

The Crystal and Molecular Structure of Sodium D-Tartrate Dihydrate*

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Sodium D-tartrate dihydrate crystallizes in the space group $P2_12_12_1$ with $a=11.460$, $b=14.670$, $c=4.954$ Å. The unit cell contains four units of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$. The structure was solved by means of the alpha synthesis using sodium positions established from a 3-D sharpened Patterson map. The preliminary analysis was carried out with Weissenberg intensity data, and the structure was finally refined with diffractometer data, to an R index of 0.035. The two parts of the tartrate ion consisting of groups $\text{C}(\text{H})\text{O}(\text{H})\text{COO}$ are not identical. The molecules are held in the structure by intermolecular hydrogen bonds formed through water.

Introduction

The tartrate ion consists of two planar halves each having a carboxyl group, a tetrahedral carbon and a hydroxyl oxygen atom. The two halves are oriented in such a manner that the four carbon atoms lie in a plane. The interesting feature in this configuration is the alignment of the carboxyl groups with respect to the $\text{CCO}(\text{H})$ plane. Even though the carboxyl groups have restricted freedom of rotation around the C-C bond, they are always found to be coplanar with $\text{CCO}(\text{H})$ of the same half (Beevers & Hughes, 1941; Beevers & Stern, 1950; Sadanaga, 1950; Parry, 1951; Sprenkels, 1956; van Bommel & Bijvoet, 1958). A conformational analysis of tartrates and tartaric acids (whose structures have been determined by X-ray analysis) has revealed small deviations of the order of $\pm 10^\circ$ resulting from the rotation of the carboxyl group away from the plane of $\text{CCO}(\text{H})$. The present study was undertaken to find how the orientation of the carboxyl group in the tartrate ion is influenced by the environment. The compounds for this study were so chosen that (1) the radii of the cations were nearly the same; and (2) the number of water molecules increased step by step. The first three tartrates whose structures have been solved are sodium tartrate dihydrate, strontium tartrate trihydrate and calcium tartrate tetrahydrate. This paper describes the structure determination of sodium D-tartrate dihydrate.

Experimental

Single crystals of sodium tartrate were grown from an aqueous solution of the commercially available salt at

room temperature. The unit-cell dimensions and space group as previously reported (Radhakrishnan & Ramachandran, 1951) are as follows:

$$a=11.49, b=14.67, c=4.97 \text{ \AA}.$$

The density reported in the *Handbook of Chemistry* (Lange, 1944) is 1.818 g.cm^{-3} . The space group deduced from systematic absences observed in Weissenberg photographs was $P2_12_12_1$ with four units of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ in the unit cell. In the present investigation the above data were used for initial calculations. When the structure was finally refined with diffractometer data, the cell dimensions were redetermined. The new values are

$$\begin{aligned} a &= 11.460 \pm 0.005 \text{ \AA} \\ b &= 14.670 \pm 0.005 \\ c &= 4.959 \pm 0.003. \end{aligned}$$

The measurements were carried out at 24°C .

Collection of photographic data

The intensity data were collected by rotation about the short c axis by the multiple film Weissenberg equi-inclination technique. Altogether 760 reflexions spread over four layers ($hk0$, $hk1$, $hk2$ and $hk3$) were recorded, using nickel-filtered copper radiation. The data were corrected for Lorentz and polarization effects in the usual manner and placed on an absolute scale by Wilson's method. Errors due to absorption were neglected in view of the small size of the crystal chosen.

Determination of the structure

Because of the shortness of the c axis (4.96 Å) attempts were made to solve the structure from the $hk0$ projection alone. A sharpened Patterson synthesis calculated using $hk0$ intensity data sharpened by multiplying by

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the inverse of the Lp factor yielded the position of one sodium atom only. However, a minimum function map plotted with the origin shifted to this position failed to give any clues to the structure. A 3-D Patterson synthesis sharpened by the Lp inverse was therefore computed. This synthesis employed coefficients of the type $(|F_{hkl}|^2 - \text{a constant})$ which resulted in the removal of a large positive peak from the origin. Analysis of the three Harker sections $U, V, \frac{1}{2}$; $U, \frac{1}{2}, W$; and $\frac{1}{2}, V, W$ gave the positions of the two sodium atoms. The next step was to compute a 3-D alpha synthesis. The alpha synthesis (Ramachandran & Raman, 1959) uses coefficients of the type $|F_N|^2 \cdot |F_P|$ where $|F_N|^2$ is the measured structure amplitude of the reflexion due to contributions from all atoms and $|F_P|$ is the calculated structure factor contribution from the known

