

The Crystal Structure of $\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_{2.5}$

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The structure of $\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_{2.5}$ has been determined by means of X-ray crystallographic methods. Each thallium atom is octahedrally surrounded by six oxygen atoms at an average distance of 2.22 Å. The thallium atoms form chains in the structure with the shortest distance between two thallium atoms equal to 4.01 Å. The positions of the light atoms have been determined from reflections to which the thallium atoms give no contribution.

In the course of a study of the structures of basic salts of some trivalent metals a basic thallium(III) sulfate has also been prepared. It has been described in the literature by Meyer and Wilk¹, who found that it crystallized from solutions of Tl_2O_3 in sulfuric acid containing between about 10 and 40 % H_2SO_4 . They ascribed to it the formula $\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_2$.

PREPARATION AND ANALYSIS

Dilute sulfuric acid containing about 20 % H_2SO_4 was saturated with Tl_2O_3 and the solution was placed in a vacuum desiccator. After a couple of days, colourless, rod-shaped crystals of the basic sulfate had formed and were large enough for single crystal measurements. They were filtered off on a glass filter plate and drained by being pressed between filter papers. They could not be washed with water as this immediately resulted in a hydrolysis to Tl_2O_3 .

Thallium was determined by precipitation with ammonia and weighing as Tl_2O_3 . The sulfate was determined gravimetrically as BaSO_4 . The water was determined by Hartwig-Bendig's² modification of Brush and Penfield's method as described by Kolthoff and Sandell³.

The density of the crystals was obtained from the apparent loss of weight in benzene.

	Found	Calculated for	
		$\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_2$	$\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_{2.5}$
% Tl_2O_3	63.2	64.61	63.00
% SO_3	22.4	22.65	22.09
% H_2O	15.1	12.74	14.91
Density	3.94	3.85	3.94

The analysis data show a better agreement with the formula $\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_{2.5}$ than with $\text{TlOH}_2\text{SO}_4(\text{H}_2\text{O})_2$ which was assumed by Meyer and Wilk¹. As will be shown later, only the first formula is consistent with the results of the X-ray analysis.

Table 1. Powder photograph of $\text{TlOHSO}_4(\text{H}_2\text{O})_{2.5}$. $\text{CuK}\alpha$ radiation.

hkl	$10^4 \sin^2\theta$ calc.	$10^4 \sin^2\theta$ obs.	I obs.	hkl	$10^4 \sin^2\theta$ calc.	$10^4 \sin^2\theta$ obs.	I obs.
101	78	77	w+	225	1515	1516	vw+
200	153	152	m	602	1535	1536	vw+
002	159	158	s	504	1591	1592	vvw
201	193	192	s	405	1604	1605	vw
210	245	245	vvw	042	1635	1636	m
211	285	284	vvw	241	1669		
112	289	289	vvw	142	1673	1671	w
202	312	310	m	603	1733	1734	vvw
020	369	369	m	620	1745	1745	vw+
103	396	395	w	306	1773	1773	vvw
121	447	447	vvw	621	1785		
311	476	476	vw	242	1788	1787	m
302	503	502	w	143	1872	1873	vw
203	510	509	m	622	1904	1904	w
220	522	522	s	425	1973	1974	vw
022	528	528	s	107	1984		
221	562	562	s	243	1986	1986	w
122	566	566	m	604	2011	2011	vvw
004	635	635	w-	207	2098		
401	651	651	m	623	2102	2102	vw
222	681	681	m	441	2127		
303	701	702	vw-	416	2133	2130	w+
411	744	744	vw	244	2264	2263	vw
123	765			127	2353	2352	w-
114	766	765	vw	506	2385	2387	vw
204	788	787	w-	443	2445		
322	872	873	vvw	800	2447	2445	w+
223	879			145	2507		
214	880	880	w+	704	2508	2509	vvw
403	969	968	m	723	2599		
304	979			714	2601		
420	981	980	vw	336	2604	2602	vvw
230	983			802	2605		
024	1004	1004	vw	245	2622	2624	vvw
421	1020	1021	m	625	2738		
105	1031	1030	vw	731	2743	2741	vvw
124	1042	1044	vvw	606	2805		
502	1115	1115	vvw	352	2809		
205	1146	1146	vvw	345	2813	2811	vw
224	1157	1158	w	137	2814		
305	1337			820	2816		
423	1338	1340	m	821	2855		
414	1339			732	2862	2858	vvw
324	1348	1349	vw	641	2892		
600	1376	1376	vvw	813	2896		
125	1400	1400	w-	616	2898	2897	vw-
601	1416	1417	vw	507	2901		
006	1429	1429	vvw	822	2974	2973	vw
040	1476	1478	m	318	2977		

