Sodium Carbonate Heptahydrate

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Abstract

$Na_2CO_3 . 7H_2O$, FW 232·09, crystallizes in the ortho-rhombic space group *Pbca* with $a = 14·492$ (7), $b = 19·490$ (5), $c = 7·017$ (3) Å, $V = 1981·9$ Å^3, $Z = 8$ and $D_x = 1·559$ Mg m^{-3}. The crystal structure has been determined with 1230 observed X-ray diffractom-eter data by full-matrix least-squares calculations to $R = 6·7\%$. The packing arrangement in the crystal unit cell is characterized by two types of Na–water octahedra. These are connected edgewise to produce endless, linear chains $[Na(H_2O)_4]_n^{n+}$. The chains are cross-linked by $[Na_2(H_2O)_{10}]^{2+}$ units. This network extends largely in the *bc* plane and contains interstices which are filled by carbonate anions. The O atoms of the latter are hydrogen bonded to three or four water molecules.

Introduction

Several thermodynamic investigations have been performed to determine the transition temperature of the different hydrates of sodium carbonate (Richards & Fiske, 1914; Bauer & Dorland, 1952). These studies have shown that the stable hydrates are the deca-hydrate between 271·0 and 305 K, the heptahydrate between 305 and 308·5 K, the monohydrate between 308·5 and 382 K; above 382 K, the anhydrous sodium carbonate exists. Other coordination complexes of sodium carbonate with water described in the literature are probably mixtures of these basic hydrates (*Gmelin's Handbuch der Anorganischen Chemie*, 1927).

The crystal structure of $Na_2CO_3 . 10H_2O$ (Soda) has been discussed by Taga (1969), and that of $Na_2CO_3 . H_2O$ by Wu & Brown (1975). The heptahydrate we describe here is thermodynamically unstable below a temperature of 305 K. From 273–283 K, it occurs predominantly in the β modification, and between

283–305 K, the α modification is found (*Gmelin's Handbuch der Anorganischen Chemie*, 1927).

As the crystals of the heptahydrate were obtained in the temperature range 279–281 K, we infer that they belong to the β modification.

Experimental

In the course of our attempts to synthesize salts of symmetrical monothiopyrophosphate, we obtained a solid consisting of approximately 80% Li_2CO_3, and 20% Li_3PO_4, Li_3PSO_3, and the presumed tetralithium symmetrical monothiopyrophosphate. The solid (2–6 mg) was dissolved in 0·25 ml 1 M NaOH. and stirred for 30 min at 278 K with 0·5 g Dowex 50 W-X2 ion-exchange resin in the sodium form. The resin was separated by centrifugation and the solution placed in an ethanol-saturated atmosphere at 279–281 K. Crystals appeared after 2–4 d as colorless needles with rectangular cross-section. They do not contain the symmetrical monothiopyrophosphate we were after but rather sodium carbonate heptahydrate, the crystal structure of which has not been described before.

Data collection

Single crystals, isolated at 279 K, were immersed in paraffin oil to prevent decomposition (Dunsmore & Speakman, 1963; Kofler, 1950) and mounted in quartz capillaries. Space group *Pbca* and preliminary cell constants were obtained from precession and Weissen-berg photographs.

A crystal of size 0·35 × 0·50 × 0·25 mm was used for determination of final cell constants (given in the *Abstract*) on a four-circle Stoe diffractometer. With Ni-filtered Cu $K\alpha$ radiation, a data set consisting of 1421 reflections ($2\theta < 117°$) was collected in the ω-scan mode, each scan covering 60 steps 0·01° wide, with a measuring time of 0·3 s per step.

Three standard reflections monitored every 100 data points did not show significant variation. All data were corrected for Lorentz and polarization factors and subjected to an empirical absorption correction (North, Phillips & Mathews, 1968).

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Structure solution and refinement

The positions of the Na and water oxygen (OW) atoms could be determined by direct methods, using *MULTAN* 80 (Main *et al.*, 1980). Positional parameters were refined initially with isotropic thermal parameters (Busing, Martin & Levy, 1977), weights according to counting statistics, and scattering factors taken from *International Tables for X-ray Crystallography* (1974). On inclusion of the carbonate anion, located from a difference Fourier map, the R index reduced to 0·098 using anisotropic thermal parameters. The positions of all H atoms could be derived from a subsequent difference Fourier map. In the last refinement, including the H atoms with isotropic temperature factors and omitting 28 reflections suffering from secondary extinction, R converged at 6·7%. Atomic coordinates and isotropic temperature factors are given in Table 1.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38009 (10 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 and isotropic temperature factors B* ($Å^2$)

B values of Na, O and C were obtained from the anisotropic β values: $B = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$; those of the H atoms are based on least-squares refinements. Figures in parentheses refer to the last digit given and are calculated from the correlation matrix.

