Hydrogen Bonding in Potassium Hydrogen meso-Tartrate. A Low-Temperature X-ray Study

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A crystal-structure analysis of potassium hydrogen *meso*-tartrate was carried out at -160° C. The crystals are triclinic (*P* $\overline{1}$) with Z = 4. Cell dimensions are $a=9\cdot33\pm0\cdot01$, $b=10\cdot29\pm0\cdot01$, $c=9\cdot09\pm0\cdot01$ Å, $\alpha=80\cdot71\pm0\cdot05$, $\beta=108\cdot77\pm0\cdot05$ and $\gamma=130\cdot95\pm0\cdot05^{\circ}$. The crystal is in fact a racemate, since the *meso*-tartaric molecules themselves are disymmetric. The conformation of one of the carboxyl groups is quite unusual, as the OH bond is in the *anti* position with respect to the C=O bond. The hydrogen bond scheme is of a mixed A/B type with three short hydrogen bonds. One of the hydrogen atoms is found in an acentric position in an A-type bond, that is as a rule supposed to be symmetrical.

Introduction

In crystal structures of potassium meso-tartrate (Kroon, Peerdeman & Bijvoet, 1965), in several modifications of meso-tartaric acid (Bootsma & Schoone, 1967) and in the dimethyl ester of meso-tartaric acid (Kanters & Kroon, 1972) the same conformation of the meso-tartaric acid molecule is always found, viz. a skew ethane conformation around the central C-C bond. As one might expect the same disymmetric conformation in the acid salts of meso-tartaric acid, there is the problem how the non-equivalence of the cai boxyl groups in mesotartaric molecules will manifest itself in these salts. For that reason the structure determination of potassium hydrogen meso-tartrate was undertaken. Because of the importance of the hydrogen position the analysis was carried out at liquid-nitrogen temperature.

Experimental

Crystals of potassium hydrogen *meso*-tartrate were obtained from an aqueous solution at room temperature. The cell dimensions were determined on a Nonius diffractometer with Mo K α radiation ($\lambda = 0.7107$ Å) and found to be: $a = 9.33 \pm 0.01$, $b = 10.29 \pm 0.01$, $c = 9.09 \pm$ 0.01 Å, $\alpha = 80.71 \pm 0.05$, $\beta = 108.77 \pm 0.05$, $\gamma = 130.95 \pm$ 0.05° . The measurements were carried out at -160° C; the working temperature was maintained by immersion of the crystal in a stream of cold gaseous nitrogen surrounded by an envelope of dry nitrogen at room temperature. The *a* axis was chosen parallel to the direction of elongation of the crystal. The Delaunay-reduced cell can be obtained by the transformation matrix

	/1	1	0\
S =	0	ī	0
	0/	0	1/

and has cell dimensions a' = 8.19, b' = 10.29, c' = 9.09Å, $\alpha' = 99.29$, $\beta' = 99.42$ and $\gamma' = 120.65^{\circ}$. With four molecules in the unit cell the calculated density (2.01 g.cm⁻³) agrees well with the density determined by flotation (1.99 g.cm⁻³). The space group was assumed to be $P\overline{1}$ and this choice was justified by the results of the structure determination.

The 5308 independent integrated intensities up to $\theta = 34^{\circ}$ were taken on a 3-circle Nonius automatic diffractometer with the θ -2 θ scan technique, using zirconium-filtered Mo K α radiation. Corrections were made for Lorentz and polarization factors. An absorption correction was applied, taking into account the irreg ular shape of the crystal ($\mu = 8.3 \text{ cm}^{-1}$; minimum and maximum dimensions were 0.2 and 0.5 mm respectively).

