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The Crystal Structures of Potassium Mesotartrate Dihydrate and the Isomorphous Rubidium Salt

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Potassium mesotartrate dihydrate and the isomorphous rubidium salt crystallize in space group $P\bar{1}$ with cell constants $a=7\cdot05$, $b=6\cdot87$, $c=11\cdot16$ Å, $\alpha=95\cdot87°$, $\beta=103\cdot27°$, $\gamma=62\cdot22°$ and $a=7\cdot11$, $b=6\cdot93$, $c=11\cdot5$ Å, $\alpha=96\cdot0°$, $\beta=101\cdot6°$, $\gamma=61\cdot8°$ respectively. The structures were determined by two-dimensional Patterson and Fourier syntheses and refined by least squares, using F_{0kl}, F_{h0l} and F_{hk0} data. The final R values are 0·080 and 0·074 respectively. The mesotartrate ion is present in an asymmetric conformation, the characteristic features of which (planar halves, ethane conformation) resemble those of the active stereoisomer. The crystal is a 'racemate' because of the presence of both 'antipodes', so-called conformational isomers, in one ordered single crystal. There are notable differences between the corresponding intermolecular distances in the two isomorphous structures with the systematic exception of the O–H · · · O distances, which are remarkably equal.

Introduction

Up till now many X-ray investigations have been carried out on structures that contain the active molecules or ions of tartaric acid (*e.g.* Beevers & Hughes, 1941; Beevers & Stern, 1950; Sadanaga, 1950; Parry, 1951; van Bommel, 1956; Sprenkels, 1956). Notwithstanding the different packing of the molecules, in all structures the same conformation* has been found, namely two planar halves in such an orientation that the carbon chain is planar.

In mesotartaric acid the configuration around one of the central carbon atoms is opposite with respect to that of tartaric acid. In the former the conformation in which the two halves as well as the carbon chain are planar, which implies a centrosymmetrical molecule, seems unfavourable because of short intramolecular distances. We decided to determine the structure of a mesotartrate to see whether indeed the planarity of one or more groups is abandoned and to gain an insight into the relative stability of the planar groups.

From crystal symmetry ($P\bar{1}$) and number of molecules in the unit cell (2) Schneider (1928) concluded that the mesotartrate ion was present in an asymmetric form. Although this statement was not strictly justified on the basis of these data it has been confirmed by the results of the present investigation.

Experimental

The cell constants of potassium mesotartrate were determined with Cu $K\alpha$ radiation by means of a General Electric apparatus equipped with a single-crystal orienter and a scintillation counter. The results are: $a=7\cdot05$, $b=6\cdot87$, $c=11\cdot16$ Å, $\alpha=95\cdot87°$, $\beta=103\cdot27°$ and $\gamma=62\cdot22°$. The space group was assumed to be $P\bar{1}$, and this choice of space group was corroborated by the structure determination. The unit cell contains two molecules; density calculated: 1·89 g.cm^{-3}, measured: 1·89 g.cm^{-3}. The corresponding constants of the isomorphous rubidium salt, determined from rotation and zero level Weissenberg photographs taken with Cu $K\alpha$ radiation, are: $a=7\cdot11$, $b=6\cdot93$, $c=11\cdot5$ Å, $\alpha=96\cdot0°$. $\beta=101\cdot6°$ and $\gamma=61\cdot8°$. $D_m=2\cdot38$ g.cm^{-3} and $D_x=2\cdot41$ g.cm^{-3}. In the latter case the reciprocal angle α^* appeared to be acute (89·4°), whereas the same angle in potassium mesotartrate is obtuse (90·3°), making the indexing somewhat troublesome.

Equatorial Weissenberg photographs (Cu $K\alpha$ radiation) around all three axes were taken on a Nonius integrating Weissenberg camera; the intensities were recorded on film packs. For all photographs the crystal was ground to a cylinder around the rotation axis. The intensities were measured by means of a microdensitometer and corrected for Lorentz, polarization and absorption factors in the usual way.

