+x$, - <i>y</i> , 1- <i>z</i>
iii	$-\frac{1}{2}+x$, - <i>y</i> , - <i>z</i>	vii	<i>x</i> , $\frac{1}{2}+y$, 1- <i>z</i>
iv	$-\frac{1}{2}+x$, $\frac{1}{2}-y$, 1+ <i>z</i>	viii	<i>x</i> , $-\frac{1}{2}+y$, - <i>z</i>
	ix	$\frac{1}{2}+x$, $\frac{1}{2}-y$, <i>z</i>	
	x	<i>x</i> , $\frac{1}{2}+y$, - <i>z</i>	
	xi	<i>x</i> , <i>y</i> , -1+ <i>z</i>	
	xii	$\frac{1}{2}+x$, - <i>y</i> , - <i>z</i>	
	xiii	$\frac{1}{2}+x$, $\frac{1}{2}-y$, -1+ <i>z</i>	
Na ions			
Na(1)-O(3 ^{ix})	2.332 (6)	Na(2)-O(1 ^{vi})	2.299 (8)
Na(1)-O(4)	2.426 (5)	Na(2)-O(1 ^{xiii})	2.313 (7)
Na(1)-O(3)	2.451 (6)	Na(2)-O(4)	2.385 (6)
Na(1)-O(2 ^{ix})	2.465 (6)	Na(2)-O(2 ^{xiii})	2.478 (8)
Na(1)-O(2)	2.526 (6)	Na(2)-O(2 ^{xiii})	2.519 (7)
Na(1)-O(1)	2.573 (6)	Na(2)-O(3 ^{ix})	2.822 (7)
Na(1)-O(4 ^x)	3.175 (6)	Na(2)-O(4 ^{xiii})	2.932 (6)
ave. Na(1)-O	2.564 (6)	ave. Na(2)-O	2.537 (7)
CO ₃ ²⁻ ion			
C—O(2)	1.277 (4)	O(1)—C—O(2)	119.8 (2)
C—O(1)	1.278 (3)	O(1)—C—O(3 ⁱ)	120.0 (2)
C—O(3 ⁱ)	1.286 (3)	O(2)—C—O(3 ⁱ)	120.2 (2)
Angles around:			
<i>E</i> ₁	Na(2 ^{xiii})	O(2)	Na(1 ^{ix})
<i>E</i> ₂	Na(2 ⁱ)		H(2 ^{xiii})
<i>A</i> ₁	Na(1)		Na(1 ⁱ)
<i>A</i> ₂	H(1 ^{vi})		Na(2 ^{ix})
C—O— <i>E</i> ₁	132.4 (4)	C—O— <i>E</i> ₂	127.0 (4)
C—O— <i>E</i> ₂	129.4 (4)	<i>E</i> ₁ —O— <i>E</i> ₂	98.0 (2)
<i>E</i> ₁ —O— <i>E</i> ₂	98.0 (2)	C—O— <i>A</i> ₁	90.4 (3)
C—O— <i>A</i> ₁	90.4 (3)	C—O— <i>A</i> ₂	99.7 (3)
C—O— <i>A</i> ₂	99.7 (3)	<i>E</i> ₁ —O— <i>A</i> ₁	99.3 (2)
<i>E</i> ₁ —O— <i>A</i> ₁	99.3 (2)	<i>E</i> ₁ —O— <i>A</i> ₂	73.4 (3)
<i>E</i> ₁ —O— <i>A</i> ₂	73.4 (3)	<i>E</i> ₂ —O— <i>A</i> ₁	84.9 (2)
<i>E</i> ₂ —O— <i>A</i> ₁	84.9 (2)	<i>E</i> ₂ —O— <i>A</i> ₂	89.2 (3)
<i>E</i> ₂ —O— <i>A</i> ₂	89.2 (3)	<i>A</i> ₁ —O— <i>A</i> ₂	169.9 (3)
<i>A</i> ₁ —O— <i>A</i> ₂	169.9 (3)	O(1)—C—O(2)	108.1 (4)
		O(1)—C—O(3 ⁱ)	120.0 (2)
		O(2)—C—O(3 ⁱ)	120.2 (2)
		Na(1 ^{ix})	Na(1 ⁱ)
		Na(2 ^{xiii})	Na(2 ^{ix})
		Na(1)	Na(1)
		Na(2 ^{ix})	Na(2 ^{ix})
		108.1 (4)	140.2 (4)
		127.0 (4)	109.3 (4)
		98.0 (2)	103.6 (3)
		92.5 (3)	115.0 (3)
		98.4 (3)	84.5 (2)
		87.8 (1)	92.6 (2)
		82.7 (2)	83.1 (2)
		90.4 (2)	78.7 (3)
		88.1 (2)	74.8 (3)
		167.3 (2)	151.3 (2)

Table 3 (cont.)

