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The Crystal and Molecular Structure of Disodium Maleate Monohydrate

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Disodium maleate monohydrate crystallizes from $DMSO/H_2O$ in the form of thick plates. The space group is $C2/c$ and the cell dimensions are $a = 20.979$ (4), $b = 10.004$ (3), $c = 6.369$ (1) Å, $\beta = 100.15$ (1)°. Diffractometer data to $2\theta = 80°$ (Mo $K\alpha$) were collected. The structure was solved by symbolic addition and refined by full-matrix least-squares methods to final weighted and unweighted R values of 0.048 and 0.033 respectively. The four atoms of the carbon spine are nearly coplanar. One carboxylate ion is twisted by 66.0° about its C–C bond and the other is rotated $-16.9°$. Bond lengths within and between the carboxyl groups are dissimilar. Both sodium ions have five oxygen atoms as coordinators in a distorted square-pyramidal arrangement. The water molecule links the organic di-ions together in a hydrogen-bonded helical array. A comparison is made with the recently reported structure of Li_2 maleate.$2H_2O$.

Introduction

The conformation adopted by a *cis*-dicarboxylic alkene structural unit (I) represents a compromise between the attractive forces arising from the presence of an intramolecular hydrogen bond and the repulsions which are engendered by the unusual shortness of the $O–H\cdots O$ linkage.

(I)
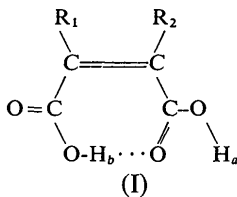
(*a*) $R_1 = R_2 = H$: maleic acid.
(*b*) R_1, $R_2\cdots C_6H_8$: bicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylic acid.
(*c*) $R_1 = R_2 = H$, H_a absent: maleate monoanion.
(*d*) $R_1 = H$, $R_2 = Cl$, H_a absent: chloromaleate monoanion.
(*e*) $R_1 = {}^-OOCCH_2$, $R_2 = H$, H_a absent: *cis*-aconitate dianion.
(*f*) $R_1 = R_2 = H$, H_a, H_b absent: maleate di-anion.

In the fully protonated forms I(*a*) (Shahat, 1952; James & Williams, 1974*b*) and I(*b*) (Hechtfischer,

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Steigemann & Hoppe, 1970) the internal angles of the quasi-cyclic system are considerably opened, the internal hydrogen bond is asymmetric and the carboxyl groups are slightly twisted out of the plane of the double bond. The maleate monoanion has been shown to have its internal bond angles similarly opened and the carboxyl groups similarly twisted so that the two central oxygen atoms are on the same side of the plane of the carbon atoms. A central position for the hydrogen atom of the internal hydrogen bond has been demonstrated in two cases (Ellison & Levy, 1965; Darlow & Cochran, 1961) and implied in one other (Glusker, Orehowsky, Casciato & Carrell, 1972). The results of Darlow and Cochran on potassium hydrogen maleate have been confirmed at a higher precision by a recent refinement based on diffractometer data by Dr P. W. Codding in this laboratory. That intermolecular interactions are important in determining whether or not the internal hydrogen bond is symmetric is demonstrated by the fact that short but definitely asymmetric hydrogen bonds have been found in two further structural studies of the maleate monoanion (James & Williams, 1971; 1974*a*). The only unequivocal demonstration of a centred hydrogen bond in the unsubstituted hydrogen maleate anion is that of Darlow and Cochran. However this ion is present in the crystals in a symmetric environment and the space-group symmetry of the environment creates the centred hydrogen bond, *cf.* brom-

pheniramine maleate and (+)-chlorpheniramine maleate (James & Williams, 1971; 1974a) where no site symmetry exists. A similar argument has been demonstrated for the bifluoride ion (F–H–F⁻) by Williams & Schneemeyer (1973). These workers have shown that when the bifluoride ion has no lattice-imposed symmetry an asymmetric hydrogen bond prevails.

The geometry of *cis*-alkene diacids is therefore the result of a subtle interplay of inter- and intramolecular forces and so, in order to characterize more fully this system, we have investigated the fully ionized form of maleic acid.