Structure analysis

Comparison of the Patterson projections of the isomorphous structures along the a and b axes yielded the positions of the heavy atoms. The remaining atoms could be located by applying the heavy atom method to rubidium mesotartrate. These parameters were assigned to potassium mesotartrate and submitted to a least-squares refinement (ZEBRA-program ZK-22, Schoone, 1962) with all measured reflexions except four because of extinction. After several cycles the scale factors of the different zones were readjusted. At

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* Conformation here means the rotational arrangement of the atoms around the carbon–carbon single bonds (Eliel, 1962).

a later stage allowance was made for hydrogen atoms placed on positions that were determined by geometrical considerations and were confirmed by difference Fourier syntheses (subtracting all atoms except hydrogen, employing low order terms only: $\sin\theta/\lambda \le 0\cdot3$). During the following refinement of the structure the positions of the hydrogen atoms and their temperature factors, tentatively put at a value of 3·0 Å², remained fixed. Application of weights according to $w^{-1}=1+(1\cdot6-0\cdot1F_o)^2$ did not give rise to significant shifts. Final difference Fourier syntheses with all terms included and all atoms subtracted gave no indication of anisotropic thermal motion.

Ultimate electron density projections of the potassium salt are shown in Fig. 1; in calculating these projections the reflexions affected by extinction were given a value corrected according to: $I_{\text{corr.}}=\exp\,(11\cdot10^{-5}I_0)$. The atomic scattering factors used for all structure factor calculations are those of Sagel (1958) for rubidium, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for potassium, oxygen and carbon and McWeeny (1951) for hydrogen. The structure factors observed and calculated are given in Table 1; the final value of the conventional R index is 0·080, the unobserved reflexions and those that suffer from extinction excepted. In order to be able to compare the isomorphous structures in some more detail rubidium mesotartrate was refined in the same way, though in the calculations hydrogen atoms were omitted. The refinement reduced the R value to 0·074 (465 ndependent F_{0kl}, F_{h0l}, F_{hk0} and F_{hhl} data). In Table 2 the final parameters of both potassium mesotartrate and rubidium mesotartrate are listed.

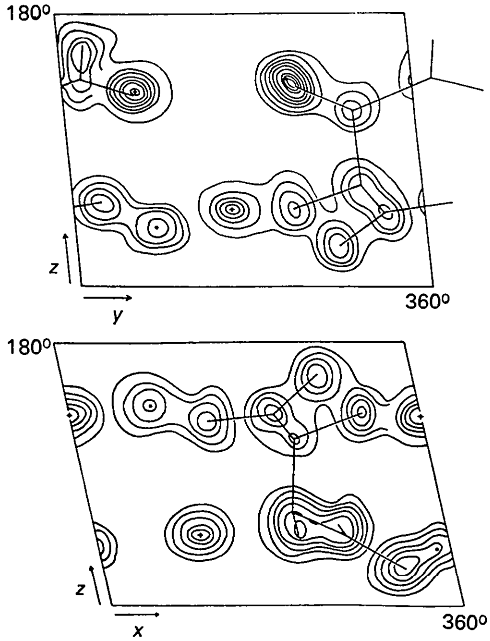

Fig. 1. Final electron-density projections along [100] and [010]. Contours are drawn from 3 e.Å^{-2} with intervals of 2 e.Å^{-2}, for the potassium atoms from 10 e.Å^{-2} with intervals of 5 e.Å^{-2}. Crosses and dots represent potassium atoms and water molecules respectively.

Table 1. *Observed and calculated structure factors of potassium mesotartrate dihydrate*

Values listed are $5F_o$ and $5F_c$. Minus sign on F_o signifies 'less than'.
Reflexions marked with an asterisk were omitted from the refinement because of extinction.

