

1978). As a consequence, the bridging Si—O—Si angle of $129(1)^\circ$ is rather small.

For comparison we may note that in the various rare-earth pyrosilicate modifications the $[\text{Si}_2\text{O}_7]$ groups occur mainly in two configurations (Felsche, 1973): (1) A centrosymmetric staggered configuration is met in the thortveitite-type silicates (type C'), such as $\text{Yb}_2\text{Si}_2\text{O}_7$, and in type D , as realized in $\text{Er}_2\text{Si}_2\text{O}_7$. In this configuration the Si—O—Si angle is 180° . (2) A non-centrosymmetric eclipsed configuration, similar to the one in $\text{Sm}_4\text{S}_3\text{Si}_2\text{O}_7$, is also found in type A [$\text{Sm}_2\text{Si}_2\text{O}_7$: Si—O—Si = $129.7(10)$ and $136(1)^\circ$; Si—Si = $2.99(2)$ and $3.05(2)$ Å] (Smolin *et al.*, 1970), type E [$\text{Eu}_2\text{Si}_2\text{O}_7$: Si—O—Si = $158.3(4)^\circ$; Si—Si = $3.28(1)$ Å] and type G pyrosilicates [$\text{Pr}_2\text{Si}_2\text{O}_7$: Si—O—Si = $131.7(4)^\circ$; Si—Si = $2.96(1)$ Å] as well as in $\text{Na}_3\text{ScSi}_2\text{O}_7$ [Si—O—Si = $136.0(4)^\circ$; Si—Si = $3.12(1)$ Å] (Felsche, 1973).

Structures containing a mixture of sulfide and silicate ions appear to be rather seldom. We are aware only of three examples, namely helvite $\text{Mn}_4(\text{BeSiO}_4)_3\text{S}$ (Holloway, Giordano & Peacor, 1972), $\text{Ag}_8\text{S}_2\text{SiO}_4$ (Schultze-Rhonhof, 1974) and $\text{Ca}_{22}(\text{SiO}_4)_8\text{O}_4\text{S}_2$ (Dent Glasser & Lee, 1981). Geometrically, the $\text{Sm}_4\text{S}_3\text{Si}_2\text{O}_7$ structure would also be appropriate for such exotic compounds as $\text{Ca}_2\text{Ln}_2^{3+}(\text{P}_2\text{O}_7)\text{S}_3$ or $\text{Ln}_2^{3+}\text{Zr}_2(\text{Al}_2\text{O}_7)\text{S}_3$.

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Neutron Diffraction Study of Sodium Sesquicarbonate Dihydrate

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Abstract. $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, $M_r = 220.0$, monoclinic, $C2/c$, $a = 20.36(2)$, $b = 3.48(1)$, $c = 10.29(1)$ Å, $\beta = 106.48(1)^\circ$, $Z = 4$, $D_x = 2.147$ Mg m^{-3} . The final R value after full-matrix least-squares refinement was 0.040 for 754 observed reflections. In this structure, water molecules and $(\text{CO}_3 \cdot \text{H} \cdot \text{CO}_3)^{3-}$ anions form a two-dimensional hydrogen-bonded network. The $(\text{HC}_2\text{O}_6)^{3-}$ anion is almost planar and consists of two CO_3^{2-} anions linked by an H atom with

an $\text{O} \cdots \text{H} \cdots \text{O}$ distance of 2.46 Å. Least-squares refinements revealed that this H atom is dynamically disordered between two equivalent sites separated by 0.211(9) Å.

Introduction. The crystal structure of sodium sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, was first determined by Brown, Peiser & Turner-Jones (1949) with single-crystal X-ray diffraction data. It was refined

later by Bacon & Curry (1956) with two-dimensional single-crystal neutron diffraction data and also by Candlin (1956) with two-dimensional X-ray diffraction data. In this structure there is a very strong hydrogen bond in the symmetric $(\text{HC}_2\text{O}_6)^{3-}$ anion. Bacon & Curry (1956) suggested that the H atom in this bond is disordered. This study, using three-dimensional single-crystal neutron diffraction data, was undertaken to improve the accuracy of the structural parameters and to find evidence for disordering of the H atom in the anion.

Data were collected on a crystal with dimensions $1 \times 2 \times 10$ mm using an automated four-circle diffractometer at the National Bureau of Standards Research Reactor. The long axis of the crystal was oriented approximately parallel to the ϕ axis of the diffractometer. The crystal orientation and cell dimensions were determined by a least-squares refinement of the setting angles of 15 strong reflections. Three-dimensional diffraction data were collected within the limiting scattering angle of 120° with 1.27 \AA neutrons. A total of 1674 reflections in the hemisphere were measured and merged to 932 unique reflections of which 754 had $I \geq 2\sigma(I)$ and were subsequently used for refinement. The data were not corrected for absorption because the neutron transmission was greater than 80% for all measured reflections.

