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A Direct Determination of the Crystal Structure of the β Form of Trilaurin

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The unit cell of the β form of trilaurin, $C_{39}H_{74}O_6$, was determined from X-ray single-crystal and powder-photograph data. It is triclinic, contains two molecules, and has the dimensions

$$a=12{\cdot}31\pm0{\cdot}10,\quad b=5{\cdot}40\pm0{\cdot}06,\quad c=31{\cdot}77\pm0{\cdot}10\ \text{A.};$$

$$\alpha=94^\circ\ 16'\pm33',\quad \beta=96^\circ\ 52'\pm18',\quad \gamma=99^\circ\ 12'\pm1^\circ\ 46';$$

density calculated 1·027, observed 1·04 g.cm.$^{-3}$.

Application of subcell theory yielded the angle of tilt and the positions of the hydrocarbon chains.

Introduction

Triglycerides occur as constituents of vegetable and animal fats. Although the glycerides have been intensively studied, the lack of single crystals has hitherto prevented any attempts at structure determination. The investigations have been limited chiefly to X-ray diffraction powder patterns, polymorphism and thermal data. According to the nomenclature of Clarkson & Malkin (1948), there exist four polymorphic forms of the saturated triglycerides: the vitreous form; the α form, giving sharp long spacings and diffuse short spacings; and the β' and β forms, each having a characteristic sharp, powder diffraction pattern. The β form is the most stable at room temperature.

The present investigation is concerned with the β form of trilaurin, a single crystal of which was grown from benzene solution.

Preparation

Trilaurin was prepared in our laboratories by esterification of pure lauric acid (obtained by fractionation of palm kernel fatty acids) and glycerol at 180° C. in the presence of p-toluene sulphonic acid under nitrogen. The washed sample was recrystallized three times from ethanol. It had a melting point of 46·4° C., saponification value of 263·6 (theory 263·8), and a zero iodine value, hydroxyl value and acid value.

X-ray powder photographs

Powder photographs of samples of trilaurin were taken using nickel-filtered Cu $K\alpha$ radiation and a 12·5 cm. diameter focusing camera of the Frevel type described by Vand (1948). These showed patterns similar to those given for the β form of saturated triglycerides by Clarkson & Malkin (1934). Table 1 gives the intensities and spacing of the observed reflexions.

Table 1. *Intensities and spacings of reflexions from a powder photograph of the β form of trilaurin*

Intensity	Spacing (A.)	Main-cell index*	Subcell index
2	15·85	002	—
20	10·49	003	—
1	8·30	$10\bar{3}$	—
4	7·83	004	—
1	6·18	104, $20\bar{1}$	—
1	5·81	$20\bar{3}$, $10\bar{5}$, $20\bar{2}$	—
20	5·36	010, $01\bar{1}$, 202	—
20	5·20	006, $01\bar{2}$, 011	—
6	4·92	$20\bar{4}$, $10\bar{6}$, $01\bar{3}$	—
1	4·80	012, $1\bar{1}3$	—
400	4·55	$20\bar{5}$, 106, $11\bar{2}$, $11\bar{3}$	010
20	4·38	204	—
1	4·22	$20\bar{6}$	—
20	4·09	$30\bar{1}$, 300	—
200	3·853	$\bar{2}1\bar{3}$, $10\bar{8}$, $20\bar{7}$	$\bar{1}10$
300	3·728	302	100
40 D	3·593	$30\bar{5}$, 303	—
10 D	3·398	$10\bar{9}$, 304	—
2	3·289	—	—
20 D	3·144	$20\bar{9}$, $1,0,\overline{10}$	—
4 D	2·974	$40\bar{2}$, $40\bar{3}$, 306, $40\bar{4}$	—
1	2·832	—	—
1	2·743	403	—
20	2·571	405, $\bar{1}2\bar{5}$, 411	$\bar{1}20$, 110
2	2·416	223	020
4	2·363	$\bar{3},1,10$	$\bar{1}11$
2	2·291	$1,0,\overline{12}$, $4,0,\overline{10}$	001
4 D	2·242	$1,0,\overline{14}$, $0,1,12$	011
2	2·186	$4,0,\overline{11}$	$10\bar{1}$
2	2·143	$\bar{2}27$	—
2	2·080	$4,0,\overline{12}$	—
2	2·059	$\bar{2}28$	$\bar{1}21$
1	1·978	$2,1,\overline{15}$	$01\bar{1}$
4	1·930	$\bar{4}2\bar{8}$, 604	$\bar{2}20$, 200
2	1·777	—	021, $11\bar{1}$, $\bar{2}21$
2	1·670	—	120
2	1·632	—	$20\bar{1}$, 111

D = diffuse line.

