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Crystal structure of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. By TOORU TAGA, *Department of Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto, Japan*

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The crystal structure of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ has been determined by the application of a symbolic addition procedure, assuming a centrosymmetric space group $C2/c$. The actual space group is Cc with four chemical units in the unit cell. The structure is characterized by the presence of $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$ units, consisting of two sodium-water octahedra, and contains disordered carbonate ions.

The crystal structure of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (washing soda) has been determined in order to clarify the role of the water molecules in the structure.

Crystals used for the experiment were obtained by recrystallization at room temperature from aqueous solution.

The crystal data are as follows:

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, monoclinic, space group Cc (No. 9), $Z=4$; cell dimensions, $a=12.83 \pm 0.02$, $b=9.026 \pm 0.009$, $c=13.44 \pm 0.05$ Å and $\beta=123.0 \pm 0.5^\circ$ (pseudo-

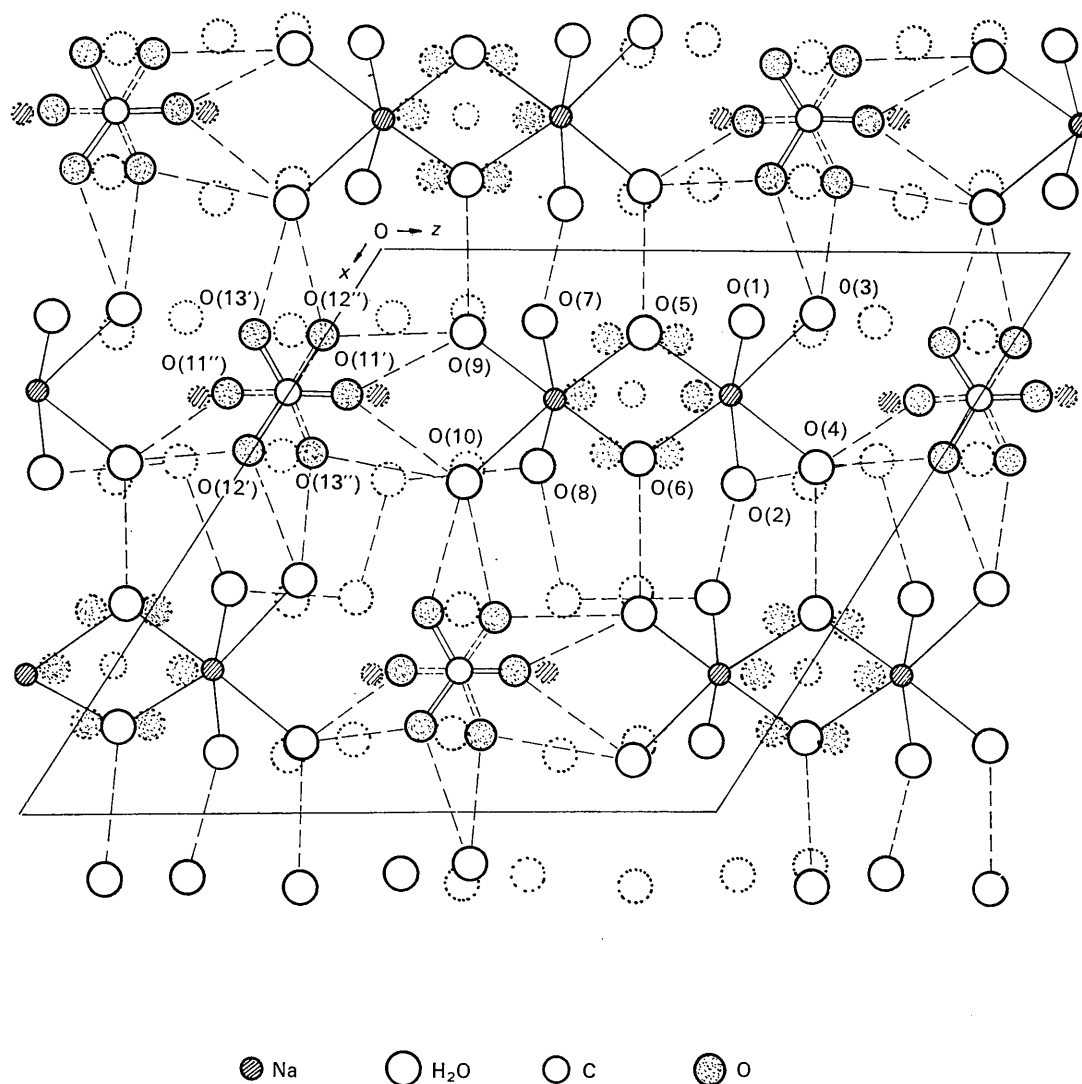


Fig. 1. Projection of the structure along the b axis. The group of atoms shown by full circles is situated at about $\frac{3}{4}b$, and that by dotted circles lies at about $\frac{1}{4}b$. Hydrogen bonds are indicated by dashed lines.

hexagonal); $D_m = 1.46 \text{ g.cm}^{-3}$ (at 31°C), $D_x = 1.455 \text{ g.cm}^{-3}$.