atoms. This synthesis has been shown to be closely related to the 'vector convergence method' of solving the structure (Ramachandran, 1964), and is identical with the 'weighted sum function' of Buerger (1959). The alpha synthesis computed with the phases from the two sodium atoms revealed ten more atoms. A structure factor calculation involving $2\text{Na} + 10\text{C}$ atoms was made, and the electron density Fourier synthesis computed with additional phase information from these ten atoms revealed the remaining two atoms also.

The structure was refined by the least-squares method using the block-diagonal approximation with isotropic thermal parameters for all atoms, the R index at the end of nine cycles of refinement being 0.13. While the correctness of the proposed structure was beyond doubt, the bond distances and angles needed improvement and it was thought worthwhile to collect more precise X-ray intensity data to obtain the necessary accuracy of results.

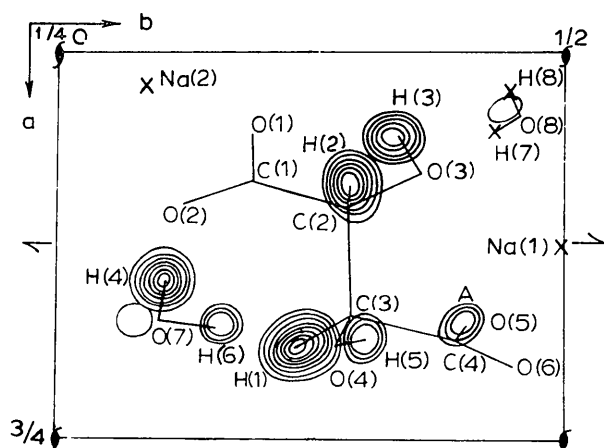


Fig. 1. A composite diagram of sections of three-dimensional electron density difference Fourier ρ_3 viewed down the c axis. Contours are drawn at intervals of $0.05 \text{ e.}\text{\AA}^{-3}$ starting from $0.2 \text{ e.}\text{\AA}^{-3}$.

Collection of counter data

The intensity data were collected with a General Electric XRD-5 X-ray unit equipped with a single-crystal orienter (Furnas, 1957) and a scintillation counter, using $\text{Cu } K\alpha$ radiation isolated by balanced Ni and Co filters. The 2θ , φ and χ settings of all reflexions within the copper sphere were computed on an IBM-650 machine, but the angles were set manually. The integrated intensity from each reflexion was recorded by moving the crystal from $\theta - 1.5^\circ$ to $\theta + 1.5^\circ$ where θ is the Bragg angle for the reflexion. Altogether 1060 reflexions out of 1121 possible for copper radiation were scanned in this manner. The intensities were corrected for Lorentz and polarization effects in the usual way and placed on an absolute scale by Wilson's method. Errors due to absorption, which were small,

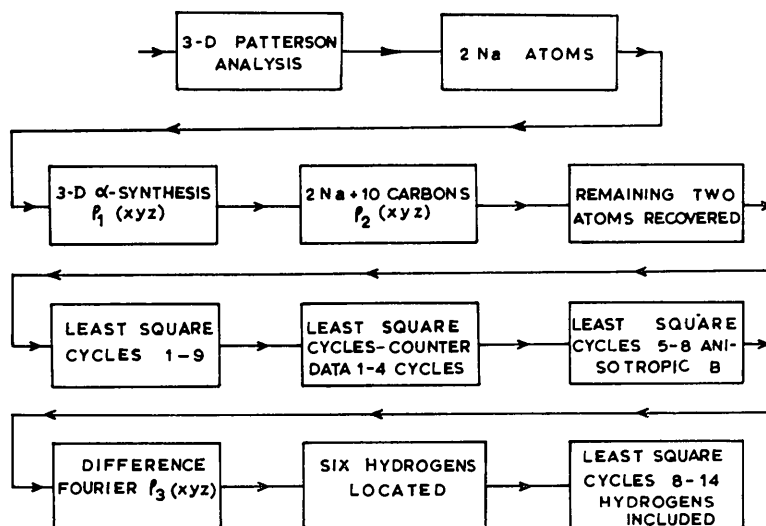


Fig. 2. An outline of the procedures adopted in the analysis of the structure and its refinement.

were neglected, but an empirical extinction correction was applied to about 20 very strong reflexions using the relation:

$$I(\text{corrected}) = \frac{I(\text{uncorrected})}{1 - KI(\text{uncorrected})}$$

where $K = 1 \times 10^{-5}$.