* Not exhaustive; indices of reflexions known to be weak from single-crystal photographs are omitted.

An average value of c^* of $0{\cdot}03185\pm0{\cdot}00004$ A.$^{-1}$ was obtained from three photographs. Thus the long spacing d is 31·40 A.

The long spacings of the even members of the series obey a linear law $d=pN+q$, where N is the number of

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carbon atoms in the chain, and p, q are constants. Clarkson & Malkin (1934) give the following list of long spacings for the β form of the even series of saturated triglycerides:

N	d (A.)
10	26·8
12	31·2
14	35·8
16	40·6
18	45·0

The values of p and q determined by the method of least squares are: $p=2{\cdot}29\pm0{\cdot}013$, $q=3{\cdot}82\pm0{\cdot}18$.

Taking the distance between alternate carbon atoms, given by Vand, Aitken & Campbell (1949), as 2·604 A., we obtain for the sine of the angle of tilt,

$$\sin\tau=2{\cdot}29/2{\cdot}604=0{\cdot}8794,$$

and therefore $\tau=61°\,35'$, when calculated from the increment of the long spacings.

Determination of crystal data

A single crystal of the β form of trilaurin was grown from a solution in benzene by evaporation at room temperature. The crystal grew in the form of a flat plate.

A series of rotation photographs and of zero- and n-layer moving-film Weissenberg photographs was taken along the a and b axes, using Ni-filtered Cu $K\alpha$ radiation. The following data were obtained:

Molecular formula: $C_{39}H_{74}O_6$.
Molecular weight: 638·98.
Unit cell: triclinic.

$a=12{\cdot}31\pm0{\cdot}10$, $b=5{\cdot}40\pm0{\cdot}06$, $c=31{\cdot}77\pm0{\cdot}10$ A.;
$\alpha=94°\,16'\pm33'$, $\beta=96°\,52'\pm18'$, $\gamma=99°\,12'\pm1°\,46'$.

Two molecules per unit cell.
Density calculated: $1{\cdot}027\pm0{\cdot}014$ g.cm.$^{-3}$.
Density measured: 1·04 g.cm.$^{-3}$.
No systematically absent reflexions.
Space group C_1^1–$P1$ or C_i^1–$P\bar{1}$.
Number of electrons = 712 per unit cell.

Estimation of intensities and structure-factor determination

Estimation of intensities was made visually by the multiple-film method of de Lange, Robertson & Woodward (1939). From these intensities the structure factors were calculated, taking account of the correcting factor for n-layer equi-inclination photographs. No absorption corrections were applied owing to the smallness of the crystal. The values of the structure factors were brought to an absolute scale by comparison with the calculated values at a later stage of the calculations.

Application of subcell theory to trilaurin

It was shown by Vand (1951) that if a unit cell of a crystal has a periodic distribution of matter which can be described by a much smaller subcell, great simplifications can be introduced in the structure determination. As the molecule of trilaurin contains hydrocarbon chains which are periodic structures, subcell theory is applicable.

On marking the observed structure factors against the points of the reciprocal lattice, it was found that a three-dimensional reciprocal sublattice could be drawn through the points of large structure factors (see Fig. 1, only the ($h0l$) layer is shown with one sublattice layer marked). The corresponding repeat unit in real space is the subcell of trilaurin. In a subcell region, $\rho(x)=\rho(r)$ for all vectors $x=u+ts+r$, where u is a vector to the origin of the subcell region, t is the repetition operator which multiplies a three-vector s representing the subcell edges, and r is the vector within the subcell from its origin. The following relation between the structure factors F_h of the main cell and F_H of the subcell is valid;

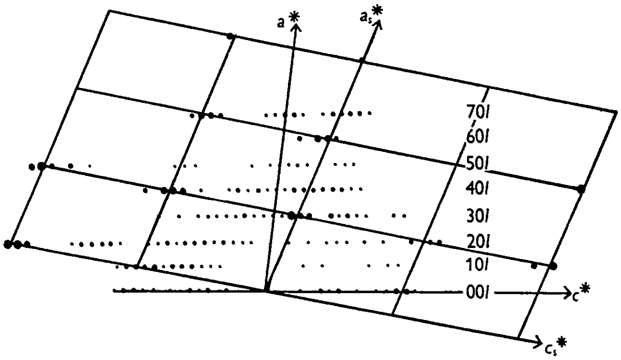

Fig. 1. The ($H0L$) plane of the reciprocal sublattice.