The space group can be approximated by the centrosymmetric space group $C2/c$ (No. 15), judging from the statistical test. The cell dimensions differ slightly from those reported by Dunsmore & Speakman (1964) but this discrepancy may be due to the difference in the temperature at which measurements were made.

Intensities were visually estimated from Weissenberg photographs about the b and c axes recorded with $\text{Cu } K\alpha$ radiation. An absorption correction ($\mu r = 0.52$) was applied. The data were reduced to an absolute scale by the Wilson method and the normalized structure factors $|E|$ were obtained. The number of independent observed reflexions is 1263.

The structure was determined by the application of a symbolic addition procedure (Karle & Karle, 1966) assuming the centrosymmetric space group $C2/c$. Approximate positions of the Na atoms and $\text{O}(\text{H}_2\text{O})$ atoms were revealed from the E map from 110 reflexions for which the signs had been determined. In the subsequent analysis, noncentrosymmetric space group Cc was taken instead of $C2/c$. The positional parameters of these atoms were refined by several cycles of least-squares calculations, and an electron density map was synthesized. From this map it was found that the carbonate ion occupies a centrosymmetric position [(c) or (d)] in the space group $C2/c$ and that it is disordered between two orientations rotated in its own plane. Six cycles of diagonal least-squares refinements including these disordered carbonate ions reduced the R index to 0.18. The atomic parameters at this stage are listed in Table 1.

In this crystal all the water molecules are coordinated with sodium and each sodium ion is surrounded by six water molecules. The crystal structure may be considered to be a distorted NaCl type structure composed of $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$ and CO_3^{2-} ions (Fig. 1). The $[\text{Na}_2(\text{H}_2\text{O})_{10}]^{2+}$ ion consists of two sodium-water octahedra which share an edge (Fig. 2). The average sodium-water distance is 2.44 \AA , which is

Table 1. *Positional parameters and isotropic thermal parameters*

	x	y	z	B
Na(1)	0.240	0.225	0.128	1.7 \AA^2
Na(2)	0.252	0.270	-0.128	1.9
O(1)	0.125	-0.012	0.091	3.0
O(2)	0.376	0.440	0.208	2.0
O(3)	0.093	0.312	0.175	1.7
O(4)	0.374	0.121	0.322	1.8
O(5)	0.139	0.374	-0.058	2.2
O(6)	0.355	0.125	0.047	2.0
O(7)	0.128	0.049	-0.215	2.5
O(8)	0.372	0.502	-0.080	2.4
O(9)	0.120	0.376	-0.332	2.7
O(10)	0.399	0.187	-0.186	2.7
C	0.250	0.754	0.000	1.0
O(11')	0.266	0.718	0.097	3.5
O(12')	0.344	0.793	-0.003	2.5
O(13')	0.139	0.794	-0.096	2.0
O(11'')	0.253	0.834	-0.073	4.6
O(12'')	0.151	0.675	-0.001	3.8
O(13'')	0.336	0.809	0.093	4.1

quite normal. These pairs of octahedra are linked by hydrogen bonds to form a three-dimensional framework in the crystal. The carbonate ion is located in a wide space within this framework and it is disordered over two orientations, in either of which the carbonate ion is hydrogen-bonded with the surrounding water molecules. This crystal structure is different from that of sodium sulphate decahydrate (Ruben, Templeton, Rosenstein & Olovsson, 1960) or borax (Morimoto, 1956) in which the octahedra of water molecules form infinite chains.

It has been reported that the dielectric dispersion behavior of this substance is similar to that of ice crystals (Kiriyaama & Saito, 1953). In the hydrogen-bond framework found here, such dispersion may possibly be due to proton transfer, as in ice.

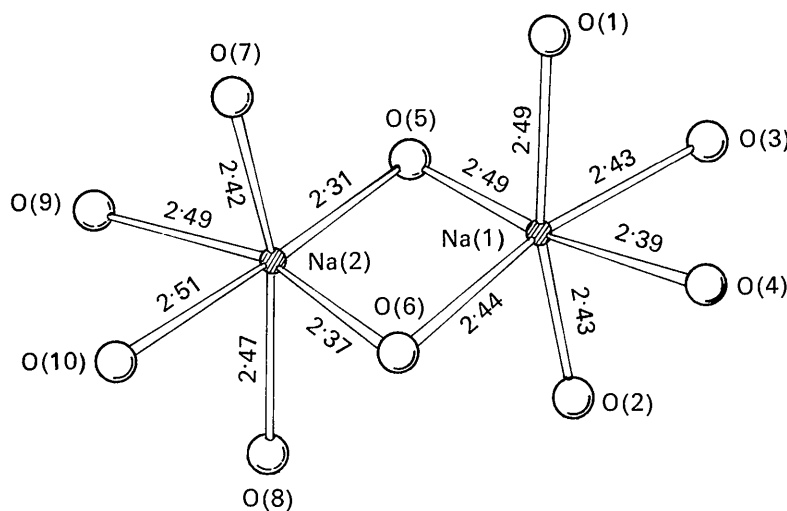


Fig. 2. The pair of water octahedra around the sodium ions.