H₂O molecule [predictions of Brown & Shannon (1973) given in brackets]

H(1)—O(4)	0.967 (10) [0.93]	H(2)—O(4)	0.988 (9) [0.96]
H(1)—O(1 ⁱⁱ)	1.987 (9) [2.1]	H(2)—O(3 ^{viii})	1.699 (8) [1.7]
O(4)···O(1 ⁱⁱ)	2.905 (6)	O(4)···O(3 ^{viii})	2.677 (7)
O(4)—H(1)···O(1 ⁱⁱ)	157.9 (8)	O(4)—H(2)···O(3 ^{viii})	169.9 (8)
H(1)—O(4)—H(2)	102.6 (7)	H(2)—O(4)—Na(2 ⁱ)	87.9 (4)
H(1)—O(4)—Na(2)	118.9 (6)	H(2)—O(4)—Na(1 ^{viii})	52.8 (4)
H(1)—O(4)—Na(1)	112.9 (5)	Na(2)—O(4)—Na(1)	91.2 (2)
H(1)—O(4)—Na(2 ⁱ)	59.7 (5)	Na(2)—O(4)—Na(2 ⁱ)	162.9 (3)
H(1)—O(4)—Na(1 ^{viii})	80.9 (5)	Na(2)—O(4)—Na(1 ^{viii})	78.2 (2)
H(2)—O(4)—Na(2)	108.5 (5)	Na(1)—O(4)—Na(2 ⁱ)	75.2 (2)
H(2)—O(4)—Na(1)	123.8 (6)	Na(1)—O(4)—Na(1 ^{viii})	165.6 (2)
		Na(2 ⁱ)—O(4)—Na(1 ^{viii})	116.9 (2)

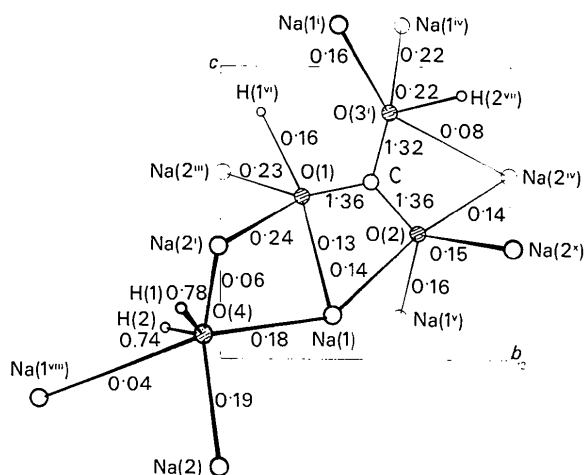


Fig. 1. The environments of CO_3^{2-} and H_2O in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ projected down *a*. Numbers are bond valences. Atoms are labelled according to the convention used in Table 3. The oxygen atoms are shaded.

in trigonal bipyramidal coordination axially disposed bonds are generally weaker than the equatorial bonds. Furthermore, the trigonal bipyramids are all similarly disposed with respect to the CO_3 group, their axes all lying between 24 and 43° of the CO_3 plane. Fig. 1 shows how Na(1) and Na(2) each form two axial bonds to the same CO_3^{2-} group, one lying above and the other lying below the CO_3^{2-} plane.

The environment of the water oxygen atom is also shown in Fig. 1. There are two strong (but significantly different) O—H bonds (0.78 and 0.74 v.u.) and two

weaker O—Na bonds (0.18 v.u.) arranged approximately tetrahedrally. In addition, there are two very weak O—Na bonds (0.05 v.u.) almost opposite the other two O—Na bonds.

Our hydrogen positions lie between the preferred set proposed by Dickens *et al.* (1970) (set 3) and those proposed by Baur (1972). The Na(2)—H(1) distance is 2.537 Å which is considerably longer than that of 2.42 Å reported by Dickens *et al.* and longer than the average Na—O distance (2.50 Å) thus satisfying the criterion proposed by Baur (1972) that no hydrogen atoms will be located in the edges of the coordination polyhedra around cations. The O—H bond lengths agree with the predictions made by Brown & Shannon (1973) for this structure (see Table 3).

We thank Drs H. D. Grundy and M. R. Anderson for assistance with the diffractometer and the National Research Council of Canada for the financial support of this work.

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