The initial parameters for refinement were taken from Bacon & Curry (1956). Anisotropic refinement of the model resulted in a final R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.040 and R_w ($= [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$) of 0.029. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The e.s.d. of F_o was determined from the formula $\sigma = [\sigma_s^2 + (kF)^2]^{1/2}$, where σ_s is the e.s.d. based on counting statistics and k is a constant (0.005 for this study). A weighting scheme based on the robust-resistant technique (Nicholson & Prince, 1978) was used. An isotropic secondary-extinction parameter as described by Zachariasen (1968) was included in the refinement (largest factor, $F_c/F_{\text{corr}} = 0.64$, for the $10,0,2$ reflec-

tion). The neutron scattering lengths $b(\text{Na}) = 3.62$, $b(\text{C}) = 6.648$, $b(\text{O}) = 5.803$, and $b(\text{H}) = -3.74$ fm were used. All computations were made using the program *RFINE* (Finger & Prince, 1975). Table 1* lists the final atomic parameters of the ordered hydrogen model (a disordered hydrogen model will be discussed later).

Discussion. The packing and atom labeling are shown in Fig. 1. All bond lengths and angles, including hydrogen bonds, are listed in Table 2. The carbonate group is essentially planar with atomic distances from the mean plane less than 0.005 \AA . This group, however, is distorted from ideal threefold symmetry with O—C—O bond angles ranging from 116.4 to 123.5° and C—O bond lengths ranging from 1.26 to 1.31 \AA . The O atom in the longest C—O bond is that involved in the very short hydrogen bond. Two carbonate groups are hydrogen bonded to a common H atom at the symmetry center of the anion by an unusually strong $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bond with an $\text{O} \cdots \text{H}$ distance of $1.232(1) \text{ \AA}$. The result is a complex

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36965 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and equivalent isotropic thermal parameters (\AA^2) with estimated standard deviations in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Na(1)	0.00000	0.74786 (57)	0.25000	1.13 (4)
Na(2)	0.15059 (7)	0.16359 (44)	0.42612 (22)	1.44 (3)
C	0.09303 (3)	0.26524 (19)	0.10317 (9)	0.73 (2)
O(1)	0.15103 (4)	0.39845 (28)	0.10200 (12)	1.29 (2)
O(2)	0.05433 (4)	0.12980 (28)	0.98823 (12)	1.22 (2)
O(3)	0.07258 (4)	0.25364 (23)	0.20797 (11)	1.00 (2)
O(4)	0.21207 (5)	0.66563 (31)	0.35376 (14)	1.55 (2)
H(1)	0.19149 (9)	0.59393 (54)	0.25966 (27)	2.46 (4)
H(2)	0.25913 (8)	0.73060 (57)	0.36351 (28)	2.60 (4)
H(3)	0.00000	0.00000	0.00000	2.33 (4)

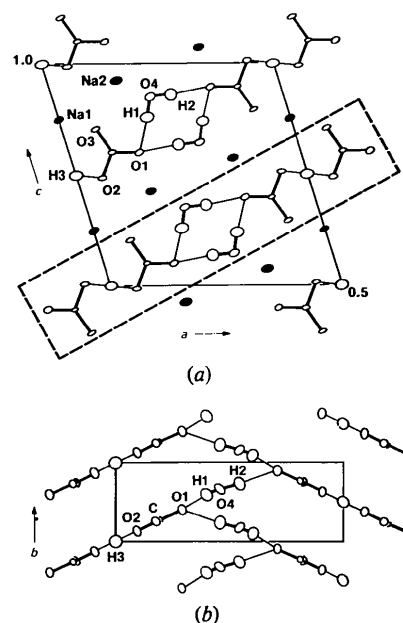


Fig. 1. Packing and hydrogen bonding in sodium sesquicarbonate dihydrate (ORTEP: Johnson, 1965). (a) The (010) projection of one-half of the unit cell. This figure shows that the Na^+ cation layer and the anion layer [marked by broken lines and consisting of $(\text{CO}_3, \text{H}_2\text{CO}_3)^{3-}$ ions and water molecules] are oriented parallel to the (101) plane and interleave each other. (b) The projection of the anion layer onto the (101) plane, showing a two-dimensional hydrogen-bonded network.