Refinement

Four cycles of least-squares refinement (block-diagonal) were carried out with isotropic thermal parameters for all atoms, bringing the R index down to 0.057. The

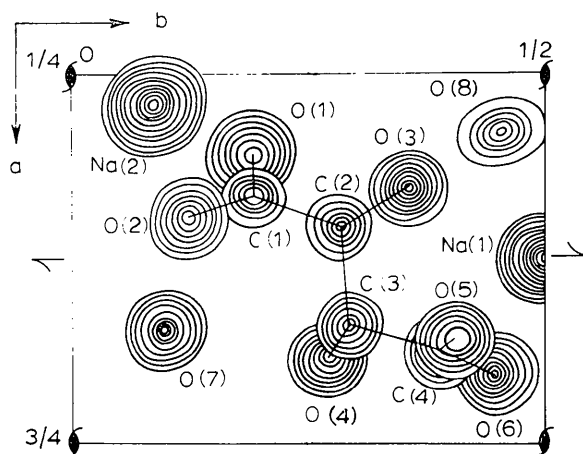


Fig. 3. Composite diagram of sections of the final three-dimensional electron density distribution viewed down the c axis. Contours are drawn at intervals of $1 \text{ e.}\text{\AA}^{-3}$.

atoms were now given anisotropic thermal parameters and a few more cycles of refinement were performed. An electron density difference Fourier synthesis computed at this stage revealed six out of eight hydrogen atoms clearly with peak heights ranging from $0.6 \text{ e.}\text{\AA}^{-3}$ to $0.3 \text{ e.}\text{\AA}^{-3}$. The map showed one extra peak (A) of height $0.33 \text{ e.}\text{\AA}^{-3}$ situated about 0.9 \AA away from O(5), but the possibility of this peak being a hydrogen atom was ruled out for two reasons. The total size of the peak was not as much as that of the other accepted hydrogen peaks. Further, the near equality of the C–O bonds of the carboxyl group ($1.248, 1.251 \text{ \AA}$) rules out the possibility that O(5) is protonated. The two hydrogen atoms belonging to the water molecule O(8) were fixed purely from geometrical considerations and therefore cannot be considered as definitely established. The composite 3-D electron density difference Fourier map viewed down the c -axis is shown in Fig. 1. In the final round of refinement (6 cycles) all the hydrogen atoms were also included. For this purpose the data were compressed by applying a cut-off which omitted from the refinement all reflexions whose F_o 's were less than 4. The final R index was 0.035. The process of the structure analysis and refinement is given in Fig. 2 and the final 3-D electron density distribution viewed down the c axis is shown in Fig. 3.

The values of observed and calculated structure factors obtained from the final cycle are given in Table 1, the coordinates of the atoms and their estimated standard deviations in Table 2 and the anisotropic thermal parameters in Table 3. The intramolecular bond lengths and angles with their standard deviations are given in Tables 4 and 5 respectively. The atomic scattering factors used in this refinement were taken from *International Tables for X-ray Crystallography* (1962).

Table 2. Final coordinates (fractional) of the atoms with mean standard deviations

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Na(1)	0.4921	0.4956	0.6553	0.001 Å	0.001 Å	0.001 Å
Na(2)	0.2933	0.0905	0.3877	0.001	0.001	0.001
O(1)	0.3563	0.1953	0.7183	0.002	0.002	0.002
O(2)	0.4423	0.1266	1.0677	0.002	0.002	0.002
O(3)	0.4040	0.3587	0.8894	0.002	0.002	0.002
O(4)	0.6307	0.2751	0.7638	0.002	0.002	0.002
O(5)	0.6086	0.4041	1.3706	0.002	0.002	0.002
O(6)	0.6521	0.4476	0.9528	0.002	0.002	0.002
O(7) (<i>W</i>)	0.5951	0.1009	0.5265	0.002	0.002	0.002
O(8) (<i>W</i>)	0.3282	0.4564	1.3989	0.002	0.003	0.003
C(1)	0.4140	0.1944	0.9300	0.002	0.002	0.003
C(2)	0.4548	0.2871	1.0402	0.002	0.002	0.003
C(3)	0.5881	0.2947	1.0265	0.002	0.002	0.002
C(4)	0.6207	0.3899	1.1241	0.002	0.002	0.002
H(1)	0.624	0.252	1.129			
H(2)	0.427	0.290	1.241			
H(3)	0.367	0.334	0.748			
H(4)	0.549	0.112	0.377			
H(5)	0.614	0.306	0.644			
H(6)	0.602	0.160	0.562			
*H(7)	0.362	0.408	0.544			
*H(8)	0.253	0.446	0.362			