Experimental

Disodium maleate was prepared by adding an excess of NaOH pellets to a concentrated solution of the acid in H_2O. On cooling and standing the syrupy solution solidified into a mass of very tiny needles. A sample of this preparation was dissolved in DMSO with the addition of a small amount of H_2O. Platy crystals of good quality were obtained by allowing the water to evaporate from this solution. An irregular specimen of maximum dimensions $0.5 \times 0.6 \times 0.08$ mm was mounted so as to rotate about an axis parallel to the plate surface. Weissenberg and precession photography revealed $2/m$ diffraction symmetry and the systematic absences hkl: $h+k=2n+1$; $h0l$: $h=2n+1$, $l=2n+1$; $0k0$: $k=2n+1$. The space-group ambiguity between Cc and $C2/c$ was later resolved. A data summary for this compound is given in Table 1. The unit-cell parameters were initially obtained photographically and were refined as part of the alignment process on a Picker FACS-1 diffractometer. Diffraction data were collected on this instrument using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) to $2\theta_{max}$ $=80°$. In total, 4157 independent and space-group-permissible reflexions were measured of which 2871 (69%) had net intensities which satisfied the criterion that net I be greater than $3\sigma(I)$. Normalized structure factors were calculated using the whole data set and an examination of their distribution statistics allowed the centrosymmetric space group $C2/c$ to be chosen for subsequent work. These E-distribution statistics compared very well with the theoretical values given by Karle, Dragonnette & Brenner (1965).

Table 1. *Crystallographic data for disodium maleate monohydrate*

Formula	$C_4H_2O_4 . H_2O . Na_2$
Molecular weight	180.07
Space group	$C2/c$
a	20.979 (4) Å
b	10.004 (3)
c	6.369 (1)
β	100.15 (1)°
V	1371.56 Å³
z	8
$\bar{\mu}$(Mo $K\bar{\alpha}$)	2.86 cm⁻¹

The structure invariants 800, 10,0,2 and 26,0,2 were assigned phases on the basis of the space-group speci-

fic $\sum_1$ formula given below. This equation and the associated probability formula were derived by inspection from the general method of Main (1971).

$$S\{E_{2h02l}\} \approx S\{ \sum (-1)^l(|E_{hkl}|^2 - 1)\},$$

$$P^+_{2h02l} = \tfrac{1}{2} + \tfrac{1}{2} \tanh \left\{ \frac{\sigma_3}{2\sigma_2^{3/2}} |E_{2h02l}| \sum_l (-1)^l(|E_{hkl}|^2 - 1)\right\}.$$

The probabilities that this procedure assigned the correct phase in the above three cases were 91.8%, 98.3% and 97.2% respectively. Phase angles of 0° were assigned to the origin-specifying reflexions $\overline{5}91$ and $\overline{24},4,3$ thus giving five reflexions in the starting set. This set was expanded to 488 phased E's by the symbolic addition procedure (Karle & Karle, 1966) using the technique of Hall & Ahmed (1968) to define and evaluate the symbols. The 11 largest peaks in a subsequent Fourier synthesis proved to represent the structure and a conventional R value of 21.2% was obtained when these were used as the basis of a structure-factor calculation. A difference Fourier map computed after several cycles of isotropic least-squares refinement clearly showed the four hydrogen atoms of the structure in peaks of positive difference density ranging from 0.81 to $1.02 e$ Å⁻³. In the final model all non-hydrogen atoms were described with anisotropic thermal ellipsoids and the hydrogen atoms assigned isotropic B values (Å²). Full-matrix least-squares (Busing, Martin & Levy, 1962) and difference Fourier techniques were employed to refine the model to final weighted and unweighted R values of 0.048 and 0.033 respectively. During the least-squares part of this refinement the structure factors were weighted with terms derived, at the data reduction stage, from the expression $| w = 2F_o/[T+(kI)^2 + B]^{1/2}$ (Peterson & Levy, 1957). In this expression T, I and B are the total, net and background counts respectively for the reflection, k is a small constant (0.04 in this case) which is included to allow for minor experimental errors. For the carbon atoms the scattering-factor table was derived from a set of analytical coefficients (Cromer & Mann, 1968) and corrected by incorporation of the term $\Delta f' = 0.005$ e (Cromer & Liberman, 1970). For the oxygen of the water molecule the
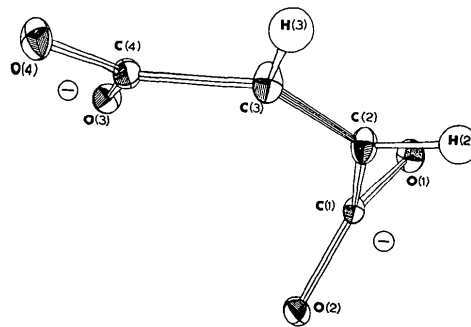