$$F_h=F_h^0+LF_H\exp\left(2\pi i x_m h\right), \tag{1}$$

where F_h^0 is the contribution of the non-subcell atoms, which will be neglected in the following calculation;

$$L=\prod_j\frac{\sin\pi N^jH_j}{\sin\pi H_j} \tag{2}$$

is an oscillating function of the Laue type; and

$$x_m=u+\tfrac{1}{2}\sum_j\left(N^j-1\right)s_j \tag{3}$$

is the vector to the centroid of the subcell origins (a block-shaped subcell region of edges N^js_j is assumed).

Trilaurin has two molecules per unit cell, so that two subcell regions are to be expected. If the main cell has a centre of symmetry, $F_H=A_H\pm iB_H$, the + and − signs being taken for the top and bottom subcell regions, respectively. Neglecting F_h^0, we have

$$F_h=2L\left(A_H\cos 2\pi x_m h-B_H\sin 2\pi x_m h\right). \tag{4}$$

From the consideration of the structure we can easily see that the centroid of the subcell origins of one of the subcell regions is not far from a point (0, 0, $\tfrac{1}{4}$) of the main cell. The subcells have a centre of symmetry, but if we choose their origin not at the centre of symmetry we are at liberty to choose it arbitrarily and thus shift the centroid of the origins. Let us choose the centroid at $(0, 0, \frac{1}{4})$. Substituting this in (4), we obtain for F_h the following values:

$$F_h=\begin{cases}+2LA_H\\-2LB_H\\-2LA_H\\+2LB_H\end{cases}\quad\text{for}\quad h_3=\begin{cases}4n\\4n+1\\4n+2\\4n+3.\end{cases}$$

If we plot $|F_h|$ as a function of h_3 (i.e. Miller index l), we obtain two curves for odd and even h_3. Their maxima correspond to maxima of L and give us $|A_H|$ and $|B_H|$ of the subcell. Substitution in $F_H^2=A_H^2+B_H^2$ gives the values of $|F_H|$, which remain the same wherever the origin of the subcell is chosen.

The subcell structure can be now solved and the signs of F_H relating to a centrosymmetrical subcell determined. However, at the beginning of our calculation we have chosen the subcell origin in a general position, so that the following relations are valid:

$$A_H/|F_H|=\cos\alpha,\quad B_H/|F_H|=\sin\alpha,$$

where $\alpha=2\pi qH$ and q is a vector from $(0, 0, \frac{1}{4})$ to the nearest centre of symmetry of the subcell.

The angle α can be determined, giving the vector q. Signs of A_H and B_H can now be calculated, giving finally the signs of the main-cell structure factors F_h.

Dimensions of the subcell

To determine the parameters of the subcell, the following procedure was adopted:

Considering h_k and H_q as vectors in reciprocal space, both of which can be evaluated for example graphically, we can obtain the coefficients of a transformation operator σ, given by $h_k=\sigma_k^q H_q$, as the components of the edges of the reciprocal subcell on the reciprocal main cell. These coefficients are obtained graphically. The quantity σ is a three-vector operator which is the inverse of s. Hence s was obtained from the relation $s_i^k\sigma_k^q=\delta_i^q$, the numerical values obtained being

$$\begin{bmatrix}s_1^1 & s_2^1 & s_3^1\\ s_1^2 & s_2^2 & s_3^2\\ s_1^3 & s_2^3 & s_3^3\end{bmatrix}=\begin{bmatrix}0{\cdot}3153 & 0 & -0{\cdot}0541\\ -0{\cdot}241 & 1 & 0{\cdot}130\\ 0{\cdot}0230 & 0 & 0{\cdot}0690\end{bmatrix}.$$

From these coefficients, the absolute length of the subcell edges in Ångström units, and the subcell angles, were calculated as follows:

The geometry in the main cell can be expressed by a fundamental double tensor g_{mn} which is obtained from the main-cell edges and angles. The numerical value of this tensor is

$$\begin{bmatrix}g_{11} & g_{12} & g_{13}\\ g_{21} & g_{22} & g_{23}\\ g_{31} & g_{32} & g_{33}\end{bmatrix}=\begin{bmatrix}151{\cdot}648 & -10{\cdot}633 & -46{\cdot}780\\ -10{\cdot}633 & 29{\cdot}168 & -12{\cdot}767\\ -46{\cdot}780 & -12{\cdot}767 & 1009{\cdot}546\end{bmatrix}$$

