

# 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  $-160^{\circ}\text{C}$ . The crystals are triclinic ( $P\bar{1}$ ) with  $Z=4$ . Cell dimensions are  $a=9.33 \pm 0.01$ ,  $b=10.29 \pm 0.01$ ,  $c=9.09 \pm 0.01$  Å,  $\alpha=80.71 \pm 0.05$ ,  $\beta=108.77 \pm 0.05$  and  $\gamma=130.95 \pm 0.05^{\circ}$ . 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 carboxyl groups in *meso*-tartaric 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  $K\alpha$  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,  $\alpha=80.71 \pm 0.05$ ,  $\beta=108.77 \pm 0.05$ ,  $\gamma=130.95 \pm 0.05^{\circ}$ . The measurements were carried out at  $-160^{\circ}\text{C}$ ; 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

$$S = \begin{pmatrix} 1 & 1 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and has cell dimensions  $a'=8.19$ ,  $b'=10.29$ ,  $c'=9.09$  Å,  $\alpha'=99.29$ ,  $\beta'=99.42$  and  $\gamma'=120.65^{\circ}$ . With four molecules in the unit cell the calculated density ( $2.01 \text{ g.cm}^{-3}$ ) agrees well with the density determined by flotation ( $1.99 \text{ g.cm}^{-3}$ ). The space group was as-

sumed to be  $P\bar{1}$  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  $\theta-2\theta$  scan technique, using zirconium-filtered Mo  $K\alpha$  radiation. Corrections were made for Lorentz and polarization factors. An absorption correction was applied, taking into account the irregular 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

	<i>x</i>	<i>y</i>	<i>z</i>
K(1)	0.22316 (4)	0.43397 (3)	0.12891 (3)
K(2)	0.25520 (4)	0.82925 (3)	0.27170 (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 (4)	0.765 (3)
H(6)	$\frac{1}{2}$ (0)	$\frac{1}{2}$ (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:  $\exp [-(10^{-5} \sum_i \sum_j h_i h_j \beta_{ij})]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
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)	427	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

Table 2 (cont.)

	$B$ ( $\text{\AA}^2$ )	$\rho$ ( $\text{e.}\text{\AA}^{-3}$ )
H(3)	2	0.42
H(6)	5	0.31*
H(7)	0	0.58
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  $\sin \theta/\lambda = 0.4 \text{ \AA}^{-1}$ ); 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  $\sin \theta/\lambda = 0.4 \text{ \AA}^{-1}$  and all atoms subtracted showed no peaks greater than  $0.2 \text{ e.}\text{\AA}^{-3}$ . 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  $0.2 \text{ e.}\text{\AA}^{-3}$  and  $0.4 \text{ e.}\text{\AA}^{-3}$  respectively. For carbon-carbon bonds these values were  $0.4 \text{ e.}\text{\AA}^{-3}$  and  $0.6 \text{ e.}\text{\AA}^{-3}$ . Evidently, these effects are due to the use of inadequate spherical scattering factors.

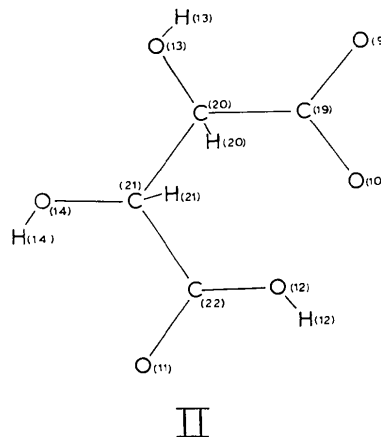
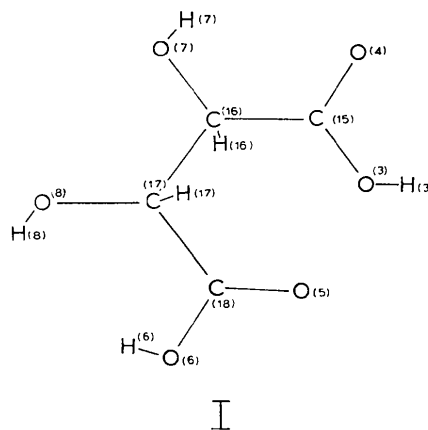
Fig. 1. Numbering scheme for the two independent *meso*-tartrate molecules.