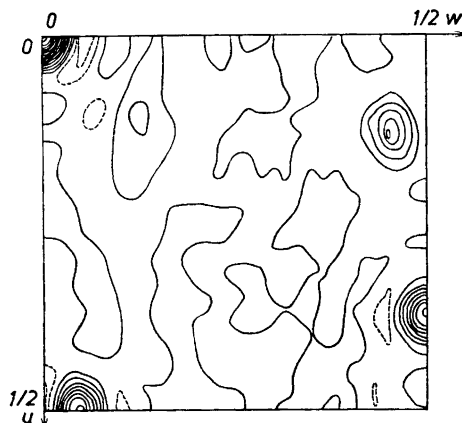


Fig. 1. Patterson projection $P(uvw)$ calculated from the intensities of the $h0l$ -reflections.

UNIT CELL AND SPACE GROUP

The crystals have orthorhombic symmetry which was shown by rotation and Weissenberg photographs taken with CuK -radiation for two of the axes ($0kl-4kl$ and $h0l-h4l$). The dimensions of the unit cell were calculated to be $a = 12.5 \text{ \AA}$ $b = 8.0 \text{ \AA}$ and $c = 12.1 \text{ \AA}$. From powder photographs in a Guinier focusing camera (Table 1) the following more accurate values for the cell dimensions were obtained ($\text{CuK}\alpha$ radiation, $\lambda_{\text{CuK}\alpha_1} = 1.54050 \text{ \AA}$)

$$\begin{aligned} a &= 12.453 \pm 0.005 \text{ \AA} \\ b &= 8.019 \pm 0.005 \text{ \AA} \\ c &= 12.224 \pm 0.005 \text{ \AA} \\ V &= 1220.7 \text{ \AA}^3 \end{aligned}$$

According to the observed density, the unit cell must contain 8 formula units of $\text{TlOHSO}_4(\text{H}_2\text{O})_{2.5}$.

The reflections systematically absent were such that

$$\begin{aligned} 0kl &\text{ was observed only for } k + l = 2n \\ hk0 &\text{ was observed only for } h = 2n \end{aligned}$$

This is characteristic for the space groups No 62: $Pnma$ and No 33: $Pn2_1a$.

Intensities were estimated visually and were corrected for Lorentz and polarization factors. No absorption corrections were applied but only very small crystals were used (about 0.1 mm in length).

POSITIONS OF THE THALLIUM ATOMS

On the rotation photograph around the b -axis the odd layer lines were very weak, and the intensities did not seem to increase for the higher layer lines. Therefore the positions of the Tl-atoms may be described by a unit cell with a b -axis of only half that of the structure as a whole.

For the determination of the x and z coordinates the $h0l$ -intensities were used to calculate the Patterson projection $P(upw)$. $P(upw)$ shows three sharp maxima which can be ascribed to the Tl-atoms (Fig. 1). For the space group $Pnma$ this can be explained by the point position $8(d)$ which gives the vectors:

$(2x, 2z)$	weight 1
$(2x-\frac{1}{2}, \frac{1}{2})$	» 2
$(\frac{1}{2}, 2z-\frac{1}{2})$	» 2

By comparison with the maxima in $P(upw)$ the following coordinates were obtained:

$$x = 0.064 \qquad z = 0.226$$

All other coordinate possibilities can be transferred to these by shifting the coordinate system half a unit along one of the axes.

As it was possible to place the Tl-atoms in $Pnma$ it was first tried to solve the structure by means of this space group.

The Tl-atoms give no or at least only a very small contribution to the reflections $h1l, h3l, \dots$ and the y -coordinates must therefore be very close to $y = 0$ and $y = \frac{1}{2}$.