h	k	l	c.Fo	c.Fc
0	0	1	−10	−5
		2	68	−62
		3	−15	−3
		4	440	−649*
		5	−20	−8
		6	142	147
		7	36	−35
		8	153	155
		9	−20	6
		10	118	−125
		11	−15	30
		12	59	−63
		13	−10	5
0	1	0	41	52
		1	136	−191*
		−1	104	−111
		2	106	115
		−2	94	−84
		3	−15	15
		−3	135	134
		4	64	60
		−4	71	77
		5	131	143
		−5	52	−49
		6	−20	2
		−6	−20	−14
		7	37	−34
		−7	91	−85
		8	−20	−23
		−8	119	−127
		9	67	−64
		−9	96	97
		10	−20	0
		−10	−20	16
		11	70	69
		−11	43	47
		12	29	−28
		−12	54	66
		13	−15	14
		−13	37	−39
0	2	0	151	−143
		1	70	−61
		−1	204	203
		2	202	245
		−2	217	−229
		3	311	−404*
		−3	110	−102
		4	64	53
		−4	81	72
		5	67	63
		−5	70	−65
		6	114	−107
0	2	−6	128	114
		7	231	231
		−7	155	162
		8	63	56
		−8	36	−36
		9	76	−60
		−9	44	48
		10	58	53
		−10	72	−70
		11	80	−72
		−11	78	−87
		12	56	−54
		−12	35	26
		13	37	51
		−13	−10	3
0	3	0	128	−124
		1	45	−48
		−1	52	−44
		2	67	−67
		−2	189	189
		3	−15	−7
		−3	38	31
		4	145	148
		−4	−15	−11
		5	−20	−19
		−5	108	106
		6	−20	5
		−6	163	−152
		7	44	−42
		−7	43	43
		8	86	−77
		−8	57	51
		9	30	−15
		−9	56	−53
		10	−15	13
		−10	62	47
		11	37	31
		−11	20	−18
		12	42	49
		−12	38	−49
0	4	0	−15	23
		1	124	128
		−1	76	−74
		2	−20	2
		−2	49	44
		3	131	119
		−3	57	−51
		4	70	51
		−4	65	−72
		5	164	−158
		−5	100	99
		6	−20	7
0	4	−6	47	−51
		7	113	−102
		−7	31	19
		8	32	−26
		−8	22	18
		9	109	102
		−9	88	−89
		10	−15	−9
		−10	−15	−4
		11	−10	15
		−11	−10	12
0	5	0	76	81
		1	180	−174
		−1	102	93
		2	64	−47
		−2	26	−19
		3	−20	−8
		−3	160	150
		4	−20	−20
		−4	102	−108
		5	143	127
		−5	109	−100
		6	94	77
		−6	−20	−8
		7	42	−39
		−7	90	−81
		8	−15	11
		−8	42	47
		9	67	−61
		−9	62	75
		10	29	−31
		−10	−15	0
0	6	0	−20	−17
		1	56	−54
		−1	44	−35
		2	67	61
		−2	112	−113
		3	−20	31
		−3	71	68
		4	−20	−32
		−4	42	38
		5	24	27
		−5	31	32
		6	42	−33
		−6	77	77
		7	31	−30
		−7	36	−37
		8	38	54
		−8	38	−44
0	7	0	61	−56
		1	32	25
		−1	83	83
0	7	2	33	−22
		−2	34	24
		3	86	−83
		−3	−15	−14
		4	44	34
		−4	40	41
		5	−10	2
		−5	46	−53
1	0	0	20	−16
		1	24	21
		−1	139	−148
		2	115	127
		−2	77	71
		3	227	245
		−3	122	125
		4	24	−27
		−4	32	−30
		5	81	70
		−5	107	−92
		6	72	−68
		−6	84	−76
		7	89	−85
		−7	182	−191
		8	−20	1
		−8	67	70
		9	36	−43
		−9	71	60
		10	26	−32
		−10	23	25
		11	41	45
		−11	79	82
		12	21	15
		−12	−15	−24
		13	−10	2
		−13	23	−25
2	0	0	83	−75
		1	31	−31
		−1	84	−86
		2	60	−55
		−2	57	−51
		3	223	264*
		−3	93	91
		4	92	94
		−4	94	−81
		5	20	14
		−5	−20	15
		6	44	38
		−6	−20	−12
		7	165	−169