 Table 1. Final fractional positional parameters and their estimated standard deviations in parentheses

	Х	r	z
K(1)	0.22316(4)	0.43397(3)	0.12891(3)
$\mathbf{K}(2)$	0.25520(4)	0.82925(3)	0.27170(3)
(-)	0 20020 (1)	0 02/23 (3)	021110(3)
O(3)	-0.0747(1)	-0.0928(1)	0.7540(1)
O(4)	0.0122(1)	0.1267(1)	0.8874(1)
O(5)	0.0464(1)	0.2216(1)	0·5578 (1)
O(6)	0.3225(1)	0.4131(1)	0.4904 (1)
O(7)	0.3944(1)	0·3293 (1)	0.8942 (1)
O(8)	0.4788(1)	0·2618 (1)	0·6648 (1)
C(15)	0.0532(2)	0·0647 (1)́	0.8227(1)
C(16)	0.2644(2)	0·1615 (1)	0·8197 (1)
C(17)	0.2809(2)	0.1802(1)	0.6538(1)
C(18)	0.2118(2)	0.2780(1)	0.5621(1)
H(3)	-0.195(4)	$-0.147(\dot{4})$	0.765 (3)
H(6)	½ (O)	+ (0)	$\frac{1}{2}(0)$
H(7)	0.414 (3)	0.323(3)	0.982(2)
H(8)	0.476 (3)	0.241(3)	0.582(2)
H(16)	0.300 (3)	0.094(3)	0.871(2)
H(17)	0.193 (3)	0.069 (3)	0.606 (2)
O(9)	0.4149 (1)	0.2724 (1)	0.2057 (1)
O(10)	0.5199 (1)	0.1805(1)	0.4194(1)
O(11)	0.8326 (1)	0.2704(1)	0.0320(1)
O(12)	0.5653 (1)	0.0873 (1)	0.1181(1)
O(13)	0.7779 (1)	0.5094 (1)	0.1654 (1)
O(14)	1.0565 (1)	0.4664 (1)	0.3077 (1)
C(19)	0.5476 (2)	0.2745 (1)	0.3067(1)
C(20)	0.7596 (2)	0.4083 (1)	0.2948(1)
C(21)	0.8500 (2)	0.3299 (1)	0.2870(1)
C(22)	0.7476 (2)	0.2256 (1)	0.1316(1)
H(12)	$\frac{1}{2}(0)$	0 (0)	0 (0)
H(13)	0.741 (3)	0.561(3)	0.173(2)
H(14)	1.116 (3)	0.440 (3)	0.365 (2)
H(20)	0.836 (3)	0.478 (3)	0.388 (2)
H(21)	0.832 (3)	0.256 (3)	0.366 (2)

 Table 2. Final anisotropic thermal parameters of the non-hydrogen atoms and the isotropic thermal parameters and peak heights of the hydrogen atoms

The anisotropic temperature factor for an atom is of the form: exp $[-(10^{-5} \sum_i \sum_j h_i h_j \beta_{ij})]$.

	β_{11}	β_{22}	β33	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$		β_{11}	β_{22}	β33	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
K(1)	418	505	344	441	55	368	K(2)	783	479	347	866	25	143
O(3)	416	304	441	288	- 14	381	O(9)	410	465	328	530	124	241
O(4)	570	431	415	680	104	425	O(10)	694	460	291	741	243	496
O(5)	550	506	419	711	160	189	O(11)	540	652	383	446	-304	374
O(6)	635	392	403	578	349	393	O(12)	453	361	392	250	-242	283
O(7)	432	326	224	346	-20	145	O(13)	623	384	325	722	240	447
O(8)	469	508	312	628	94	354	O(14)	325	429	333	465	- 105	-11
C(15)	444	303	288	427	148	272	C(19)	456	320	242	450	-9	255
C(16)	401	284	234	382	96	225	C(20)	42 7	305	225	428	13	183
C(17)	417	350	246	453	89	241	C(21)	396	317	238	436	- 32	98
C(18)	539	323	221	468	31	145	C(22)	432	332	283	499	-81	148



	$B(Å^2)$	<i>ϱ</i> (e.Å⁻3)
H(3)	2	0.42
H(6)	5	0.31*
H(7)	0	0.28
H(8)	0	0.52
H(16)	0	0.65
H(17)	0	0.69
H(12)	3	0.45
H(13)	0	0.46*
H(14)	0	0.46
H(20)	0	0.71
H(21)	0	0.69

* Value at special position.