POSITIONS OF THE SULFATE GROUPS

The unit cell of the space group $Pnma$ has mirror planes in $y = \pm \frac{1}{4}$. As the distance between them is only 4.01 Å the SO_4 -groups cannot be situated between the planes, which would have required an interplanar distance not less than about 4.3 Å. The SO_4 -groups must then be in the mirror planes and the S-atoms and two of the four O-atoms of the SO_4 -group must be in point positions 4(c). The other two O-atoms must be outside the mirror planes and therefore have the same x and z parameters. In an electron density projection on this plane they should therefore give a maximum about 0.85 Å from the peak of the sulfur atom and of approximately the same height.

From the structure factors for the Tl-atoms, calculated with the above coordinates, all the signs of the intensities of the $h0l$ -reflections were determined and the projection of the electron density on the xz -plane, with the contribution from the Tl-atoms subtracted, was calculated.

$$\rho'(xpz) = \sum_h \sum_l [F_{\text{obs}}(h0l) - F_{\text{Tl}}(h0l)] \cos 2\pi(hx + lz)$$

F_{Tl} are the calculated structure factors for the Tl-atoms multiplied by the factor $\sum F_{\text{obs}} / \sum |f_{\text{Tl}} A_{\text{Tl}}|$. (The temperature factor obtained by means of the expression $F_{\text{obs}} = c \cdot F_{\text{calc}} \exp(-B \sin^2 \Theta / \lambda^2)$ was negligible. Probably the temperature factor is cancelled by the absorption effects).

Fig. 2 shows $\rho'(xpz)$. There are two double maxima in the projection:

$$\begin{array}{l} A \left\{ \begin{array}{ll} x = 0.236 & x = 0.162 \\ z = 0.343 & z = 0.367 \end{array} \right. \text{ (Distance 0.97 \AA)} \\ B \left\{ \begin{array}{ll} x = 0.374 & x = 0.440 \\ z = 0.382 & z = 0.397 \end{array} \right. \text{ (Distance 0.84 \AA)} \end{array}$$

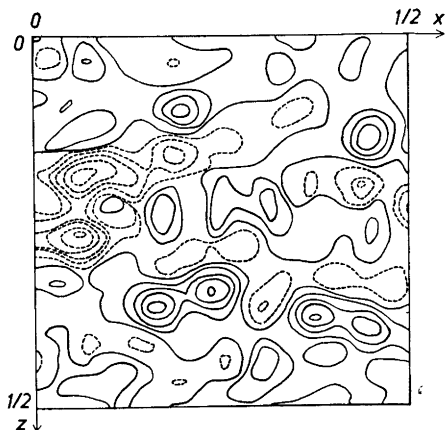


Fig. 2. The electron density projection $q'(xpz)$ calculated from the structure factors of the $h0l$ -reflections with the contribution from the thallium atoms subtracted. Dashed lines indicate negative regions.

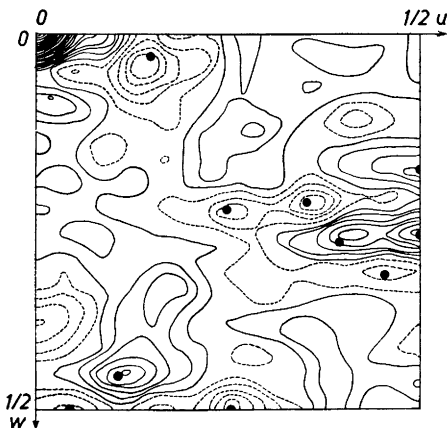


Fig. 3. The generalized Patterson projection $P_1(uw)$ calculated from the intensities of the $h1l$ -reflections. The dots indicate the positions of S-S-vectors.

The heights of the maxima are approximately the same and are also the same as might be expected for one sulfur or two oxygen atoms.