* No evidence in the difference Fourier map

Table 3. Final anisotropic thermal parameters

Temperature factor

$$\exp \{-10^{-4}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	33	19	186	-4	-8	2
Na(2)	30	18	138	-1	-9	7
O(1)	41	30	222	-17	-39	-35
O(2)	40	16	248	-4	22	-12
O(3)	34	21	313	4	-38	2
O(4)	37	19	109	2	9	-24
O(5)	34	20	106	-3	0	-8
O(6)	37	17	122	-13	6	6
O(7) (W)	49	24	247	11	1	-18
O(8) (W)	40	81	314	-6	-32	5
C(1)	24	19	162	-12	28	-18
C(2)	23	16	188	0	11	-17
C(3)	26	13	98	-6	11	-15
C(4)	14	15	131	-3	4	3

Table 4. Intramolecular bond distances with estimated standard deviations

		$\sigma(l)$
C(1)-O(1)	1.240 Å	
C(1)-O(2)	1.249	
C(4)-O(5)	1.248	
C(4)-O(6)	1.251	0.004 Å
C(2)-O(3)	1.414	
C(3)-O(4)	1.420	
C(1)-C(2)	1.540	
C(2)-C(3)	1.533	0.004
C(3)-C(4)	1.526	
C(2)-H(2)	1.05	
C(3)-H(1)	0.90	
O(3)-H(3)	0.89	
O(4)-H(5)	0.77	
O(7)-H(4)	0.92	
O(7)-H(6)	0.89	
O(8)-H(7)	1.07	
O(8)-H(8)	0.89	

Distances between non-bonded atoms in the molecule

O(1)···O(3)	2.601 Å
O(4)···O(6)	2.708
O(1)···O(2)	2.223
O(5)···O(6)	2.224

Discussion of the structure

The tartrate ion

The tartrate ion (Fig. 4) consists of two planar halves C(2)O(3)C(1)O(1)O(2) and C(3)O(4)C(4)O(5)O(6) which are so oriented that the four carbon atoms lie in a plane with the interplanar angle $69^\circ 24'$. The chemically equivalent bonds are (1) C(1)-C(2) and C(3)-C(4); (2) the four C-O bonds of the carboxyl groups and (3) the two C-OH bonds. The differences in bond lengths within each group are too small to have any significance. The details of the least-squares planes fitted to the three planar groups along with the deviations of the atoms from each plane are given in Table 6.

Table 5. Intramolecular bond angles and their estimated standard deviations

	Angle	$\sigma(\theta)$
O(1)-C(1)-O(2)	127.5°	0.3°
O(5)-C(4)-O(6)	125.7	
O(1)-C(1)-C(2)	116.9	
O(2)-C(1)-C(2)	115.5	
O(5)-C(4)-C(3)	115.8	0.3
O(6)-C(4)-C(3)	118.3	
C(1)-C(2)-C(3)	110.5	
C(1)-C(2)-O(3)	110.0	
O(3)-C(2)-C(3)	109.5	
C(2)-C(3)-O(4)	111.6	0.3
O(4)-C(3)-C(4)	113.0	
C(2)-C(3)-C(4)	107.2	
H(2)-C(2)-O(3)	110.2	
H(1)-C(3)-O(4)	102.9	
H(4)-O(7)-H(6)	92.0	
H(7)-O(8)-H(8)	112.1	
H(3)-O(3)-C(2)	108.4	
H(5)-O(4)-C(3)	120.2	