The length $|a|$ of a vector a whose components a^r are expressed as fractions of the main-unit-cell edges is then given by $|a|=\sqrt{(g_{mn}a^m a^n)}$, and the angle Θ_{ab} between the vectors a and b is given by

$$|a|\,|b|\cos\Theta_{ab}=g_{rs}a^r b^s. \qquad (5)$$

Using the above equations, we obtained the following dimensions for the subcell edges and angles:

$$a_s=4{\cdot}287,\quad b_s=5{\cdot}40,\quad c_s=2{\cdot}45\text{ A.};$$
$$\alpha_s=74^\circ\,45',\quad \beta_s=108^\circ\,2',\quad \gamma_s=117^\circ\,24'.$$

Thus the subcell is triclinic, containing two CH_2 groups per unit cell. Consideration of the symmetry of a hydrocarbon chain yields the subcell space group C_i^1–$P\bar{1}$.

Estimation of subcell structure factors

The values of $|A_H|$ and $|B_H|$ were determined, as discussed in the section on subcell theory. From these F_H^2 was given by $A_H^2+B_H^2$, and $\tan\alpha$ by $\pm B_H/\pm A_H$, where $\alpha=2\pi qH$. The values of F_H are shown in Table 2. Owing to the ambiguity in sign of $\tan\alpha$, there are eight possibilities for q. Only four of these need be considered as they alone give the centroid of the subcell region in the neighbourhood of $(0, 0, \frac{1}{4})$. These four possibilities reduce to two in practice as the other two imply a shift of half the c axis of the main cell, i.e. a choice of the origin of the main cell at $(0, 0, 0)$ or $(0, 0, \frac{1}{2})$, which is trivial. The two solutions are $q_x=0{\cdot}05$, $q_z=-0{\cdot}05$; or $q_x=0{\cdot}05$, $q_z=0{\cdot}45$ in subcell fractionals.

Determination of the subcell structure

From the dimensions of the subcell given above, we can see that the hydrocarbon chains lie along the c_s axis of the subcell, and the plane of the chains is approximately parallel to the b_s axis. Since there are only two CH_2 groups per centrosymmetrical subcell, the signs of F_H were easily determined by trial. A Fourier synthesis of the b_s-axis projection of the subcell was then made (Fig. 2). It gave the x and z co-ordinates of the CH_2 groups in the subcell. A further projection along the c axis gave the y co-ordinate. These co-ordinates were refined by a modified steepest-descents formula, minimizing a function R_4, discussed by Vand (1949).

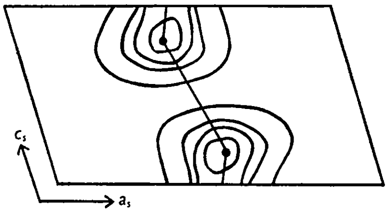

Fig. 2. Synthesis of the subcell; b-axis projection.

The fractional subcell co-ordinates finally obtained were $x=0{\cdot}0395$, $y=0{\cdot}6021$, $z=0{\cdot}1991$. The other CH_2 group is given by $(-0{\cdot}0395, -0{\cdot}6021, -0{\cdot}1991)$. Observed and calculated subcell structure factors are shown in Table 2.

Table 2. *Observed and calculated subcell structure factors*

(HKL)	F_o	F_c	(HKL)	F_o	F_c	(HKL)	F_o	F_c
001	2·2	1·9	011	2·6	1·8	021	3·2	−3·0
002	2·6	−1·2	012	1·2	1·4	022	0·9	−1·0
100	7·8	9·9	$0\bar{1}\bar{1}$	3·1	−3·7	120	0·4	−0·1
101	1·4	0·3	110	2·6	−4·3	121	1·9	−1·8
102	1·1	−1·0	111	1·5	1·6	$\bar{1}21$	4·9	−3·2
$10\bar{1}$	5·6	3·0	$11\bar{1}$	2·2	−3·3	$\bar{1}22$	2·1	−1·5
$10\bar{2}$	1·9	−0·9	210	0·9	−1·1	$\bar{2}21$	1·5	−1·7
200	5·0	3·5	211	0·9	1·2	$\bar{2}22$	1·6	−1·4
202	0·5	−0·4	$21\bar{1}$	0·7	−1·9	020	1·2	1·8
$20\bar{1}$	3·2	1·9	$\bar{1}10$	6·2	−9·6	$\bar{1}20$	3·3	3·6
300	1·0	1·2	$\bar{1}11$	0·8	0·5	$\bar{1}2\bar{1}$	2·0	2·4
$30\bar{1}$	1·1	1·4	$\bar{1}12$	1·6	1·6	$\bar{2}20$	1·8	2·9
010	7·2	−9·3	$\bar{2}12$	1·2	1·3	$\bar{2}2\bar{1}$	0·7	1·6