Structure determination

On successful location of the potassium ions from a three-dimensional Patterson analysis followed by repeated cycles of structure-factor calculations and Fourier syntheses the positions of all the non-hydrogen atoms were found. The hydrogen atoms showed up in a difference Fourier synthesis (terms up to $\sin \theta / \lambda = 0.4$ $Å^{-1}$; their peak heights are given in Table 1. Scaling factor, positional parameters, the anisotropic temperature factors of the non-hydrogen atoms and the isotropic temperature factors of the hydrogen atoms were submitted to a least-squares block-diagonal refinement. All structure factors were given unit weight. All the temperature factors of the hydrogen atoms except for those belonging to the carboxyl groups became slightly negative. For this reason they were put equal to zero and kept constant during the further refinement. No extinction correction was applied, but five strong reflexions suspected of being weakened by this effect were given zero weight. Scattering factors were in the form of the analytical expression given by Moore (1963).

Tables 1 and 2 show the final structural parameters. Table 3 compares the structure factors observed and calculated.

The final *R* value is 0.035. A difference Fourier synthesis with terms up to $\sin\theta/\lambda = 0.4$ Å⁻¹ and all atoms subtracted showed no peaks greater than 0.2 e.Å⁻³. In the difference Fourier synthesis with all 5303 structure

factors a systematic effect cropped up. Near the centres of the covalent bonds there was an appreciable residual electron density. The minimum and maximum values for carbon–oxygen bonds amounted to 0.2 e.Å^{-3} and 0.4 e.Å^{-3} respectively. For carbon–carbon bonds these values were 0.4 e.Å^{-3} and 0.6 e.Å^{-3} . Evidently, these effects are due to the use of inadequate spherical scattering factors.



Fig. 1. Numbering scheme for the two independent *meso*-tar-trate molecules.

Table 3. Observed and calculated structure factors

The reflexions suspected of extinction and omitted from the refinement are marked with an asterisk.

The colums of each group are $h_{k,l}$, $|10F_{o}|$, $10F_{c}$.