From purely geometrical reasons it is difficult to decide which of the maxima comes from the sulfur atom and which from the oxygen atoms, particularly as the coordinates obtained could be expected to be only approximate because of the influence of the heavy thallium atoms. It should, however, be possible to reduce the contribution from the two oxygen atoms relative to the sulfur atom by calculating a generalized Patterson projection $P_1(uw)$ from the intensities of the $h1l$ -reflections to which the Tl-atoms do not contribute:

$$P_1(uw) = \frac{1}{A} \sum_h \sum_l |F(h1l)|^2 \cos 2\pi(hu + lw)$$

The vectors in $P_1(uw)$ are equal to the vectors in the $(h0l)$ -projection multiplied by the factor $\cos 2\pi(y_1 - y_2)$. For vectors between atoms in the planes $y = \pm \frac{1}{4}$, *i.e.* the sulfur atoms, this will not reduce the size of the maxima but the signs for vectors between atoms in different planes will be negative. The maxima from vectors between atoms in the planes $y = \pm \frac{1}{4}$ and those oxygen atoms from the SO_4 -groups which are in the position $8(d)$ will be reduced to about half the magnitude they would have had in the $h0l$ -projection. Atoms in the planes $y = 0$ and $y = \frac{1}{2}$ will not contribute at all.

The vectors between the sulfur atoms must therefore have the largest relative contribution to $P_1(uw)$ and the corresponding maxima should be easily recognized.

Within the point position $4(c)$ the following two vectors occur with only one variable:

$$u = 2x - \frac{1}{2}, w = \frac{1}{2} \text{ (with negative sign)}$$

$$u = \frac{1}{2}, w = 2z - \frac{1}{2} \text{ (with positive sign)}$$

From Fig. 3 it can be seen that for both $u = \frac{1}{2}$ and $w = \frac{1}{2}$ there are two maxima which probably come from the S-atoms and from which the following parameters can be calculated:

$$x = 0.377 \qquad z = 0.383$$

$$x = 0.228 \qquad z = 0.340$$

A comparison with the coordinates obtained from $\rho'(xpy)$ shows that the parameters of the sulfur atoms must be:

$$\text{A } x = 0.228 \qquad \text{B } x = 0.377$$

$$z = 0.340 \qquad z = 0.383$$

By means of these values the other vectors between the sulfur atoms were calculated and Fig. 3 shows that they also occur in the projection with their correct signs. Because of the great number of vectors in the projection it cannot be used for determining the coordinates of other atomic positions.

The positions of the sulfate groups are now approximately determined as having the following parameters (the coordinates for the O-atoms in 4(c) have been obtained by assuming the dimensions of the SO_4 -group to be O—O = 2.4 Å and S—O = 1.5 Å):

$$\begin{array}{l} \text{SO}_4 \text{ (A) } 4 \text{ S in } 4(\text{c}) : x = 0.228 \quad y = 1/4 \quad z = 0.340 \\ \quad \quad \quad 8 \text{ O in } 8(\text{d}) : x = 0.162 \quad y = 0.10 \quad z = 0.367 \\ \quad \quad \quad 4 \text{ O in } 4(\text{c}) : x = 0.26 \quad y = 1/4 \quad z = 0.22 \\ \quad \quad \quad 4 \text{ O in } 4(\text{c}) : x = 0.33 \quad y = 1/4 \quad z = 0.41 \\ \\ \text{SO}_4 \text{ (B) } 4 \text{ S in } 4(\text{c}) : x = 0.377 \quad y = 3/4 \quad z = 0.383 \\ \quad \quad \quad 8 \text{ O in } 8(\text{d}) : x = 0.440 \quad y = 0.60 \quad z = 0.397 \\ \quad \quad \quad 4 \text{ O in } 4(\text{c}) : x = 0.33 \quad y = 3/4 \quad z = 0.27 \\ \quad \quad \quad 4 \text{ O in } 4(\text{c}) : x = 0.29 \quad y = 3/4 \quad z = 0.47 \end{array}$$

ELECTRON DENSITY PROJECTIONS OF THE LIGHT ATOMS

From the coordinates of the SO_4 -groups the signs of most of the $h1l$ -reflections were determined and the generalized electron density projection, $\rho_1(xz)$, was calculated:

$$\rho_1(xz) = - \int_0^1 \rho(xyz) \sin 2\pi y dy = \sum_h \sum_l F(h1l) \sin 2\pi(hx + lz)$$

In this projection the electron density at each point has been multiplied by $-\sin 2\pi y$ which means that the atoms in the planes $y = \pm 1/4$ will give the same contribution as in a $h0l$ -projection, with the exception of the signs, but atoms outside these planes will give smaller contributions and atoms in the planes $y = 0$ and $y = \frac{1}{2}$ will not be seen at all.