Table 3. Observed and calculated structure factors

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

The columns of each group are h,k,l, |10F<sub>o</sub>|, 10F<sub>c</sub>.

A large table with columns for h, k, l, |10F<sub>o</sub>|, and 10F<sub>c</sub>. The table contains multiple columns of data, with some values marked with an asterisk to indicate suspected extinctions. The data points are organized in a grid-like format across the page.

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Table 3 (cont.)

Table with multiple columns of numerical data, including integers and floating-point numbers, arranged in a grid-like structure. The table contains various numerical values, some with signs, and is organized into several columns and rows.



Table 3 (cont.)

A large table of numerical data with multiple columns, likely representing a matrix or a set of coefficients. The data is organized into a grid-like structure with various numerical values ranging from -10 to 100.

### 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 *meso*-tartaric acid molecules and their estimated standard deviations in parentheses

The hydrogen atoms H(6) and H(12) are supposed to be located at special positions.

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  $\alpha$ -hydroxyl group is in a *syn* position

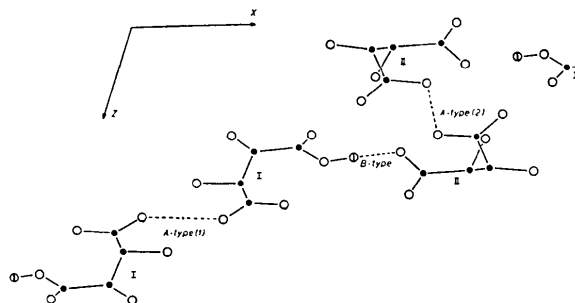


Fig. 2. Projection of part of the structure of potassium hydrogen *meso*-tartrate along the *b* axis. Hydrogen bonds are indicated by broken lines. I and II denote the independent mesotartaric acid molecules in the unit cell.

Table 4 (cont.)

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)	121.2 (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)
O(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.

	Plane through:				Plane through:			Dihedral angle	Conformation about:	
O(3)	O(4)	C(15)	C(16)	O(7)	C(15)	C(16)	1°	C(15)—C(16)	$sp^2-sp^3$	
0.004 (1)	0.015 (1)	0.013 (2)	0.004 (2)	O(8)	C(17)	C(18)	6	C(17)—C(18)	$sp^2-sp^3$	
O(5)	O(6)	C(17)	C(18)	O(13)	C(19)	C(20)	1	C(19)—C(20)	$sp^2-sp^3$	
0.002 (1)	0.002 (1)	0.001 (2)	0.005 (2)	O(14)	C(21)	C(22)	8	C(21)—C(22)	$sp^2-sp^3$	
O(9)	O(10)	C(19)	C(20)							
0.006 (1)	0.006 (1)	0.016 (2)	0.004 (2)							
O(11)	O(12)	C(21)	C(22)							
0.001 (1)	0.001 (1)	0.000 (2)	0.002 (2)							
C(15)	C(16)	C(17)		O(8)	C(16)	C(17)	4	C(16)—C(17)	$sp^3-sp^3$	
C(19)	C(20)	C(21)		O(14)	C(20)	C(21)	11	C(20)—C(21)	$sp^3-sp^3$	

Table 6. *Hydrogen bonds in the structure of K-H-meso-tartrate*

Estimated standard deviations are in parentheses.