$[\text{CO}_3 \cdot \text{H} \cdot \text{CO}_3]^{3-}$ anion in which the two mean planes of the carbonate groups are separated by 0.047 Å, and hence, the entire complex is nearly coplanar. The $(\text{HC}_2\text{O}_6)^{3-}$ anions are hydrogen bonded at each end to two water molecules with $\text{O} \cdots \text{H}$ distances of 1.736 (3) and 1.856 (2) Å. The H_2O molecule with the shorter $\text{O} \cdots \text{H}$ distance is located very close to the mean plane of the anion. The other water molecule is linked to the neighboring symmetrically identical anion (Fig. 1b) by

Table 2. Bond lengths (Å) and angles ($^\circ$), including hydrogen bonds

C—O(1)	1.272 (1)	O(1)—C—O(2)	116.4 (1)
C—O(2)	1.309 (1)	O(1)—C—O(3)	123.5 (1)
C—O(3)	1.262 (1)	O(2)—C—O(3)	120.0 (1)
O(4)—H(1)	0.972 (3)	H(1)—O(4)—H(2)	107.4 (2)
O(4)—H(2)	0.961 (2)	O(4)—H(1) \cdots O(1)	170.8 (2)
H(1) \cdots O(1)	1.736 (3)	O(4)—H(2) \cdots O(1)	173.1 (2)
H(2) \cdots O(1)	1.856 (2)	O(2) \cdots H(3) \cdots O(2)'	180.0
H(3) \cdots O(2)	1.232 (1)		
Na(1)—O(2)	2.424 (1) \times 2	(Disordered model)	
Na(1)—O(3)	2.386 (2) \times 2	O(2)—H(3)	1.128 (5)
Na(1)—O(3)	2.415 (2) \times 2	O(2)' \cdots H(3)	1.337 (5)
Na(2)—O(3)	2.374 (2)	O(2)—H(3) \cdots O(2)'	178.5 (7)
Na(2)—O(1)	2.364 (2)		
Na(2)—O(1)	2.663 (2)		
Na(2)—O(2)	2.450 (2)		
Na(2)—O(4)	2.378 (2)		
Na(2)—O(4)	2.388 (2)		

Table 3. Thermal ellipsoids of H atoms

The orientation of each principal axis is given by the angle between the axis and the O—H bond.

	Axis 1 Length (Å)/ angle ($^\circ$)	Axis 2 Length (Å)/ angle ($^\circ$)	Axis 3 Length (Å)/ angle ($^\circ$)
H(1)	0.153 (5)/12.	0.176 (5)/78.	0.198 (5)/89.
H(2)	0.161 (4)/10.	0.177 (5)/84.	0.203 (4)/81.
H(3)	0.143 (6)/81.	0.172 (7)/83.	0.196 (6)/12.

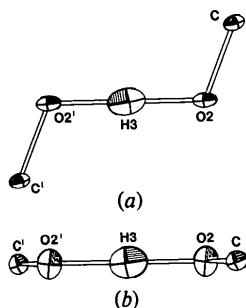


Fig. 2. The thermal ellipsoid of the H(3) atom: (a) view along the normal to the plane C—O(2) \cdots H(3); and (b) view parallel to the plane.

the same short $\text{O} \cdots \text{H}$ bond distance. Thus a two-dimensional hydrogen-bonded network of water molecules and anions is formed. Each anionic layer is adjacent to a layer consisting of Na^+ ions (Fig. 1a), and consequently $\text{Na}_3(\text{HC}_2\text{O}_6) \cdot 2\text{H}_2\text{O}$ is an ionic-type layer structure.

As stated in the *Introduction*, Bacon & Curry (1956) have found from their two-dimensional density maps that the H atom in the anion is slightly disordered. The results of our anisotropic refinement show that the thermal ellipsoid of H(3) is consistent with the density distribution of the disordered model. Since the libration amplitude should be much larger than the amplitude of the bond-stretch motion for a bonded atom, we would expect the longest principal axis to be perpendicular to the bond and the shortest axis parallel to the bond. This was found to be true for the water H atoms, as shown in Table 3. For the H(3) atom, however, the thermal ellipsoid is oriented with the longest principal axis approximately parallel to the O—H bond (Fig. 2 and Table 3), which is interpreted to result from a disordered structure.

A second model, therefore, was refined in which the H(3) atom was replaced by two isotropic half-H atoms placed centrosymmetrically about the origin and along the O(2) \cdots O(2)' direction. Preliminary refinement showed that all parameter shifts [except H(3)] were less than one estimated standard deviation from the initial parameters. Consequently, in the final cycles of refinement, only H(3) was allowed to shift with all other parameters being held in the positions of the ordered model (Table 1). The refinement converged to $R_w = 0.023$ and $R = 0.041$ that are essentially the same as in the first refinement in which a single anisotropic H(3) was assumed. The final least-squares parameters for H(3) are: $x = 0.0048$ (3), $y = 0.0121$ (10), $z = 0.0006$ (8) and $B = 2.04$ (5) Å². The direction of the split is approximately parallel (angle $\sim 7^\circ$) to the longest principal axis found in the anisotropic refinement of the H(3) atom. The hydrogen-bond parameters for the disordered model are included in Table 2. From our analysis, we conclude that H(3) is dynamically disordered between two equivalent sites separated by 0.211 (9) Å.

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