		−7	143	−118
		8	−20	−32
2	0	−8	60	49
		9	24	33
		−9	−20	−24
		10	18	15
		−10	40	42
		11	52	51
		−11	92	93
		12	−10	15
		−12	−10	10
		−13	−10	−13
3	0	0	208	209
		1	120	121
		−1	129	−132
		2	34	34
		−2	150	−159
		3	32	32
		−3	108	−106
		4	127	−129
		−4	195	−197
		5	115	−109
		−5	83	77
		6	82	78
		−6	121	106
		7	−20	−4
		−7	101	98
		8	88	90
		−8	91	61
		9	52	47
		−9	−20	−24
		10	53	−53
		−10	62	−64
		11	−10	11
		−11	45	−43
		−12	−10	8
		−13	−10	−5
4	0	0	90	94
		1	113	−106
		−1	−15	23
		2	34	−28
		−2	57	51
		3	58	−51
		−3	−15	0
		4	57	−52
		−4	96	−102
		5	79	69
		−5	29	−35
		6	−20	14
		−6	26	16
		7	25	18
		−7	25	27
		8	20	25
4	0	−8	97	99
		9	20	−17
		−9	60	57
		10	24	−25
		−10	48	−39
		−11	20	17
		−12	57	−66
		−13	31	−42
5	0	0	44	35
		1	113	−102
		−1	126	−120
		2	−20	0
		−2	48	−40
		3	139	132
		−3	162	161
		4	57	−54
		−4	18	13
		5	54	45
		−5	61	52
		6	−15	−9
		−6	63	62
		7	85	−90
		−7	137	−148
		8	−15	0
		−8	25	21
		9	−15	−5
		−9	−20	2
		−10	−15	−17
		−11	57	76
		−12	45	−32
6	0	0	19	22
		1	−20	2
		−1	−20	−15
		2	36	27
		−2	48	−47
		3	48	45
		−3	56	49
		4	18	−28
		−4	33	−36
		5	27	−23
		−5	63	70
		6	23	−23
		−6	63	70
		−7	41	−35
		−8	16	17
		−9	−10	−14
		−10	52	−65
		−11	−10	5
7	0	0	102	104
		1	−15	26
		−1	−15	1
7	0	2	20	−19
		−2	−20	3
		3	19	−11
		−3	37	−30
		4	56	−53
		−4	102	−98
		−5	24	25
		−6	−15	4
		−7	17	18
		−8	52	56
		−9	26	−18
1	1	0	136	−162
−1			137	130
2			209	221
−2			−20	26
3			69	−60
−3			128	122
4			93	83
−4			66	−59
5			135	135
−5			−20	−8
6			−15	27
−6			43	−37
7			−15	−3
−7			−10	−8
1	2	0	125	−105
−1			280	−295
2			263	−278
−2			210	−201
3			−20	−11
−3			30	26
4			61	60
−4			−20	−11
5			161	−154
−5			105	−96
6			121	−118
−6			−10	−2
7			42	38
8			−10	−15
1	3	0	−10	13
−1			23	−23
2			96	−83
−2			68	−68
3			215	−209
−3			138	−131
4			139	−139
−4			−20	17
5			45	−48
−5			−15	13
6			−15	−20
7			90	−86
8	3	0	41	−35
1	4	0	270	273
−1			77	−62
2			120	−106
−2			154	153
3			−20	17
−3			49	56
4			66	65
−4			−15	−17
5			50	52
−5			−20	−15
6			−20	−10
7			−15	−7
8			44	45
1	5	0	−15	12
−1			41	42
2			123	132
−2			91	84
3			163	161
−3			−15	−3
4			48	−36
−4			26	39
5			144	136
6			71	67
7			−15	24
8			40	32
1	6	0	54	50
−1			61	−57
2			28	23
−2			26	23
3			121	−109
−3			−15	15
4			58	61
5			100	99
6			53	−54
7			−15	−3
8			43	38
1	7	0	66	−64
−1			−15	−5
2			−20	−16
3			−20	−17
4			81	−73
5			77	−79
6			−10	−10
7			35	−27
1	8	0	23	23
2			−20	−5
3			66	−61
4			−20	−24
5			−15	−21
6			33	−25