Donor group ( <i>d</i> )	Acceptor ( <i>a</i> )	Distance <i>d...a</i>	Distance <i>H...a</i>	Angle <i>d-H...a</i>
O(3)—H(3)	O(9) ( - <i>x</i> - <i>y</i> 1- <i>z</i> )	2.543 (1) Å	1.65 (4) Å	171 (4)°
O(6)—H(6)	O(6) (1- <i>x</i> 1- <i>y</i> 1- <i>z</i> )	2.483 (2)	} <i>A</i> -type bonds	
O(12)—H(12)	O(12) (1- <i>x</i> - <i>y</i> - <i>z</i> )	2.452 (2)		
O(7)—H(7)	O(9) ( <i>x</i> <i>y</i> 1+ <i>z</i> )	2.768 (1)		2.02 (3)
O(8)—H(8)	O(10) ( <i>x</i> <i>y</i> <i>z</i> )	2.720 (1)	1.94 (3)	164 (3)
O(13)—H(13)	O(7) (1- <i>x</i> 1- <i>y</i> 1- <i>z</i> )	2.877 (1)	2.10 (3)	159 (2)
O(14)—H(14)	O(6) (1+ <i>x</i> <i>y</i> <i>z</i> )	2.838 (2)	2.07 (3)	167 (2)

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

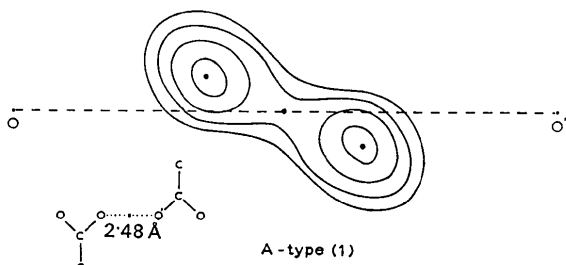


Fig. 3. Electron density in the section through donor, acceptor and H atoms in the *A*-type O(6)···O(6) hydrogen bond. Contours are in steps of 0.05 e.Å<sup>-3</sup>, starting at 0.20 e.Å<sup>-3</sup>.

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

K(1)···O(3)	( - <i>x</i> - <i>y</i> 1- <i>z</i> )	2.957 (1) Å
K(1)···O(4)	( <i>x</i> <i>y</i> -1+ <i>z</i> )	3.161 (1)
K(1)···O(6)	( <i>x</i> <i>y</i> <i>z</i> )	3.127 (1)
K(1)···O(7)	( 1- <i>x</i> 1- <i>y</i> 1- <i>z</i> )	2.763 (1)
K(1)···O(8)	( 1- <i>x</i> 1- <i>y</i> 1- <i>z</i> )	2.860 (1)
K(1)···O(9)	( <i>x</i> <i>y</i> <i>z</i> )	3.029 (1)
K(1)···O(11)	(-1+ <i>x</i> <i>y</i> <i>z</i> )	2.695 (1)
K(1)···O(13)	( 1- <i>x</i> 1- <i>y</i> - <i>z</i> )	2.643 (1)
K(1)···O(14)	(-1+ <i>x</i> <i>y</i> <i>z</i> )	2.766 (1)
K(2)···O(4)	( - <i>x</i> 1- <i>y</i> 1- <i>z</i> )	2.733 (1) Å
K(2)···O(8)	( 1- <i>x</i> 1- <i>y</i> 1- <i>z</i> )	3.053 (1)
K(2)···O(10)	( <i>x</i> 1+ <i>y</i> <i>z</i> )	2.949 (1)
K(2)···O(10)	( 1- <i>x</i> 1- <i>y</i> 1- <i>z</i> )	2.948 (1)
K(2)···O(11)	( 1- <i>x</i> 1- <i>y</i> - <i>z</i> )	2.775 (1)
K(2)···O(12)	( <i>x</i> 1+ <i>y</i> <i>z</i> )	2.950 (1)
K(2)···O(14)	(-1+ <i>x</i> <i>y</i> <i>z</i> )	2.900 (1)