The two halves of the tartrate ion projected down C(1)-C(2) and C(4)-C(3) are shown in Fig. 5. It may be observed that the group C(1)O(1)O(2) is turned away from the plane C(1)C(2)O(3) by 8° while the other group C(4)O(5)O(6) is turned away through as much as 18° from C(4)C(3)O(4). The two carboxyl oxygen atoms O(5) and O(6) are surrounded by three cations, namely Na(1), Na(2) and Na(2), in the next unit cell with the result that the resultant force due to the cations acting on the carboxyl groups appears to twist this group away from the plane C(4)C(3)O(4). The angles O(1)-C(1)-C(2) (116.9°) and O(6)-C(4)-C(3) (118.3°) are larger than the other pair O(2)-C(1)-

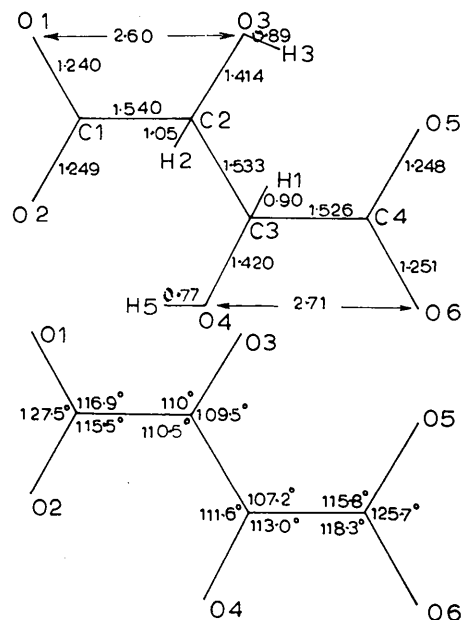


Fig. 4. Intramolecular features of the tartrate ion.

Table 6. *The deviations of the atoms from the least-squares planes* (Å)*

	Plane 1	Plane 2	Plane 3
O(1)		-0.005	
O(2)		-0.04	
O(3)			
O(4)			-0.003
O(5)			0.084
O(6)			-0.035
C(1)	-0.02	0.004	
C(2)	0.02	0.082	
C(3)	0.02	-0.054	-0.149
C(4)	-0.017		-0.096

* Plane 1	C(1)	C(2)	C(3)	C(4)
Plane 2	C(2)	O(3)	C(1)	O(1)
Plane 3	C(4)	O(5)	O(6)	C(3)

C(2) and O(5)-C(4)-C(3) (115.6° , 115.8°) respectively, a situation very similar to that encountered in α -hydroxycarboxylic acids (Kroon, 1964). The C-H distances (1.05 and 0.90 Å) are shorter than the value obtained from Raman spectra (1.08 Å). A similar trend is observed in ammonium hydrogen D-tartrate (van Bommel & Bijvoet, 1958) and D-tartaric acid (Okaya, Stemple & Kay, 1966).

Molecular packing and hydrogen bonding

The structure projected down the c axis is shown in Fig. 6. The tartrate molecules lie in a direction parallel to the a axis with the carbon atoms forming sheets parallel to the (001) plane. Intermolecular hydrogen