Fig. 1. A computer-produced diagram (Johnson, 1965) of one maleate dianion showing the conformation of the ion and the numbering scheme of this analysis.

table was similarly derived and corrected by the term $\Delta f' = 0.015$ e. All four oxygen atoms of the maleate dianion were assigned an average $(0 + 0^{-1})/2$ curve; the 0^{-1} curve was similarly obtained. The hydrogen-atom scattering-factor table was that of Stewart, Davidson & Simpson (1965). A tabulation of the observed structure amplitudes and final calculated structure factors is available.*

Results and discussion

Tables 2 and 3 contain the positional and thermal parameters used to describe the final model. Fig. 1 depicts

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30346 (71pp., 2 microfiches). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional parameters for one unique portion of the disodium maleate monohydrate structure*

	x/a	y/b	z/c
Na(1)	0·06865 (2)	−0·08777 (4)	−0·05251 (6)
Na(2)	0·19473 (2)	0·24508 (4)	−0·23141 (6)
O(1)	0·04766 (3)	0·12301 (7)	0·07167 (11)
O(2)	0·08617 (3)	0·19681 (8)	−0·21138 (11)
O(3)	0·19700 (3)	0·31393 (7)	0·12467 (10)
O(4)	0·20558 (4)	0·53586 (8)	0·15176 (14)
C(1)	0·06585 (3)	0·21468 (8)	−0·04052 (12)
C(2)	0·05716 (4)	0·35364 (9)	0·03766 (15)
C(3)	0·10179 (4)	0·44445 (8)	0·11248 (15)
C(4)	0·17352 (4)	0·42990 (8)	0·13125 (12)
O(5)*	0·17796 (3)	0·13178 (8)	0·43795 (12)
OH(1)	0·2079 (9)	0·0890 (19)	0·4287 (29)
OH(2)	0·1776 (9)	0·1856 (21)	0·3370 (31)
H(2)	0·0105 (7)	0·3765 (14)	0·0346 (23)
H(3)	0·0868 (7)	0·5355 (16)	0·1625 (22)

* This is the oxygen atom of the water molecule; the two hydrogen atoms bonded to it are designated OH(1) and OH(2).

the numbering scheme adopted here and the conformation found. Bond distances and interbond angles are given in Fig. 2. Error estimates for the molecular parameters were derived by the independent atom method from the atomic position e.s.d.'s obtained from the inverse matrix (Busing *et al.*, 1962). These e.s.d.'s are probably underestimated but are quoted here unmodified. A results summary of the least-squares planes is given in Table 4.

Table 4. *A results summary for the least-squares planes for the maleate dianion*

(a) Distances from the planes ($\text{Å} \times 10^4$)

	I	II	III
C(1)	−20*	−206*	7427
C(2)	70*	85*	3306
C(3)	−70*	−9263	5*
C(4)	22*	−22563	−13*
O(1)	−10389	64*	−639
O(2)	9988	73*	18470
O(3)	−3150	−27067	3*
O(4)	3346	−28340	5*
H(2)	−57	8584	2833
H(3)	−164	−7382	−2784

* Atom used to define the plane.

(b) Terms in the equation $lx + my + nz - p = 0$ and χ^2 values for the planes

	l	m	n	p	χ^2
I	0·1147	0·3558	−0·9275	1·1654	125·79
II	−0·8510	0·0400	−0·5236	−0·9748	1184·84
III	0·0846	0·0704	−0·9939	−0·2183	3·89

(c) Dihedral angles between the planes

Plane	I	II	III
I	0	16·9°	66·2°
II		0	63·1
III			0

Non-ionized carboxylic acids typically exhibit one C–O bond distance near 1·23 Å and the other about 1·31 Å (Dunitz & Strickler, 1968). Carboxylate anions, on the

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Table 3. *The thermal vibration parameters used in the description of the final model for disodium maleate monohydrate*

Coefficients are terms in the expression $T = \exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right]$. Values are $\times 10^5$.