Table 2. *Final structure parameters*

Atom	Potassium mesotartrate				Rubidium mesotratrate			
	x	*y*	*z*	*B*	*x*	*y*	*z*	*B*
(K/Rb) (1)	0·9983	0·2063	0·3604	2·35	0·9979	0·2069	0·3604	2·85
(K/Rb) (2)	0·2945	0·4498	0·1379	2·15	0·2941	0·4608	0·1375	2·85
Standard deviation	0·0004	0·0004	0·0003		0·0003	0·0003	0·0002	
O(1) (carb.)	0·8852	0·7420	0·0706	2·1	0·8434	0·7560	0·0683	2·8
O(2) (carb.)	0·6928	1·0775	0·1534	3·4	0·7126	1·0753	0·1653	3·3
O(3) (hydr.)	0·5727	0·6216	0·1381	3·3	0·5794	0·6438	0·1384	3·9
O(4) (hydr.)	0·8534	0·6560	0·3667	2·0	0·8346	0·6697	0·3550	3·1
O(5) (carb.)	0·3836	1·2004	0·3529	2·2	0·3867	1·2123	0·3534	3·1
O(6) (carb.)	0·7401	1·0669	0·4439	2·3	0·7289	1·0727	0·4447	2·8
O(7) (water)	0·9545	0·2306	0·1063	2·9	0·9533	0·2423	0·1038	3·6
O(8) (water)	0·2358	0·6482	0·3777	3·0	0·2360	0·6548	0·3852	3·5
C(1)	0·7092	0·8817	0·1309	2·6	0·7270	0·8911	0·1358	3·2
C(2)	0·5669	0·8214	0·1845	2·1	0·5754	0·8370	0·1848	2·4
C(3)	0·6204	0·8240	0·3232	2·9	0·6245	0·8333	0·3169	3·1
C(4)	0·5800	1·0463	0·3775	2·6	0·5795	1·0556	0·3735	2·5
Standard deviation	0·0020	0·0020	0·0015		0·0030	0·0030	0·0020	
H(1)[C(2)]	0·41	0·92	0·16	3·0				
H(2)[C(3)]	0·51	0·79	0·35	3·0				
H(3)[O(3)]	0·74	0·50	0·12	3·0				
H(4)[O(4)]	0·96	0·65	0·37	3·0				
H(5)[O(7)]	0·04	0·21	0·05	3·0				
H(6)[O(7)]	0·83	0·16	0·12	3·0				
H(7)[O(8)]	0·31	0·48	0·38	3·0				
H(8)[O(8)]	0·28	0·77	0·44	3·0				

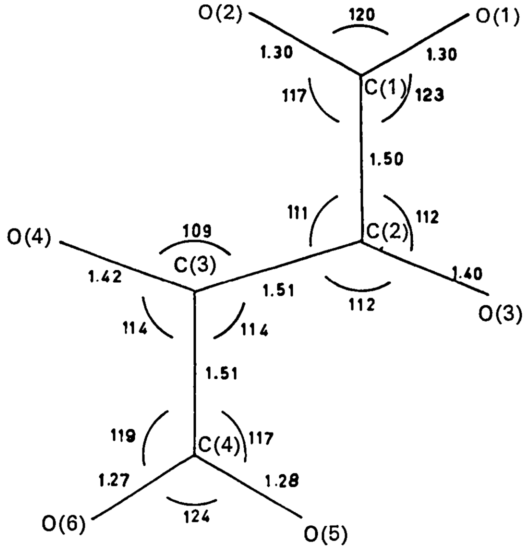

Fig. 2. Bond distances and bond angles in the mesotartrate ion.

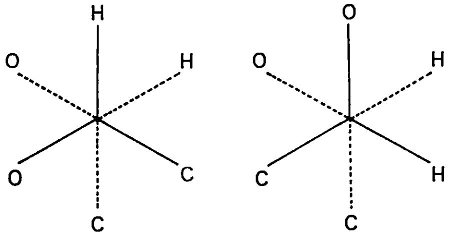

Fig. 3. Newman projections of the mesotartrate ion along the central C–C bond.

Discussion

The mesotartrate ion

The molecular dimensions, as determined in potassium mesotartrate, are shown in Fig. 2. The standard deviations of these quantities deduced from the calculated e.s.d. (Cruickshank, 1960) of the positional parameters amount for the bond lengths to 0·02 Å and for the bond angles to 1·5°. From this we can conclude that the bond lengths and the bond angles do not differ significantly from the usual values.

The groups C(1)C(2)O(1)O(2) and C(3)C(4)O(5)O(6) are planar within the experimental error and just as in all other α-hydroxycarboxylic acids (Jeffrey, 1952) the α-hydroxyl oxygen atom lies nearly in the same plane (see Table 3, first and second columns). This general, hitherto not clearly understood, feature in various structures may be an indication that this phenomenon is not restricted to the crystalline state. An investigation on a larger scale concerning this planarity by studying a variety of suitable crystalline compounds is in progress in our laboratory.

Table 3. *Deviations of atoms from median planes*

Median planes through:

C(1)C(2)O(1)O(2)		C(3)C(4)O(5)O(6)		C(2)C(3)C(4)O(3)	
C(1)	0·02 Å	C(3)	0·00 Å	C(2)	0·06 Å
C(2)	0·00	C(4)	0·00	C(3)	0·05
O(1)	0·02	O(5)	0·00	C(4)	0·05
O(2)	0·00	O(6)	0·00	O(3)	0·06
O(3)	0·22	O(4)	0·17		

The conformation of the mesotartaric acid molecule, here determined for the first time, is an asymmetric one. The asymmetry is probably caused by the rigidity of the end groups, for a symmetric form with planar halves would be unlikely because of too short intramolecular contacts. The molecule assumes an ethane conformation (see the Newman projections in Fig. 3), which means that the external bonds of the central pair of carbon atoms are directed to the vertices of a trigonal antiprism. A perspective drawing of the molecule is shown in Fig. 4. Contrary to the situation in the molecules of tartaric acid, in which all four atoms lie in one plane, here three of the carbon atoms [C(2), C(3) and C(4)] are coplanar with one of the hydroxyl groups [O(3)] (compare Table 3, column 3).