All the computations were made with FORTRAN programs written by the author for the KDC II.

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The crystal structure of the ion exchanger zirconium bis(monohydrogen orthoarsenate) monohydrate.*

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The crystal structure of the synthetic ion exchanger zirconium bis(monohydrogen orthoarsenate) monohydrate, $Zr(HAsO_4)_2 \cdot H_2O$, has been determined. The crystals are isomorphous with the monoclinic α -zirconium phosphate and have cell dimensions $a = 9.178(4)$, $b = 5.378(2)$, $c = 16.55(1)$ Å and $\beta = 111.30(5)^\circ$. The calculated density with $Z = 4$ is 3.395 g.cm^{-3} compared with an observed density of 3.3 g.cm^{-3} . The structure was refined to an R value of 9.0% by the block-diagonal method. Anisotropic thermal parameters were obtained by refinement only on those reflections for which $\sin^2 \theta \leq 0.35$. The average zirconium-oxygen bond length is 2.075 Å (2.07 Å in the phosphate). The arsenate groups deviate considerably from tetrahedral symmetry but the deviations are similar to those of the phosphate groups in α -zirconium phosphate. The average arsenic-oxygen bond distance for non-hydrogen bearing (bridging) oxygen atoms is 1.655 Å. The cation sieving behavior of zirconium arsenate is discussed on the basis of its structure.

Introduction

The crystal structure of α -zirconium bis(monohydrogen orthophosphate) monohydrate (α -ZrP), $Zr(HPO_4)_2 \cdot H_2O$, has been determined as part of a fundamental study of synthetic, inorganic ion exchange compounds (Clearfield & Smith, 1969). Crystals isomorphous with this phosphate include the compounds commonly called titanium and hafnium phosphate and zirconium arsenate. All of these compounds, when crystalline, exhibit ion sieving behavior. In acid solutions titanium phosphate readily exchanges lithium and sodium ions, partially exchanges potassium ion and excludes rubidium and cesium ions (Alberti, Cardini-Galli, Constantino & Torracca, 1967). α -ZrP crystals exchange lithium, sodium and potassium ions but exclude rubidium and cesium ions (Clearfield & Stynes, 1964) while zirconium arsenate exchanges with these ions and also partially exchanges rubidium but not cesium ions (Clearfield, Smith & Hammond, 1968; Torracca, Constantino & Massucci, 1967).

The structure of α -ZrP is a layered one (Clearfield & Smith, 1969). The layers are arranged relative to one another in such a way as to create zeolite-like cavities within the crystal lattice. The initial stage of exchange involves diffusion of unhydrated or partially hydrated ions into the cavities (Clearfield, Duax, Medina, Smith & Thomas, 1969). Thus, the size of the entrances into the cavities apparently determines the size of the cations which can enter the lattice.

In α -ZrP these are such as to permit a spherical ion of 2.64 Å diameter or smaller to pass. This size correlates well with the observed sieving behavior. It was therefore of interest in determining the structures of other isomorphous crystals to see whether the correlation persists. A further incentive for doing these structures was the possibility of locating the hydrogen atoms which were not determined in the zirconium phosphate structure.

This paper reports on the crystal structure of the isomorphous zirconium arsenate (α -ZrAs).

Experimental

The preparation of microcrystals and their composition has been previously described (Clearfield, Smith & Hammond, 1968). Larger crystals suitable for X-ray diffraction studies were grown from the microcrystals by heating them at 150–160 °C in sealed tubes containing 1M arsenic acid and 6M nitric acid. The crystals were thin hexagonal platelets elongated parallel to the b axis.

The unit-cell dimensions were determined from a least-squares fit of back reflection Weissenberg data corrected for film shrinkage. The crystals are monoclinic with $a = 9.178(4)$, $b = 5.378(2)$, $c = 16.55(1)$ Å, $\beta = 111.30(5)^\circ$. The values in parentheses represent the uncertainty in the last significant figure. This primitive cell is one-third the size of the previously reported cell (Clearfield, Smith & Hammond, 1968). The difference arises from the location of the c axis. In the previous work the direction of the reported c axis is actually that of c^* . The density was determined on a single crystal by the flotation method in diiodomethane, the liquid being slowly warmed until the crystal remained suspended. The value found was 3.3 g.cm^{-3} ; the calculated with $Z = 4$ is 3.395 g.cm^{-3} .

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