(a) The non-hydrogen atoms

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	99 (1)	562 (4)	1257 (8)	32 (1)	74 (2)	−10 (4)
Na(2)	87 (1)	535 (4)	1281 (8)	4 (1)	60 (2)	−80 (4)
O(1)	122 (1)	448 (6)	1587 (15)	−30 (3)	85 (3)	211 (7)
O(2)	113 (1)	758 (7)	1263 (14)	−60 (2)	145 (3)	−302 (8)
O(3)	100 (1)	449 (5)	1285 (14)	46 (2)	55 (3)	−70 (6)
O(4)	153 (2)	507 (6)	2285 (20)	−126 (2)	236 (4)	−333 (9)
C(1)	62 (1)	369 (6)	1034 (14)	−10 (2)	34 (3)	−41 (7)
C(2)	83 (1)	400 (7)	1799 (20)	18 (2)	91 (4)	−128 (9)
C(3)	101 (1)	347 (6)	1834 (21)	22 (2)	97 (4)	−218 (9)
C(4)	94 (1)	388 (6)	939 (13)	−21 (2)	73 (3)	−103 (7)
O(5)	104 (1)	659 (7)	1537 (16)	19 (2)	132 (3)	40 (8)

(b) The hydrogen atoms

	B_{iso}
OH(1)	4·45 (40) Å^2
OH(2)	4·90 (43)
H(2)	3·03 (30)
H(3)	3·51 (30)

other hand, are expected to have more nearly equal bonds of intermediate length. In the present case intermediate distances are shown but the bonds within each group are not equal and there is a marked difference between the two carboxylate ions. Differences of 12 and 14 times the nominal 0·001 Å e.s.d. are apparent within the two groups and there is a 30σ difference between the means of the C–O distances for each group. The two longer distances are associated with the C(1), O(1), O(2) carboxylate ion which is rotated by 66·2° about the C(1)–C(2) bond (refer to Table 4). The other ionic group is rotated −16·9° about its C–C linkage and so retains approximate coplanarity with the double bond. That extensive electron delocalization from the ethylenic bond to the more coplanar carboxylate ion does not occur is inferred from the 'ideal' length of the C=C bond (Sutton, 1965) and from the fact that the two C–C linkages here are both larger than the similar bonds in maleic acid (James & Williams, 1974b). However, the nearly coplanar nature of two π-electron systems which are separated by one bond would permit some delocalization and the fact that the shorter C–C bond is to the C(4), O(3), O(4) group may imply that some transfer does occur.

A study of the nearest-neighbour positions for the oxygen atoms reveals that each carboxylate ion has one oxygen atom with approximate tetrahedral coordination and the other with a nearly trigonal pattern of ligands. Fig. 3 is a composite sketch showing the environments of the five oxygen atoms. This figure shows that the carboxyl group exhibiting the longer C–O distances [C(1), O(1), O(2)] is involved in a total of five ionic interactions whereas only three such bonds are implicated for C(3), O(3), O(4). Both hydrogen bonds from the water molecule are to this latter group and these facts may be important in rationalizing the different bond lengths. Manojlović & Speakman (1967) have pointed out that the sum of the C–O bond distances in carboxyl groups, whether ionized or not, is close to 2·52 Å. The 2·514 Å sum for C(4)–O(3) and C(4)–O(4) is within normal bounds but the value of 2·574 Å for C(1), O(1), O(2) is significantly larger. Craven, Cusatis, Gartland & Vizzini (1973) have produced evidence which indicates that a slight lengthening of the bond between a hydrogen-bond accepting carbonyl oxygen and its carbon atom accompanies hydrogen-bond formation. The intricate and highly interconnected nature of the present system defies a simple interpretation in terms of either the results of Craven et al. (1973) or the more general charge-redistribution ideas deduced from theoretical studies (Kollman & Allen, 1972).

Oxygen atoms O(3) and O(4) are not involved in hydrogen bonding so the explanation for the larger bond sum of this carboxyl group might be found in the entirely cationic environment of the group. Coppens, Cooper & Larsen (1972) have shown that in an ionic compound the ions had considerably less than the full unit net electric charge formally resident on them. It is thought that this is a general property of ionic struc-

tures. In the present case this may be interpreted to mean that the bonding capability of O(1) and O(2) is diminished because there has been a transfer of electrons from the oxygens to the sodium ions in compliance with this microscopic electroneutrality principle. The C(1)–O(1) and C(1)–O(2) bonds would therefore be lengthened.