17 -8	110 -118 38 -30 23 -10 5 1 ² 1 -168 14 -10	10 -> -	4 46 -47 13 17 19 12 113 -108 11 180 -176 10 51 40	• -3	27 -28 135 -122 136 129 48 84 91 90	3 -2 -	44 44 454 444 416 -419 306 295 254 251	1 ⁰ -2 -9 -9 -9 -9	30 36 138 -144 44 -45 141 -146 97 -05	• -1 • ;	171 -175 175 184 101 102 114 113 27 -17	3 9 -17		10	0 4 20 0 -12 34 -11 0 -10 05	24 32 4 97 343
17 -4 -1 -1 -1	1 1 1 1 2 4 3 48 -51 2 82 -00 1 120 -117 4 129 -121 5 94 6		97 98 131 135 7 67 67 6 11 -1 7 57 0	10	211 -214 26 -25 39 39 58 61 21 -27		109 100 271 -271 33 20 71 77	-4 -3 -2 -1	21 22 250 253 107 107 217 -222 73 -72	11 7 -1 -17 -14 -13 -12	17 -35 80 84 18 -11 77 -76 117 -118	-1	0 10 17 9 120 -131 9 40 -32 7 95 99 • 411 401		-8 19 -7 89 -5 49 -4 109 -3 37	23 -87 -41 -109 37
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10 -7 -	74 -77 178 -138 152 -149 15 -13		1 11 -41 2 15 58 3 73 -73 4 17 -48 5 15 48		128 -129 307 300 289 281 19 -27 287 -203	• •2 •1 -1 -1 -1	92 -49 104 -105 26 -25 24 -21 10 -9	*: -2 -12 +11 +10 2	49 -47 117 110 11 8 33 -26 90 69	-1	423 -430 155 -159 35 -27 73 -05		0 204 -202 1 58 68 2 181 175 3 54 51 4 232 227	**	3 129 4 57 0 -10 13 -9 12 -8 40	-124 -94 -11 -2 34
-	1 40 51 0 96 101 1 54 -40 1 15 -118	11 -5 -	181 180 44 -39 3 79 -25 48 -01 3 127 124	-	81 81 282 -208 48 36 170 179 110 121		102 -103 211 203 70 73 70 -80 257 -251	·7 -7 -10 	49 45 173 -152 45 38 44 42 71 50	1	24/ 271 77 /0 16V -1/0 103 -100 8V -75		9 44 -33 8 293 -294 7 328 -341 8 103 102 9 77 78		-7 34 -4 20 -9 24 -4 53 -3 142	-37 -31 -29 57
	21 -18 227 119 60 -62 7 25 29	12 -3 -	3 52 51 2 42 -32 1 127 145 0 112 110		195 -189 44 -81 50 47 17 - 302 -308		31 38 300 -302 404 -402 211 217 1140 1194	-4 -5 -4 -3 -7	100 162 20 23 113 -112 114 -113		A5 -V3 2 -7 204 200 105 102 76 -74	1 1 1 1	0 34 41 1 125 124 2 117 117 3 17 -17 5 94 95		-2 70 -1 71 0 111 1 44 2 60	-40 -104 37 -84
'1 -7 -1 -1 -1	37 -30 3 27 27 2 62 5 21 5	5 -4	3 52 51 4 27 31 5 16 -13 5 245 250	1	50 -61 140 149 52 52 24 11		251 258 108 100 210 -208 3 191 -190 4 330 -129	-1 0 1 2	110 -:04 8 1 21 -10 111 -06	10 * -1 -14 -13 -12 -12	87 -83 122 -119 23 -25 84 82 172 1/2	-1 -1 -1 -1 -1	4 110 117 3 20 -30 7 48 -44 1 18 23 0 92 -91	17	0 -7 10 -6 10 -5 65 -4 80 -3 24	27
27 -7 -1 -1 -1	70 -40 2 114 118 3 3 34		e 70 -78 7 78 81 8 11 7 9 254 -251 0 63 -88	* -3 -1 -1 -1 -1	104 105 36 35 140 -141 32 -35		5 65 7p 167 158 7 116 114 108 111	1	87 84 371 -305 117 -128 447 356	-10	101 100 00 08 10V -108 274 -225 177 -130		• 52 -47 8 125 127 7 367 368 6 95 -58 5 14 -19	-1	-2 133 1 4 229 10 41	-130 10 730 30
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	2 -1 -46 45 -51 7 200 199 42 -44 148 -155	-	4 394 342 3 9 -9 2 349 -343 1 172 168 1 144 -140	-	307 -298 316 318 403 340	-	74 -71 40 -30 25 -10 47 -44		208 -207 430 -431 331 -325 446 434 109 -108		8 -8 210 -218 86 -97 37 38 78 -80		$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-3 420 -2 453 -1 200 0 90	-411 474 -196 100
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	4 33 37 5 211 211 70 73 8 112 -112	-	10 196 -200 9 67 /5 17 -13 17 -13 12 -312	-	211 -209 233 -232 173 173		200 200 99 -57 10 -6 10 -7	1 -1 -11 -10 -11 -11	19 38 19 -66 114 -112 18 -99	-	76 -75 272 -276 56 61 175 177		7 85 -84 5 128 126 3 343 -541 2 92 93	•	1 -14 31 -13 129 -12 108 -11 298 -10 92	-31 -132 -108 306
10 -0 -1 -1 -1	4 44 -51 3 84 87 2 94 94 1 97 -95		-5 472 465 -4 130 -121 -3 232 -234 -2 72 70		71 72 14 14 328 324 140 123	• -2 -1	11 -6 17# 170 48 -67 40 62	-10	143 144 1•7 112 63 84 73 -60		82 -83 60 -81 9 -1 104 -103	•	1 436 431 0 174 173 1 232 233 2 19 24 3 18 16		-9 19 -8 69 -7 54 -4 158 -5 209	-13 74 -54 -145
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• -3 -15 -14 -13 -12	73 78 51 56 36 41 66 65		300 200 110 114 102 -97 73 70	4 5 7	101 -104 167 -149 33 35 48 53	-13 -12 -11 -10	127 -123 195 -192 59 52 233 232	8 9 10 11	136 -137 103 101 90 88 60 55	-12	56 54 69 -68 226 233 264 266		100 100 70 83 120 122 10 -10		6 32 6 87 18 190 11 12	27 27 87 195
-10	141 -145 80 -7 105 101 84 87		101 -106 97 -55 136 137 26 29		22 -14 50 -53 146 -143 43 -40		9 -16 51 -34 28 30 187 -193	-14 -13 -12 -11 -10	72 74 49 49 234 -240 124 -126 159 159		491 -442 316 -301 60 -94 102 156 284 301	• • • • • • • •		3	13 71 1 -15 49 -14 46 -13 26	-134 -73 -47 -63 22
-9	16 19 237 238 139 -138 157 -138	11 -4 -1	12 12 108 -108	-10	133 12+ 85 82 199 -144 98 -97	-2	220 237 164 170 161 146 62 63	-8	172 124 247 -755 290 289 15 -4 239 -741	-2	325 323 105 -102 324 -335 375 -378	+10 -10 -10	107 106 170 184 28 17		-11 129 -10 24 -1 224	-134 25 210 -735
	70 71 44 -44 32 40 294 304	12 -4 -1 -1 -1	44	2 -2 10 10	37 -12 36 -12 30 -29 44 -44	-	234 -238 94 -94 48 51 112 108	-4 -3 -2 -1	304 -374 130 -124 145 133 12 12 224 232	; ; ;	97 99 272 -268 306 301 83 /5 25 -11		+ -79 + -79		-0 215 -5 69 -4 410 -3 139	-18 277 -48 -462 -138
,	202 -206 125 -129 34 31 68 62		40 13 104 -100 21 20 179 1/1	11 12 13 14 3 -2 -3	102 1 53 34 -33 126 -126 158 126	10 -2 -13 -12 -11	43 62 44 -61 69 -62 93 97	12334	184 184 1 4 141 -143 106 -106 22 17	11 12	115 -114 156 163 49 -55 114 111	1	124 12 44 49 104 -110 124 -127		-1 192 -1 192 -1 1 192 -1 192	141 -143 -126 462 72
•	-1 -1	1	** ••1	•2	12 -124	-10						,				- 49