	x	y	z	B
Na(1)	0·5119 (1)	0·2361 (1)	0·0584 (3)	3·3 (1)
Na(2)	0·4471 (1)	0·0577 (1)	0·3542 (3)	3·3 (1)
O(1)	0·4944 (2)	0·1153 (1)	0·0531 (5)	4·1 (1)
O(2)	0·6250 (2)	0·2542 (2)	−0·1885 (5)	3·7 (1)
O(3)	0·3959 (2)	0·2534 (2)	0·3006 (5)	3·8 (1)
O(4)	0·3132 (2)	0·1282 (2)	0·3731 (5)	3·8 (1)
O(5)	−0·0986 (2)	−0·0044 (2)	0·8700 (5)	3·4 (1)
O(6)	0·0220 (2)	0·1379 (2)	0·9275 (5)	3·7 (1)
O(7)	−0·1222 (2)	−0·0287 (2)	1·3668 (5)	3·8 (1)
C	0·7574 (3)	0·1143 (2)	0·6033 (7)	3·2 (2)
O(1)C	0·7039 (2)	0·1214 (2)	−0·5433 (5)	3·4 (1)
O(2)C	0·8304 (2)	0·0765 (2)	0·5905 (5)	3·8 (1)
O(3)C	−0·2392 (2)	−0·1436 (2)	1·2591 (5)	3·9 (1)
H(1)A	0·540 (4)	0·075 (3)	−0·009 (8)	16 (2)
H(1)B	0·427 (4)	0·096 (3)	0·012 (8)	8 (1)
H(2)A	0·139 (4)	0·204 (3)	0·148 (8)	10 (1)
H(2)B	0·672 (4)	0·212 (3)	−0·241 (8)	17 (1)
H(3)A	0·366 (4)	0·203 (3)	0·339 (8)	6 (1)
H(3)B	0·149 (4)	−0·209 (3)	0·314 (8)	12 (1)
H(4)A	0·269 (4)	0·116 (3)	0·271 (9)	5 (1)
H(4)B	0·291 (4)	0·128 (3)	0·484 (9)	11 (2)
H(5)A	0·147 (4)	0·048 (3)	0·134 (8)	16 (2)
H(5)B	0·108 (5)	−0·033 (4)	0·201 (8)	14 (2)
H(6)A	0·509 (4)	0·177 (3)	0·612 (9)	12 (2)
H(6)B	0·079 (4)	0·134 (4)	0·918 (8)	18 (2)
H(7)A	0·167 (4)	0·071 (3)	0·673 (8)	6 (2)
H(7)B	−0·142 (4)	−0·000 (3)	1·444 (8)	9 (2)

Discussion

In the crystal structure of sodium carbonate heptahydrate, all water molecules are coordinated with sodium to form octahedra consisting of $Na^+.6H_2O$. In these units, the average sodium–water distance is 2·43 (4) Å (Table 2) and the O—Na—O angles are in the range 81 to 102°, and 164 to 180°. Two kinds of structure elements generated by combination of these octahedra are evident. In one, octahedra with Na(1) ions occupying central positions are connected edgewise by two water molecules [O(3) and O(2)] to build infinite, linear chains of general formula $[Na(H_2O)_4]_n^{n+}$. Similar chains but with different edge-to-edge linkages were found in the crystal structure of borax (Morimoto, 1956).

In the second type of octahedra, Na(2) ions form dimeric clusters best described as $[Na_2(H_2O)_{10}]^{2+}$. These are composed of two edge-sharing Na–water octahedra which are also the main constituents in

Table 2. *Structural characteristics* (Å *and* deg) *of hydrogen bonds, carbonate anions and sodium water octahedra*

There are only two water–water interactions $O(1)\cdots O(7)$, $O(3)\cdots O(4)$ and all other hydrogen bonds involve carbonate oxygen. Two O—H groups, O(3)—H(3)B and O(6)A are not involved.

	O···O	O—H	H···O	O—H···O
O(1)—H(1)A···O(7)	2·827 (5)	1·09 (6)	1·73 (6)	165 (5)
O(1)—H(1)B···O(2)C	2·690 (5)	1·09 (6)	1·61 (5)	167 (4)
O(2)—H(2)A···O(1)C	2·869 (4)	0·89 (6)	1·99 (6)	165 (5)
O(2)—H(2)B···O(3)C	2·741 (5)	1·13 (6)	1·65 (6)	161 (5)
O(3)—H(3)A···O(4)	2·766 (5)	1·10 (6)	1·66 (6)	173 (4)
O(3)—H(3)B···O(3)C	3·060 (4)	0·98 (6)	2·13 (6)	158 (4)
O(4)—H(4)A···O(1)C	2·808 (5)	0·98 (6)	1·85 (6)	159 (5)
O(4)—H(4)B···O(3)C	2·811 (5)	0·84 (5)	1·98 (6)	170 (5)
O(5)—H(5)A···O(1)C	2·810 (4)	1·09 (6)	1·77 (6)	156 (4)
O(5)—H(5)B···O(2)C	2·719 (5)	0·89 (6)	1·92 (6)	148 (5)
O(6)—H(6)A		0·83 (6)		
O(6)—H(6)B···O(1)C	2·777 (5)	0·83 (6)	2·02 (6)	150 (5)
O(7)—H(7)A···O(3)C	2·909 (5)	1·09 (5)	1·82 (6)	178 (4)
O(7)—H(7)B···O(2)C	2·672 (5)	0·83 (4)	1·86 (5)	168 (6)