Both independent sodium ions of this structure reside in distorted square pyramidal sites formed by five oxygen atoms. This is not common either in terms of coordination number or arrangement of ligands for Na$^+$ (Shannon & Prewitt, 1969, and references therein) but the 2·402 Å average over the ten Na–O contact dis-
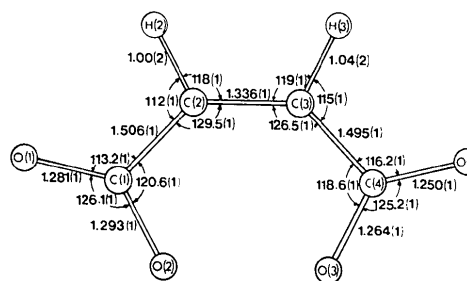

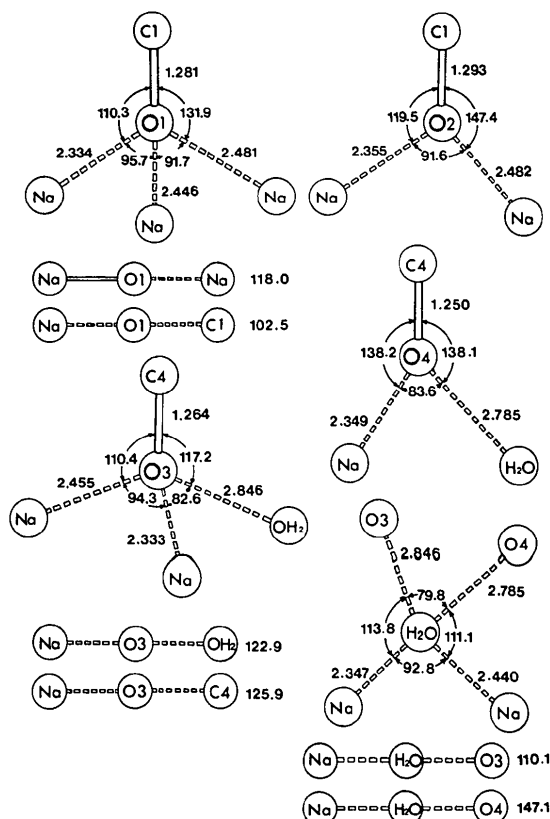Fig. 2. Bond distances and interbond angles in the maleate dianion.

Fig. 3. A diagrammatic representation of the environments of the five oxygen atoms of the Na$_2$ maleate monohydrate structure.

tances here agrees well with the 2·40 Å expectation value (Shannon & Prewit, 1969). The environments of the two sodium ions are given in Fig. 4.

That the ionic packing within this structure is complex is readily appreciated from Fig. 5. This packing diagram is a view of the structure along a direction displaced slightly from the *b* axis. The helical array of hydrogen bonds linking the maleate ions is shown only in the bottom right corner. The edge-sharing sodium ion pentahedra may be seen to run as alternate up-down-up pyramids through the figure from bottom left to middle right and in directions parallel to this.

A further point of interest is that the maleate dianions are held together in an edge-to-edge manner by Na^+ and H_2O bridges. The water molecules and sodium ions occupy spaces between the discontinuous sheets formed by this arrangement.

Because of the complexity and the obvious importance of ionic interactions in this structure, it is very difficult to decide just which factors are the more important in determining the precise conformation of the maleate dianion. However, the recent publication of the dilithium maleate dihydrate crystal structure (Town & Small, 1973) allows some deductions regarding the inherent molecular geometry of this dianion.

The conformation of the maleate dianion is essentially the same in these two different environments. In both cases the carbon spine is planar and one of the carboxylate groups is approximately coplanar with this spine. The other carboxylate group is rotated out of this plane by 66·2° in Na_2 maleate and 81·4° in Li_2 maleate.

The comparable carbon–carbon bond lengths are identical within experimental error, and the two C=C–C angles maintain their highly significant difference in the same sense. The carboxylate C–O distances show a much greater variation by comparison. In the Li_2 maleate structure the two C–O bond length sums are equivalent at 2·527 Å, but the situation is more com-