	Table 3 (cont.)	•4 •¥ 27 34 7 4 −P 20 19 −30 −30	-6 194 -197 -6 1 327 -338 -9 241 -226 - 6 4374 -179 -4 131 100 - 7 47 -39
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J. KROON AND J. A. KANTERS

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HYDROGEN BONDING IN POTASSIUM HYDROGEN meso-TARTRATE

Table 3 (cont.)

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Discussion of the structure

Intramolecular bond lengths and angles are given in Table 4 (for the numbering of the atoms in the two independent molecules see Fig. 1). Table 5 is concerned

 Table 4. Bond lengths (Å) and angles (°) in the mesotartaric acid molecules and their estimated standard deviations in parentheses

The	hydrogen	atoms	H(6)	and	H(12)	are	supposed	to	be
		locate	ed at s	specia	1 positi	ons.			

C(15)–O(3)	1.324(1)	C(19–O(10)	1.255(1)
C(15) - O(4)	1.219 (2)	C(19) - O(9)	1·271 (1)
C(18) - O(5)	1.231(2)	C(22) - O(12)	1.297 (1)
C(18)–O(6)	1.297 (1)	C(22) - O(11)	1.229 (1)
C(16)–O(7)	1.419 (1)	C(20)–O(13)	1.413 (1)
C(17) - O(8)	1.414 (2)	C(21) - O(14)	1.423(2)
C(15) - C(16)	1.526 (2)	C(19) - C(20)	1.530 (2)
C(16) - C(17)	1.534 (2)	C(20) - C(21)	1.522 (2)
C(17) - C(18)	1.535 (2)	C(21) - C(22)	1.529 (2)
O(3)H(3)	0.90 (4)		
O(6)H(6)	1.241(1)	O(12)-H(12)	1.226(1)
O(7)—H(7)	0.76 (3)	O(13) - H(13)	0.82(3)
O(8)—H(8)	0.80 (3)	O(14) - H(14)	0.79 (3)
C(16) - H(16)	0.95 (3)	C(20)-H(20)	0.94(3)
C(17)–H(17)	0.93 (3)	C(21) - H(21)	0.92 (3)

with the conformations around the carbon-carbon bonds of the molecules. The molecules occur as enantiomorphic pairs. The carboxyl group C(18)O(5)O(6)-H(6) has a conformation which to our knowledge has never been seen before in crystals. The O-H bond is in an *anti* direction with respect to the C=O bond. The same carboxyl group also deviates from the general findings that the α -hydroxyl group is in a *syn* position