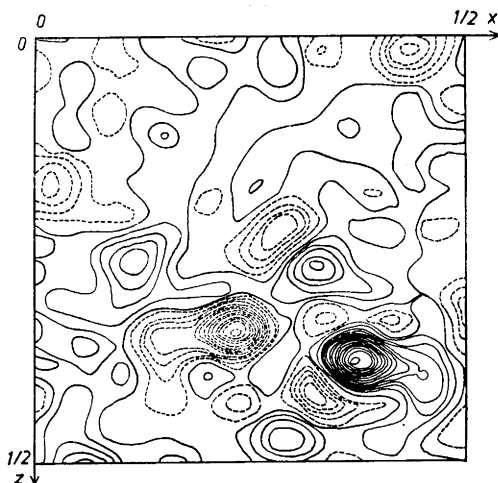


Fig. 4. The generalized electron density projection $\varrho_1(xz)$. The two large peaks come from the sulfur atoms; the negative peak (dashed lines) from S_A and the positive peak from S_B .

Fig. 4 shows the final result with all intensities from the $h1l$ -level included. The two largest maxima can be ascribed to the sulfur atoms and give the coordinates:

$$\begin{aligned} \text{A: } & x = 0.232 \quad z = 0.347 \quad (y = 1/4) \\ \text{B: } & x = 0.377 \quad z = 0.382 \quad (y = 3/4) \end{aligned}$$

Among the other maxima that can be seen in Fig. 4, the six maxima from the oxygen atoms of the sulfate groups can be identified in positions with coordinates which are in fair agreement with those calculated above.

A new projection $\varrho'_1(xz)$ with the S-atoms subtracted was now calculated:

$$\varrho'_1(xz) = \sum_h \sum_l [F_{\text{obs}}(h1l) - F_S(h1l)] \cdot \sin 2\pi(hx + lz)$$

This projection, which is shown in Fig. 5, was used for the final determination of the parameters of the oxygen atoms in the SO_4 -group:

$$\begin{aligned} \text{SO}_4 \text{ (A): } & 8 \text{ O}_1 \text{ in } 8(\text{d}) : x = 0.167 \quad y = 0.10 \quad z = 0.353 \\ & 4 \text{ O}_2 \text{ in } 4(\text{c}) : x = 0.324 \quad y = 1/4 \quad z = 0.424 \\ & 4 \text{ O}_3 \text{ in } 4(\text{c}) : x = 0.278 \quad y = 1/4 \quad z = 0.232 \\ \\ \text{SO}_4 \text{ (B): } & 8 \text{ O}_4 \text{ in } 8(\text{d}) : x = 0.439 \quad y = 0.60 \quad z = 0.390 \\ & 4 \text{ O}_5 \text{ in } 4(\text{c}) : x = 0.331 \quad y = 3/4 \quad z = 0.272 \\ & 4 \text{ O}_6 \text{ in } 4(\text{c}) : x = 0.299 \quad y = 3/4 \quad z = 0.473 \end{aligned}$$

The y -coordinates of O_1 and O_4 have been calculated from the dimensions assumed for a sulfate group. An approximate value can, however, be obtained from the electron density projection by a comparison between the heights of

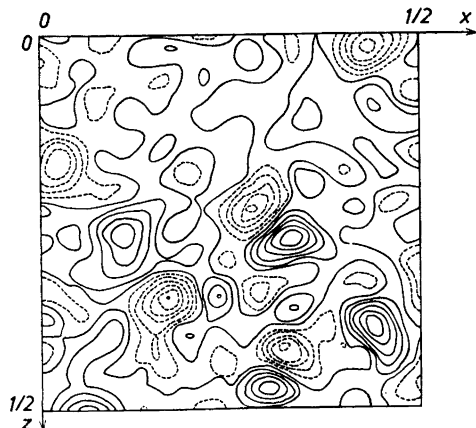


Fig. 5. The generalized electron density projection $\rho'_1(xz)$ calculated from the structure factors of the $h1l$ -reflections with the contribution from the sulfur atoms subtracted.