plex in the Na_2 maleate structure as discussed above. In the two structures the angles around the central carbon atoms of the two carboxylate groups retain the same relative magnitudes. There are however some small differences between the two sets of angles which are probably due to the different coordination pattern of the oxygen atoms. A final point of interest concerns the coordination geometry of the alkali metal ions. The smaller Li^+ ions accommodate four oxygen ligands in a distorted tetrahedral arrangement, whereas the Na^+ ions are linked to five in a distorted square pyramid. Despite this apparent requirement for more oxygen ligands by the Na_2^+ salt it actually has one water molecule per asymmetric unit, the Li_2^+ salt using two in the packing.
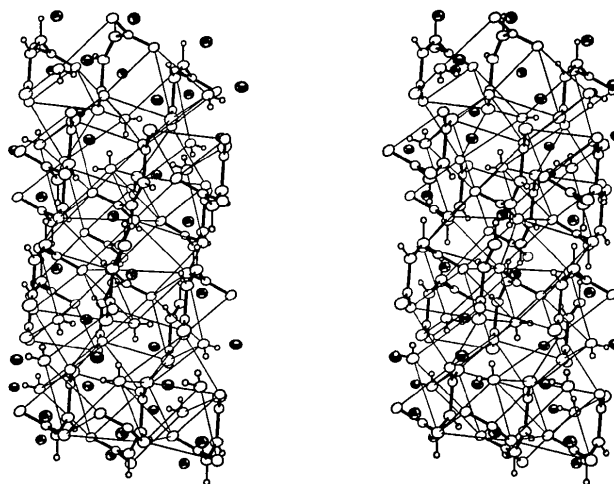

Fig. 5. A stereoscopic packing diagram of the disodium maleate monohydrate structure. In this view the crystallographic *a* axis is vertical, the *c* axis horizontal and **b** is approximately parallel to the viewers line of sight.
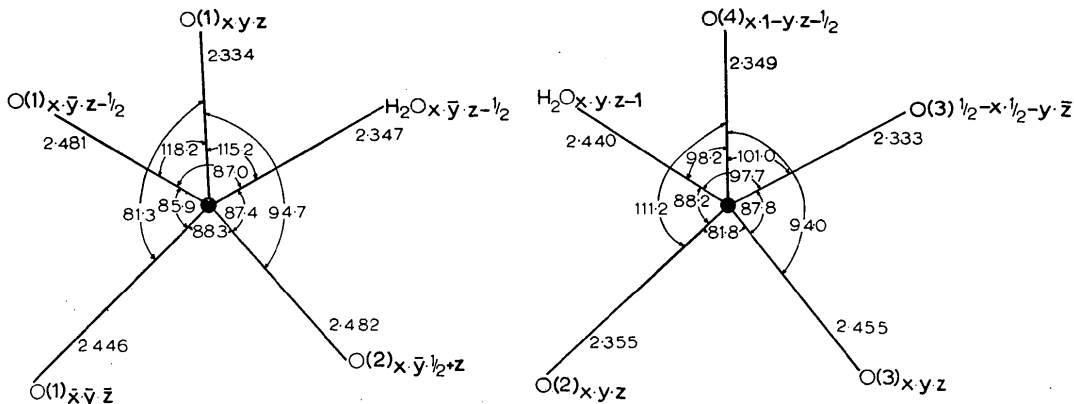

Fig. 4. A sketch showing the distances and angles of the coordination patterns of the sodium ions. (*a*) Na(1), (*b*) Na(2). Nominal e.s.d.'s for these parameters are 0·0008 Å and 0·03°.

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WILLIAMS, J. M. & SCHNEEMEYER, L. F. (1973). *Amer. Cryst. Assoc. Abs.* Ser. 2, Vol. 1, paper G5, p. 150.

The Crystal Structure of Wenkite

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The crystal structure of wenkite $(Ba,K)_4(Ca,Na)_6(Si,Al)_{20}O_{41}(OH)_2(SO_4)_3 . H_2O$, has interesting relationships with that of the zeolite offretite. Both minerals are characterized by the type of cage found in cancrinite, each cage being joined through bridges of six oxygen atoms to two identical cages, thus building up columns parallel to c. In wenkite the columns are interconnected by half-occupied face-sharing tetrahedral pairs. One barium cation is located in the cancrinite cavity enclosed in the columns; the other barium cations, calcium cations and disordered sulphate groups are located in the channels of the structure.

Introduction

Wenkite was found in the marbles of Candoglia, Italy, by Papageorgakis (1959, 1962), who studied its physical and optical properties, determined its hexagonal lattice constants and on the basis of analyses of purified material proposed the following formula:

$Ba_{4.5}Ca_{4.5}Al_9Si_{12}O_{42}(OH)_5(SO_4)_2$. Wenk (1966) refined, by least-squares calculations on powder data, the lattice constants, obtaining $a = 13·511$ (1), $c = 7·462$ (1) Å; he confirmed the diffraction symmetry of wenkite as $6/mmm$ and, by examination of the Harker concentrations on the Patterson map, determined $P\bar{6}2m$ as the most probable space group. Moreover he observed