Discussion of the chain packing

In order to visualize the packing of the chains, a section perpendicular to the chain axis is required. This section forms a plane lattice of parameters

$$a_0=\frac{1}{a_s^*}\operatorname{cosec}\gamma_s^*=4{\cdot}078\text{ A.};$$

$$b_0=\frac{1}{b_s^*}\operatorname{cosec}\gamma_s^*=5{\cdot}209\text{ A.};$$

$$\gamma_0=180^\circ-\gamma_s^*=114^\circ\,23'.$$

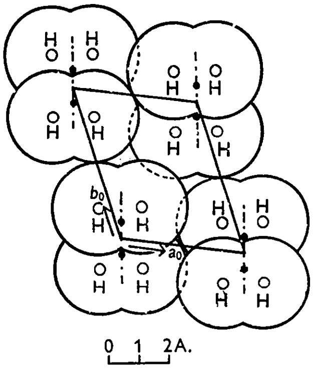

Fig. 3. The side packing of the hydrocarbon chains.

From the angles α_s, β_s of the subcell the mutual displacements along the c_s axis of the neighbouring chains were calculated (that is in a direction perpendicular to the plane of Fig. 3). Taking chain I as a reference, chain II is displaced $a_s\cos\beta_s=-1{\cdot}33$ A., and chain III $b_s\cos\alpha_s=1{\cdot}42$ A. The displacement of chain IV is thus 0·09 A. The displacement of chain II relative to I is very approximately $\frac{1}{2}c_s$. This corresponds to the hydrogen atoms of one chain falling into the troughs between the hydrogen atoms of the other chain. The packing of the hydrocarbon chains is thus triclinic; it is probable that the same packing occurs in silver soaps investigated by Vand *et al.* (1949) and in triclinic paraffins, the unit cell of which was determined by Müller & Lonsdale (1948).

Considering the hydrogen domains as spherical, it was found possible to calculate the positions of the centres of these domains (H in Fig. 3). The radius of the domains was found to be 1·5 A.

Synthesis of the main cell

In trilaurin L has the form $\dfrac{(\sin 6\pi H_3)}{(\sin\pi H_3)}\dfrac{(\sin 3\pi H_1)}{(\sin\pi H_1)}$ in the a^*c^* plane of reciprocal space. A contour map of L was drawn covering the $a_s^*c_s^*$ face of the reciprocal subcell, treating H_1 and H_3 as continuously variable. From this the sign and magnitude of L in the neighbourhood of any main-cell reflexion could be determined. In practice two sets of signs for the main-cell reflexions were obtained, corresponding to the two possibilities $(q_x, q_z)=(0{\cdot}05, -0{\cdot}05)$ or $(0{\cdot}05, 0{\cdot}45)$. Using each of these sets of signs, two main-cell b-axis projection syntheses were prepared. Choice $(q_x, q_z)=(0{\cdot}05, -0{\cdot}05)$ gave a much more reasonable picture of the trilaurin molecule, so this possibility was chosen as the correct one.

Having fixed the origin of the centrosymmetrical subcell with reference to the origin of the main cell, the x and z co-ordinates of the CH_2 groups of the chains were calculated by using the relationship $r^i=p^k s_k^i$ between main-lattice fractional co-ordinates and sublattice co-ordinates (Vand, 1950). The x and z co-ordinates so obtained (Table 3) agreed well with the observed peaks on the synthesis.