Na(1)—O(1)	2·370 (4)	Na(2)—O(5)	2·377 (4)
Na(1)—O(2)	2·411 (4)	Na(2)—O(4)	2·381 (4)
Na(1)—O(3)	2·414 (4)	Na(2)—O(5^{iv})	2·431 (4)
Na(1)—O(2^{vi})	2·424 (4)	Na(2)—O(6)	2·442 (4)
Na(1)—O(6)	2·461 (4)	Na(2)—O(1)	2·488 (4)
Na(1)—O(3^{vi})	2·478 (4)	Na(2)—O(7)	2·500 (4)

C—O(1)C	1·296 (6)	O(1)C—C—O(2)C	119·7 (4)
C—O(2)C	1·292 (6)	O(1)C—C—O(3)C	120·9 (4)
C—O(3)C	1·262 (6)	O(2)C—C—O(3)C	119·3 (4)

Symmetry code

(i) $0·5 + x, 0·5 − y, −z$ (ii) $−x, 0·5 + y, 0·5 − z$
(iii) $0·5 − x, −y, 0·5 + z$ (iv) $−x, −y, −z$
(v) $0·5 − x, 0·5 + y, z$ (vi) $x, 0·5 − y, 0·5 + z$
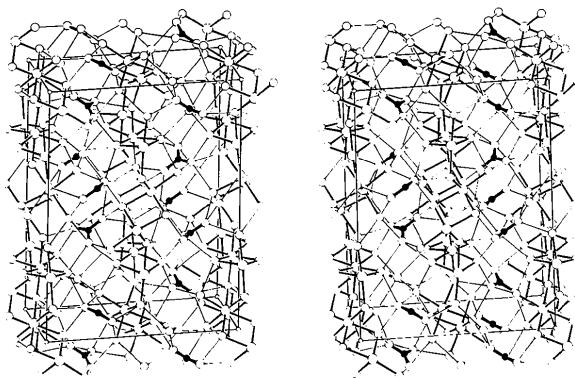(vii) $0·5 + x, y, 0·5 − z$

Fig. 1. Stereoplot of the unit cell of sodium carbonate hepta-hydrate, drawn by *ORTEP* (Johnson, 1965). Spheres of increasing size are C, O, Na with C shown filled. Covalent C—O bonds, coordinative Na···O bonds and hydrogen bridges are indicated as thick, medium and thin lines respectively.
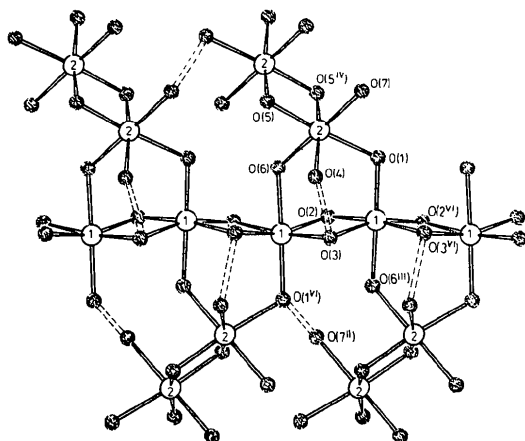

Fig. 2. Coordination octahedra formed around the sodium ions, drawn by *SCHAKAL* (Keller, 1980). Spheres with numbers 1, 2 correspond to Na atoms Na(1) and Na(2). Water oxygen atoms O*W* are labelled according to the convention used in Table 1, and hydrogen bonds are indicated by dashed lines. Symmetry-equivalent atoms are denoted by Roman numerals.

$Na_2CO_3.10H_2O$ (Taga, 1969). The dimeric units have four common water molecules with the infinite chains, two [O(1) and O(6)] on each side of the unit, and thus they serve as links between the chains. The links are in addition reinforced by hydrogen bonds between chain and dimeric-unit water molecules (Figs. 1 and 2).

This network of octahedra leaves free interstices which are filled by carbonate anions. Carbonate O atoms are connected with water molecules by hydrogen bonds in the O···O distance range 2·672 (5) to 3·060 (4) Å. Oxygen atoms O(1)C and O(3)C accept four hydrogen bonds whereas O(2)C has only three partners (Table 2).

Comparing the crystal structure of the sodium carbonate mono-, hepta- and decahydrates, we find that the carbonate anions are ordered in the mono- and

heptahydrate but twofold disordered in the deca-hydrate. The coordination of the sodium ion is octahedral in all cases, a configuration most commonly confirmed in inorganic hydrates (Kofler, 1950; Benrath & Benrath, 1929). However, in the monohydrate, the ligands of the sodium ion are water molecules as well as carbonate oxygens and, in the decahydrate, only isolated dimerically connected octahedra are found. In the heptahydrate, a more complex coordination and aggregation scheme is observed because larger systems have to build up due to the loss of water molecules. If, however, the heptahydrate is left below 273 K with water, it recrystallizes in the form of the decahydrate (Loewel, 1851).

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