The mesotartrate crystal is in fact a racemate, so that the optical inactivity is not due to internal molecular compensation, but merely a result of crystal symmetry. The persistence of the two enantiomorphous conformations of mesotartaric acid, found in all modifications of the free acid (Bootsma & Schoone, 1964), is an indication that in solution too this molecule occurs in these conformations only. Therefore two possibilities arise depending on the racemization velocity which is determined by the height of the rotational barrier. First, if the barrier appears to be high, one may succeed in separating the ‘antipodes’ of mesotartaric acid, as in the case of configurational isomers. On the other hand, if the barrier is low, this would not be possible, but by suitable chemical means, that is crystallizing mesotartaric acid with for instance an optically active base, one could convert the ‘racemic mixture’ into one ‘antipode’.

Description of the structure

Water molecules link successive mesotartrate ions into infinite chains in the [$-\mathbf{a}+\mathbf{b}+\mathbf{c}$] direction (Fig. 5). The polymers thus formed are grouped in wavy layers, on either side of which there are similar cation layers. In each anion layer both conformational isomers are present, as in the case of some racemic tartrates.

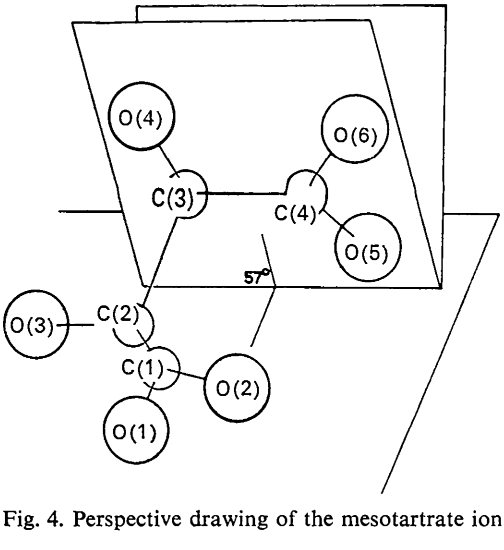

Fig. 4. Perspective drawing of the mesotartrate ion.

Table 4. *Hydrogen bonds*

Atoms involved		Potassium mesotartrate	Rubidium mesotartrate
Donor	Acceptor	Distances	
O(3)	O(7) (x, y, z)	2·85 Å	2·86 Å
O(7)	O(1) ($2-x, 1-y, -z$)	2·69	2·68
O(7)	O(2) ($x, y-1, z$)	2·68	2·70
O(4)	O(8) ($x, y+1, z$)	2·77	2·76
O(8)	O(5) ($x, y-1, z$)	2·76	2·74
O(6)	O(6) ($1-x, 2-y, 1-z$)	2·66	2·63

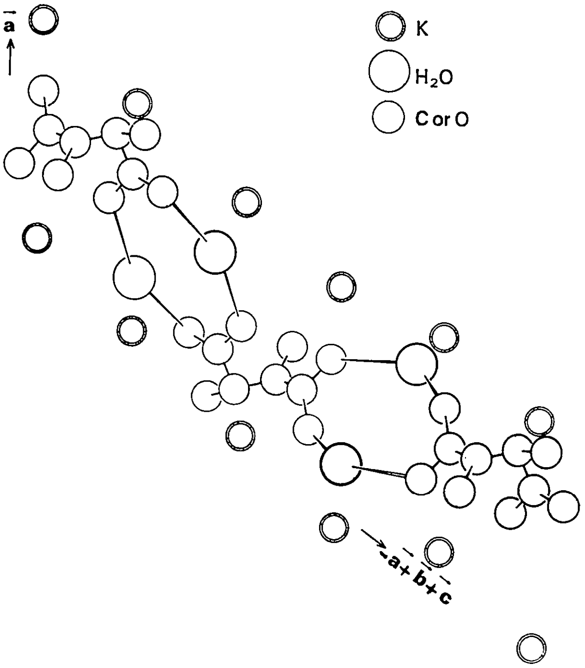

Fig. 5. A mesotartrate chain viewed along the b axis.