O(3) - C(15) - O(4)	124·8 (1)°	O(10) - C(19) - O(9)	125·1 (1)°
O(5) - C(18) - O(6)	121.5 (1)	O(12) - C(22) - O(11)	124.6 (1)
O(3) - C(15) - C(16)	112.8 (1)	O(10) - C(19) - C(20)	117.4 (1)
O(4) - C(15) - C(16)	122.3(1)	O(9) - C(19) - C(20)	117.5 (1)
O(5) - C(18) - C(17)	117.3 (1)	O(12) - C(22) - C(21)	113·0 (1)
O(6) - C(18) - C(17)	$121 \cdot 2(1)$	O(11) - C(22) - C(21)	122·4 (1)
C(15)-C(16)-O(7)	110-3 (1)	C(19) - C(20) - O(13)	113·7 (1)
D(7) - C(16) - C(17)	108.0 (1)	O(13) - C(20) - C(21)	107.1 (1)
C(18) - C(17) - O(8)	113.7 (1)	C(22) - C(21) - O(14)	111.5 (1)
O(8) - C(17) - C(16)	107.9 (1)	O(14) - C(21) - C(20)	108.1 (1)
C(15) - C(16) - C(17)	112.6 (1)	C(19)-C(20)-C(21)	113.4 (1)
C(16) - C(17) - C(18)	109.6 (1)	C(20)-C(21)-C(22)	110.3 (1)
C(15) - O(3) - H(3)	109 (2)	C(22) - O(12) - H(12)	109.4 (1)
C(18)–O(6)–H(6)	129.6 (1)	C(20)-O(13)-H(13)	108 (1)
C(16)–O(7)–H(7)	109 (2)	C(21) - O(14) - H(14)	109 (2)
C(17)–O(8)–H(8)	106 (2)	H(20)-C(20)-O(13)	111 (1)
H(16)-C(16)-O(7)	112 (2)	H(20)-C(20)-C(19)	106 (2)
H(16)-C(16)-C(15)	107 (2)	H(20)-C(20)-C(21)	106 (2)
H(16)–C(16)–C(17)	107 (2)	H(21)-C(21)-O(14)	109 (2)
H(17)C(17)O(8)	111 (2)	H(21)-C(21)-C(20)	109 (2)
H(17)-C(17)-C(16)	107 (1)	H(21)-C(21)-C(22)	108 (1)
H(17)–C(17)–C(18)	108 (2)		

Table 5. Geometry of the meso-tartaric acid molecules

Its distance from the mean plane is given below each atom in Å.

	Pla	ne throu	igh:	Dihedral angle	Conformatio	on about:			
O(3)	O(4)	C(15)	C(16)	O(7)	C(15)	C(16)	1 °	C(15)-C(16)	sp2-sp3
0.004 (1)	0.015 (1)	0.013 (2)	0.004 (2)						
O(5)	O(6)	C(17)	C(18)	O(8)	C(17)	C(18)	6	C(17) - C(18)	sp^2-sp^3
0.002 (1)	0.002 (1)	0.001 (2)	0.005 (2)						
O(9)	O(10)	C(19)	C(20)	O(13)	C(19)	C(20)	1	C(19) - C(20)	sp ² -sp ³
0.006 (1)	0.006 (1)	0.016 (2)	0.004(2)						
O(11)	O(12)	C(21)	C(22)	O(14)	C(21)	C(22)	8	C(21) - C(22)	sp ² -sp ³
0.001(1)	0.001(1)	0.000(2)	0.002(2)	. ,	• •	• •			-1 1
C(15)	C(16)	C(17)		O(8)	C(16)	C(17)	4	C(16) - C(17)	SD3-SD3
C(19)	C(20)	C(21)		O(14)	C(20)	C(21)	11	C(20) - C(21)	sp ³ -sp ³

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Table 6. Hydrogen bonds	in t	he structure of	^c K–H-meso-tartrate
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Estimated standard deviations are in parentheses.