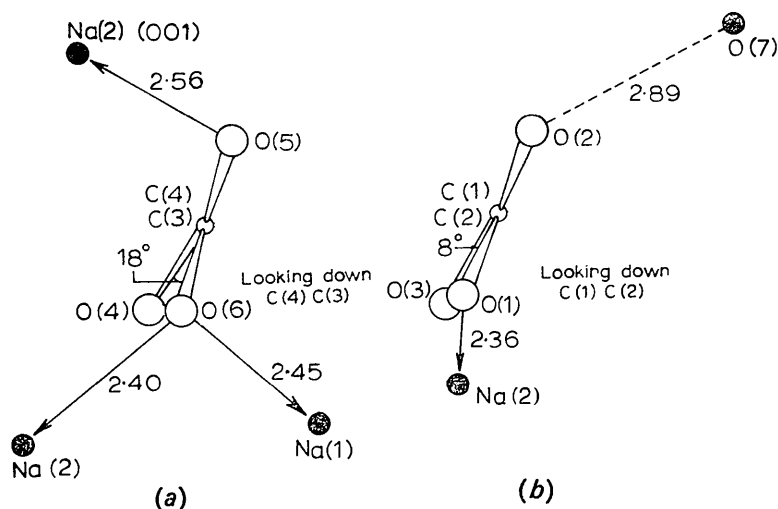
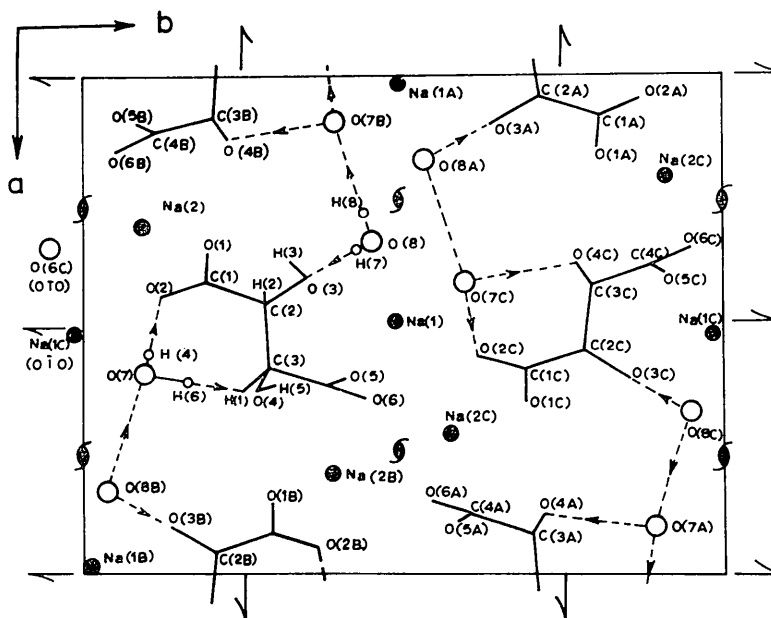


Fig. 5. The environment of the carboxyl groups viewed down (a) C(4)-C(3) and (b) C(1)-C(2).

Fig. 6. The structure of sodium D-tartrate dihydrate viewed down the c axis.

bonds formed through the water molecule stabilize the structure. The hydrogen atoms H(3) and H(5) attached to the hydroxyl oxygens are so situated (angles O(4)–H(5)–O(7) and O(3)–H(3)–O(8) are 65° and 109° respectively) that they do not participate in hydrogen bond formation.

The water molecules O(7) and O(8) have four nearest neighbours each, arranged in a distorted tetrahedral manner and in both cases one of the lone pair orbitals is found to be directed towards a cation. The water oxygen atom O(8) is 2.95 Å away from O(3) and 3.03 Å away from O(3) in the next unit cell. The hydrogen bond distances, angles and proton assignments are given in Table 7(a) and the non-bonded intermolecular distances in Table 7(b). The environments of the water molecules are shown in Fig. 7.

Table 7(a). Distances and angles involved in hydrogen bonding

Donor (OD)	Acceptor (OA)	Distance (OD)...(OA)	Angle (OD)–H...(OA)
O(7)–H(4)	O(2)	2.895 Å	147.4°
O(7)–H(6)	O(4)	2.844	160.4
O(8)–H(7)	O(3)	2.953	159.2
O(8)–H(8)	O(7B)	2.825	158.0

$\sigma(l)$ for bond distance = 0.004 Å

Angles subtended at O(2), O(3) and O(4)

C(1)–O(2)...O(7)	107.6°
C(2)–O(3)...O(8)	153.4
C(3)–O(4)...O(7)	120.8

Table 7(b). Non-bonded intermolecular distances less than 3.5 Å

For A, B etc. refer to Fig. 6

O(4)...O(2)	3.42 Å
O(3)...O(5)	3.41
O(3)...O(8)	3.03
O(8A)...O(8B)	3.31
O(5)...O(1B)	3.22
O(5)...O(2C)	3.33
O(8)...O(7C)	3.11

Coordination of sodium

Both sodium atoms in the asymmetric units exhibit sixfold coordination. The coordination octahedra have common edges O(5)–O(6) and O(2)–O(6) of length 2.99 and 3.83 Å respectively. The distances between the pairs of sodium atoms in the two cases are 2.68 and 3.62 Å respectively (Fig. 8). One of the sodium atoms Na(1) is surrounded by two water oxygen atoms, three oxygen atoms from one tartrate molecule and one oxygen atom from a second molecule. This sodium atom lies nearly in the plane formed by O(3), O(8), O(2), O(6). The other sodium atom Na(2) is surrounded by five oxygen atoms from three different tartrate molecules. Out of the twelve Na–O distances (Table 8), ten have an average value of 2.38 Å which agrees well with the sum of the ionic radii of Na⁺ and O²⁻ (2.37 Å).