Orientation of the chains within the main cell

As the axes of the chains coincide with the c_s edges of the subcells, it is an easy matter to derive the orientation of the chain axes within the main cell. Using equation (5) for the angle between two vectors, we find for the angle between the b edge of the main cell and the c_s edge of the subcell, $\alpha_0=74^\circ\,45'$. Similarly, the angle between the a edge of the main cell and c_s is $\beta_0=115^\circ\,5'$. The angles α_0 and β_0 define a 'constant direction', as discussed by Vand *et al.* (1949). The angle of tilt τ, which is the angle between c_s and the ab plane of the main cell, can then be calculated from α_0, β_0 and γ. The value obtained is $\tau=62^\circ\,7'$. This value compares well with the value $\tau=61^\circ\,35'$, obtained from the increment of the long spacings, discussed at the beginning of the paper.

The authors are indebted to Mr P. N. Williams and Mr R. Jamsett for the preparation of the trilaurin, and to Miss B. Edkins for extensive help in the calculations.

Table 3. *Atomic co-ordinates*

Hydrocarbon chains

	x/a	z/c		x/a	z/c		x/a	z/c
C_1	0·1792	0·0260	C_{13}	0·5425	0·4464	C_{25}	0·7728	0·5766
C_2	0·1824	0·0554	C_{14}	0·5393	0·4170	C_{26}	0·7760	0·6060
C_3	0·1251	0·0950	C_{15}	0·5966	0·3774	C_{27}	0·7187	0·6456
C_4	0·1283	0·1244	C_{16}	0·5934	0·3480	C_{28}	0·7219	0·6750
C_5	0·0710	0·1640	C_{17}	0·6507	0·3084	C_{29}	0·6646	0·7146
C_6	0·0742	0·1934	C_{18}	0·6475	0·2790	C_{30}	0·6678	0·7440
C_7	0·0169	0·2330	C_{19}	0·7048	0·2394	C_{31}	0·6105	0·7836
C_8	0·0200	0·2624	C_{20}	0·7016	0·2100	C_{32}	0·6137	0·8130
C_9	0·9628	0·3020	C_{21}	0·7589	0·1704	C_{33}	0·5564	0·8526
C_{10}	0·9660	0·3314	C_{22}	0·7557	0·1410	C_{34}	0·5596	0·8820
C_{11}	0·9087	0·3710	C_{23}	0·8130	0·1014	C_{35}	0·5023	0·9216
C_{12}	0·9119	0·4004	C_{24}	0·8098	0·0720	C_{36}	0·5055	0·9410

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Short Communications

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The positions of the barium atoms in hollandite.

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In a previous paper in this journal (Byström & Byström, 1950) a determination of the crystal structure of hollandite was reported. In the suggested structure, which is tetragonal or pseudotetragonal, the barium atoms occupy the positions $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. However, there are only about 1·0 barium atoms per unit cell, and so only 50 % of the positions are filled with barium atoms. Because of the length of the c axis (2·86 A.) some of the Ba–Ba distances will be very short. A statistical distribution of the barium atoms over all positions requires that on the average every fourth barium atom has another barium atom at the distance of 2·86 A., which is only a little more than twice the ionic radius.

Prof. A. Westgren has suggested to us that the barium atoms may be arranged over the same atomic sites in another way. On each tetragonal axis only every other position is occupied by barium atoms. However, the positions on one tetragonal axis are independent of the positions on the other tetragonal axes, and thus a one-dimensionally ordered but two-dimensionally disordered arrangement of the barium is obtained. This arrangement will give the same intensity distribution as that previously suggested, but as no close Ba–Ba distances are obtained in this case it is obviously preferable.

This modification of the arrangement of the barium atoms may have the consequence that the objections against water molecules in the vacant positions are less convincing (see Byström & Byström, 1950, p. 155). It is in fact possible that some of the water, which is always present in these minerals, is placed between the barium atoms (and probably forming hydrogen bonds with the surrounding oxygen atoms). The observed densities are in some cases somewhat higher than those calculated with all the water molecules among the oxygen atoms in sixteen atomic sites. This may be an indication that some part of the water lies in the positions on the fourfold axes, and leads to a modification of the general formula, thus:

$$(\mathrm{Ba, K, Pb})_{2-y}(\mathrm{H_2O})_u(\mathrm{Mn, Fe})_{8-z}(\mathrm{O, OH})_{16};$$

y is always close to unity, but may be somewhat less in the coronadites; u is probably always small and cannot possibly exceed unity; z is equal to or close to zero ($< 0·5$) in minerals hitherto analysed.

An interesting consequence of the suggested arrangement of barium atoms and vacant sites or water molecules on the fourfold axes is that atomic sites belonging to the same point position are not equivalent, as there occurs a further one-dimensional order of a period twice that of the unit cell.

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