Donor group (d)		Accept	or (a)		Distance da	Distance H···a	Angle $d-H\cdots a$
O(3)—H(3)	O(9)	(-x)	-y	(1 - z)	2·543 (1) Å	1·65 (4) Å	171 (4)°
O(6)H(6) O(12)-H(12)	O(6) O(12)	(1-x)(1-x)(1-x)(1-x)(1-x)(1-x)(1-x)(1-x)	1-y -y	$\begin{pmatrix} 1-z \\ -z \end{pmatrix}$	2·483 (2) 2·452 (2)	A-type bonds	
O(7) - H(7) O(8) - H(8) O(13) - H(13)	O(9) O(10) O(7)	$\begin{pmatrix} x \\ x \\ (1-x) \end{pmatrix}$	y y 1 y	1+z z) 1-z	2·768 (1) 2·720 (1) 2·877 (1)	2.02(3) 1.94(3) 2.10(3)	170 (3) 164 (3)
O(14)-H(14)	O(6)	(1-x) (1+x)	y = y	$\frac{1-2}{z}$	2.838(2)	2·10 (3) 2·07 (3)	159 (2) 167 (2)

with respect to the C=O bond (Kanters, Kroon, Peerdeman & Schoone, 1967).



Fig. 3. Electron density in the section through donor, acceptor and H atoms in the A-type $O(6) \cdots O(6)$ hydrogen bond. Contours are in steps of 0.05 e.Å⁻³, starting at 0.20 e.Å⁻³.

Table 7. Potassium-oxygen distances shorter than 3.25 Å and their estimated standard deviations in parentheses





Fig. 4. Projection of the cell-contents in the structure of potassium hydrogen *meso*-tartrate along the *b* axis. I and I' as well as II and II' denote the centrosymmetrically related pairs of the independent molecules. (For clarity, hydrogen atoms are omitted.)

All hydrogen bonds are intermolecular (see Table 6). The hydrogen bond scheme, as far as carboxyl coupling is concerned, is shown in Fig. 2. This acid salt belongs to an A-type as well as to a B-type (Shrivastava & Speakman, 1961). When comparing corresponding antipodes it appears that apart from the hydrogen atoms and neglecting minor deviations in molecular geometry, the carboxyl group C(15)O(3)O(4) coincides with C(19)O(9)O(10) and the group C(18)O(5)O(6) with C(22)O(11)O(12) on superimposing. It is then noteworthy that the first two groups are involved in a B-type hydrogen bond, whereas the second two groups are involved in two A-type hydrogen bonds. A closer inspection of the electron density in the A-type hydrogen bonds revealed that the maximum in at least one of these bonds lies at a significant distance from the centre of the bond (Fig. 3). The implication of this observation is discussed in more detail elsewhere (Currie & Speakman, 1970; Kroon, Kanters & Peerdeman, 1971; Kroon, Kanters, Peerdeman & Vos, 1971). The environment of the potassium ions is given in Table 7; other intermolecular contacts are of no particular interest. The projection of the cell contents along the b axis can be seen in Fig. 4.

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Mise en Évidence d'un Nouveau Type de Surstructure NaCl; Structure des Composés TNaO₂ (T=Dy, Ho, Y, Er)

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(Reçu le 18 juin 1971)

A new superstructure has been found in the compounds of NaCl-type TNaO₂ (T=Dy, Ho, Y, Er). The structure, determined by X-ray powder diffraction, is monoclinic (space group C2/c). The structure is intermediate between the FeLiO₂ Q_1 type structure and the α -NaFeO₂ type structure.

Introduction

Les composés $TNaO_2$, du lanthane au lutétium, ont fait l'objet de plusieurs publications. Suivant le rayon

ionique de la terre rare, quatre formes cristallines ont été observées. Les trois formes connues dérivent de la structure NaCl; références et types de structures sont résumés dans le Tableau 1.

Tableau	1.	Références o	et	type	de	structure	pour	les
		compos	sés	TN	аO	2		

	Т	La···Gd	Тb∙∙∙Но		Y		Er		Tm···Lu	
	Référence	(1)	(1)	(2)	(1)	(1)	(3)	(4)	(1)	
	type	Q	*	R	*	*	С	R	R	
(1)	Blasse (1966) Hoppe (1965)		Q: Qu	adratique,	type Fel	LiO ₂ Q1, Ba	rblan, Branderb	erger &		
(3) (4)	Hestermann & Murav'eva, K	& Hoppe (1968) ovba & Spitsyn		C: Cubique, type FeLiO ₂ désordonné, Posnjak & Bart (1931)						
	--- ,			<i>R</i> : Rh *: Inc	omboédric connue.	que, typ	e α-NaFeO	D ₂ , Goldsztaub	(1935)	