However, two distances Na(1)–O(3) and Na(2)–O(4) are 2.53 and 2.82 Å respectively. This effect may be a result of the repulsion of the cation by the hydrogen atoms of the hydroxyl groups O(3) and O(4). In fact, in the structure of potassium sodium DL-tartrate, 4H₂O (Sadanaga, 1950) the Na–O(H) distance (2.75 Å) is larger than the average value.

It is a pleasure to thank Professor G. N. Ramachandran for the keen interest he evinced in this work, and

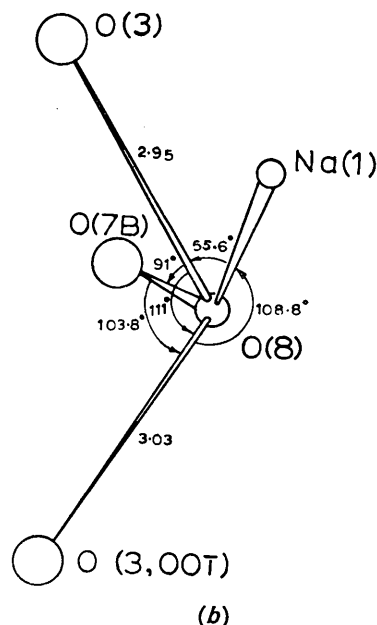
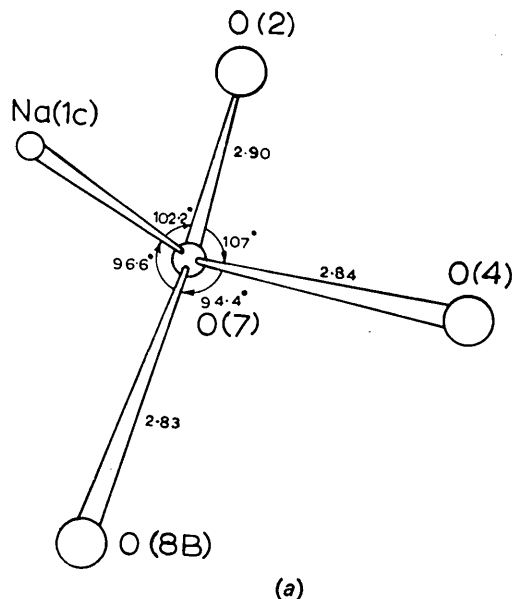


Fig. 7. The environment of the water molecules.

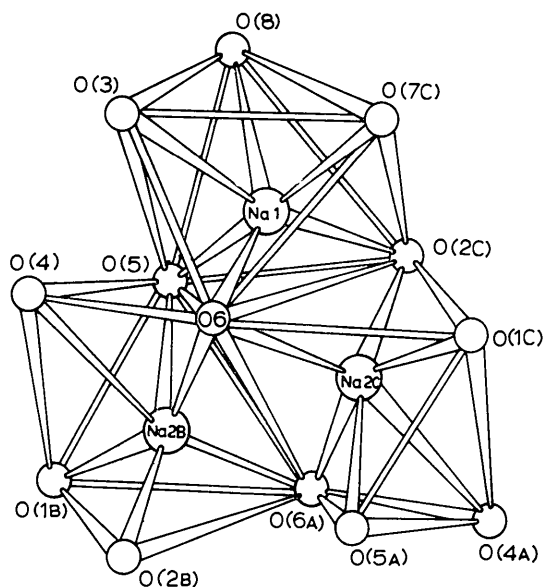


Fig. 8. The coordination octahedra of the cations.

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Table 8. Sodium–oxygen distances and their mean standard deviations

	Distance	$\sigma(1)$
Na(1)...O(3)	2.53 Å	
Na(1)...O(5)	2.36	
Na(1)...O(6)	2.45	
Na(1)...O(2C)	2.34	0.003 Å
Na(1)...O(7C)	2.42	
Na(1)...O(8)	2.34	
Na(2)...O(6B)	2.40	
Na(2)...O(5B)	2.43	
Na(2)...O(4B)	2.82	0.003
Na(2)...O(1)	2.36	
Na(2)...O(2)	2.39	
Na(2)...O(6C0T0)	2.33	
Na(2)...Na(2)	3.76	
Na(2)...Na(1)	3.68	
Na(2)...Na(1)	3.62	

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