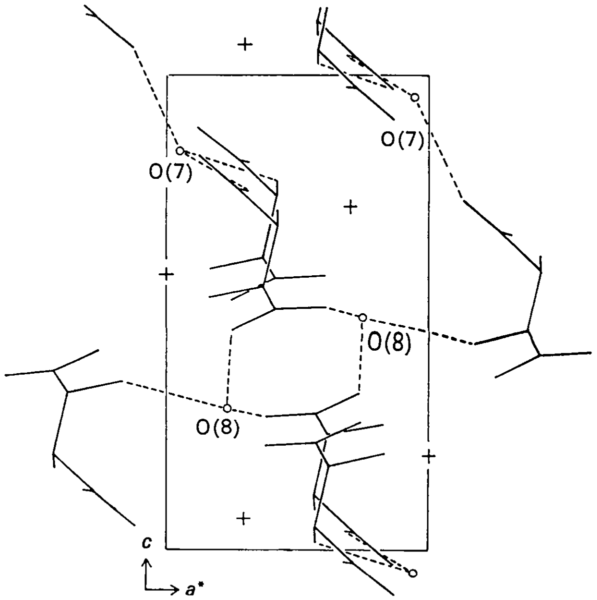

Fig. 6. Projection of the structure along the normal to **c** in the bc plane. Potassium ions are represented by crosses, water molecules by circlets and hydrogen bonds by broken lines.

Table 5. *The oxygen-surroundings of the potassium ions*

Distances to K(1)		Distances to K(2)	
Atom	Distance	Atom	Distance
O(2) $(x, y-1, z)$	3·14 Å	O(1) $(x-1, y, z)$	2·76 Å
O(4) (x, y, z)	2·75	O(1) $(1-x, y, z)$	2·79
O(5) $(x+1, y-1, z)$	2·72	O(2) $(x, y-1, z)$	2·76
O(6) $(x-1, y, z)$	2·76	O(3) (x, y, z)	2·72
O(6) $(1-x, y, z)$	2·73	O(5) $(x-1, y, z)$	2·87
O(7) (x, y, z)	2·80	O(8) (x, y, z)	2·90

Fig. 6 shows a projection of potassium mesotartrate along a non-crystallographic axis so as to make it possible to see the hydrogen-bonded ions separately. Both water molecules have three hydrogen bonds in a distorted non-planar trigonal arrangement. All hydrogen bonds are within the anion layers except for one: O(8)–O(5). The latter bond connects ions of different sheets giving the structure, to some extent, the aspect of a three-dimensional network. The hydrogen bond distances are given in Table 4. It is noteworthy that of the corresponding distances in the two isomorphous structures only the hydrogen bonds have the same lengths, whereas there are notable differences in all other intermolecular contacts.

The arrangement of the oxygen atoms around the cations is a very irregular one. Table 5 contains the distances of the potassium ions to the oxygen atoms that can be considered as the nearest neighbours.

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The Crystal Structure of Barium Tetraborate, $BaO.2B_2O_3$

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$BaO.2B_2O_3$ crystallizes in the monoclinic system, $P2_1/c$. The lattice constants are $a = 10·56$, $b = 8·20$, $c = 13·01$ Å, $\beta = 104° 57'$, and $Z = 8$.

The structure was established by Patterson projections and three-dimensional electron density syntheses utilizing the heavy atoms initially to establish some phases. The structure was refined by three-dimensional least-squares to a final $R = 10·4\%$ (observed data only).

The borate network can be described as a three-dimensional linkage of alternating six-membered single rings containing two tetrahedral boron atoms and one triangular boron atom, and double rings containing two tetrahedral boron atoms, one of them being common to both rings, and three triangular boron atoms. Each single ring is directly linked only to double rings and each double ring directly links only to single rings. The barium atoms fit into channels of this network.

Introduction

The anhydrous borates with more than 50 mole % B_2O_3 are in an important glass forming region and there is much interest in the structure of the borate groups. There have been several radial distribution (Block & Piermarini, 1964; Krogh-Moe, 1962*a*) studies of various glass compositions but the only single-crystal structure studies have been of several alkali borate compounds of lithium, cesium and potassium by