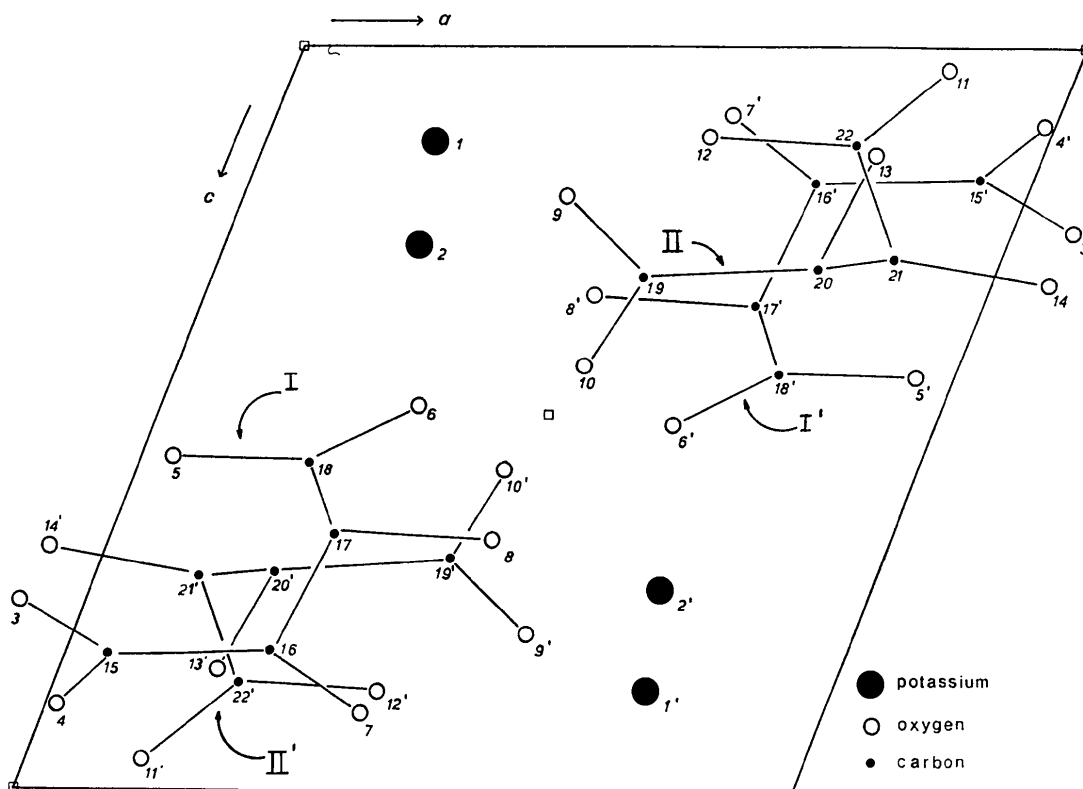


Fig. 4. Projection of the cell contents in the structure of potassium hydrogen *meso*-tartrate along the *b* axis. I and I' as well as II and II' denote the centrosymmetrically related pairs of the independent molecules. (For clarity, hydrogen atoms are omitted.)



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 TNaO<sub>2</sub> (T = Dy, Ho, Y, Er)

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A new superstructure has been found in the compounds of NaCl-type TNaO<sub>2</sub> (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 FeLiO<sub>2</sub> *Q*<sub>1</sub> type structure and the  $\alpha$ -NaFeO<sub>2</sub> type structure.

#### Introduction

Les composés TNaO<sub>2</sub>, 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 et type de structure pour les composés TNaO<sub>2</sub>

T	La...Gd	Tb...Ho	Y	Er	Tm...Lu
Référence	(1)	(1)	(2)	(1)	(1)
Structure				(1)	(1)
type	<i>Q</i>	*	<i>R</i>	*	<i>R</i>

(1) Blasse (1966)  
 (2) Hoppe (1965)  
 (3) Hestermann & Hoppe (1968)  
 (4) Murav'eva, Kovba & Spitsyn (1967)

*Q*: Quadratique, type FeLiO<sub>2</sub>*Q*<sub>1</sub>, Barblan, Branderberger & Niggli (1944)  
*C*: Cubique, type FeLiO<sub>2</sub> désordonné, Posnjak & Barth (1931)  
*R*: Rhomboédrique, type  $\alpha$ -NaFeO<sub>2</sub>, Goldsztaub (1935)  
 \*: Inconnue.