the peaks of O_1 and O_4 and the heights of the peaks of the oxygen atoms in the planes $y = \pm 1/4$, which gives the following values for the y -coordinates of O_1 and O_4 :

$$\begin{aligned} y &= 0.09_8 \text{ for } O_1 \\ y &= 0.59_8 \text{ for } O_4 \end{aligned}$$

This leads to a distance between these oxygen atoms of 2.4_4 \AA for both $SO_4(A)$ and $SO_4(B)$, which is the expected distance between the O-atoms of a sulfate group. This method of determination, however, is rather approximate. Some information about the accuracy can be obtained from the scatter of the heights of the 4-fold O-positions around the calculated mean. This gives a standard deviation of 0.013 in the y -coordinates of O_1 and O_4 .

In the electron density projection in Fig. 5 there are three further peaks of about the same height as for an oxygen atom in one of the planes $y = \pm 1/4$. The two maxima with the coordinates

$$\begin{aligned} x &= 0.024 & x &= 0.109 \\ z &= 0.170 & \text{and } z &= 0.267 \end{aligned}$$

cannot be ascribed to oxygen atoms outside the mirror planes as this would lead to a Tl—O distance less than about 1.2 \AA . Their y -coordinates must therefore be $1/4$ and $3/4$, respectively, which leads to the Tl—O distances 2.17 and 2.14 \AA . Each of these two oxygens (O_7 and O_8) is therefore in contact with two thallium atoms.

Of the thallium atoms no trace can be seen in Fig. 5 and their y -parameters must therefore be exactly or very nearly $y = 0$ and $y = \frac{1}{2}$.

The result of the analysis shows that, in addition to the 40 oxygen atoms that have already been found, there are at least 16 and probably 20 more

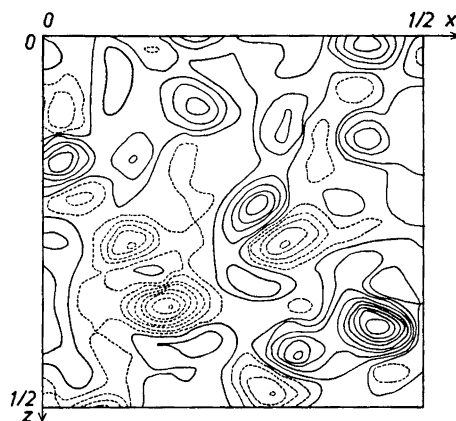


Fig. 6. The generalized electron density projection $\rho'_3(xz)$ calculated from the structure factors of the $h3l$ -reflections with the contribution from the sulfur atoms subtracted.

oxygen atoms in the unit cell. In the electron density projection in Fig. 2 there are, besides the maxima from the sulfate groups, two other maxima of about the same height. These might therefore correspond to two sets of oxygens (O_9 and O_{10}) in position 8(d).

Their coordinates are:

$$\begin{array}{l} x = 0.198 \text{ and } x = 0.447 \\ z = 0.099 \quad \text{»} \quad z = 0.142 \end{array}$$

In the electron density projection from the $h1l$ -reflections, Fig. 5, there are, however, no marked maxima corresponding to these positions, and the y -coordinates must therefore be close to $y = 0$ and $y = \frac{1}{2}$. This would give a $\text{Tl}-\text{O}$ distance of about 2.25 Å for O_9 and the rather short distance of 2.05 Å for O_{10} .

In order to obtain a more accurate value for the y -parameters the following electron density projection was calculated:

$$\rho'_3(xz) = \sum_h \sum_l [F_{\text{obs}}(h3l) - F_s(h3l)] \sin 2\pi(hx + lz)$$

This will give the same result as the corresponding projection from the $h1l$ -reflections with the exception that the electron density is now multiplied by $-\sin 6\pi y$ instead of $-\sin 2\pi y$. This will change only the signs of the maxima of the atoms in the planes $y = \pm 1/4$, but will greatly increase the maxima from atoms near — but not in — the planes $y = 0$ and $y = \frac{1}{2}$. The result is shown in Fig. 6. The projection is in the main the same as $\rho'_1(xz)$ in Fig. 5, but the maxima from the 8(d) atoms of the sulfate groups have increased by about the same factor as could be calculated from the relationship $\sin 6\pi y / \sin 2\pi y \approx 1.6$, and in the assumed positions for O_9 and O_{10} there are now marked maxima. From the heights of these maxima in relation to the heights of the maxima of the other oxygen atoms the following y -parameters can be calculated:

$$\text{O}_9 : y = -0.020 \quad \text{O}_{10} : y = -0.022$$

(An estimation of the accuracy of these parameter values, analogous to that for O_1 and O_4 , gives an approximate value for the standard deviation of about 0.003). The positions of the maxima in the xz -plane are:

$$\begin{array}{lll} O_9: & x = 0.203 & z = 0.097 \quad (\text{From the } h3l\text{-projection}) \\ & x = 0.198 & z = 0.099 \quad (\text{From the } h0l\text{-projection}) \end{array}$$

$$\begin{array}{lll} O_{10}: & x = 0.425 & z = 0.137 \quad (\text{From the } h3l\text{-projection}) \\ & x = 0.447 & z = 0.142 \quad (\text{From the } h0l\text{-projection}) \end{array}$$

In both the $h1l$ - and $h3l$ -projections (Figs. 5 and 6) there is also another maximum with the coordinates:

$$\begin{array}{lll} & x = 0.433 & z = 0.017 \quad (\text{From the } h1l\text{-projection}) \\ & x = 0.427 & z = 0.012 \quad (\text{From the } h3l\text{-projection}) \end{array}$$

This can be explained by assuming four oxygen atoms in the position 4(c). From space considerations this also seems very probable.

FINAL PARAMETERS

As the structure seems to be satisfactorily explained by means of the space group $Pnma$ no further investigation has been made with the space group $Pn2_1a$, which would also have been in accordance with the systematically absent reflections.

The positional parameters of the light atoms were refined by the method of least squares from the 82 observed $h1l$ -reflections, and independently from the 78 $h3l$ -reflections. The average values of the differences between the final parameters as calculated from the $h1l$ - and the $h3l$ -reflections, respectively, was 0.002 for the x -parameters and 0.001 for the z -parameters. The standard deviations in atomic coordinates calculated from the least squares residuals are 0.002 for S, 0.004 for O in 4(c), 0.003 for O_1 and O_4 , 0.007 for O_9 , and 0.005 for O_{10} . For the y -parameters of O_9 and O_{10} the standard deviation is 0.004 which is close to the estimation made above by comparing the heights of the maxima in the Fourier-projections. These values lead to standard deviations of about 0.06 Å for S—O and 0.07 Å for O—O distances except those involving O_9 and O_{10} for which the values are somewhat higher.

Assuming the SO_4 -group to be a regular tetrahedron a standard deviation of 0.04 Å in the S—O-distances can be calculated from the scatter around the average value of the $S_A—O_2$, $S_A—O_3$, $S_B—O_5$, and $S_B—O_6$ distances, which is close to the value calculated above. This would indicate that the estimation of the standard deviations from the least squares residuals is essentially correct in spite of the high absorption from the heavy Tl-atoms. However, the presence of these heavy atoms may introduce systematic errors that are not included in the calculations of the standard deviations and the accuracy may therefore be lower than the values indicate.

The final parameters are shown in Table 2. For the light atoms the average value of the parameters obtained from the $h1l$ - and the $h3l$ -reflections has been used. The y -parameters of O_1 and O_4 have been calculated assuming the $\text{O}_1\text{—O}_1$ and $\text{O}_4\text{—O}_4$ distances to be the same as the average value of the $\text{O}_2\text{—O}_3$ and $\text{O}_5\text{—O}_6$ distances.

Table 2. Final parameters.

		x	y	z
Tl:	8 Tl in 8(d):	0.064	0	0.226
$\text{SO}_4(\text{A})$:	4 S_A in 4(c):	0.235	1/4	0.346
	8 O_1 in 8(d):	0.164	0.09 ₉	0.361
	4 O_2 in 4(c):	0.323	1/4	0.428
	4 O_3 in 4(c):	0.286	1/4	0.232
$\text{SO}_4(\text{B})$:	4 S_B in 4(c):	0.376	3/4	0.382
	8 O_4 in 8(d):	0.441	0.59 ₉	0.393
	4 O_5 in 4(c):	0.328	3/4	0.273
	4 O_6 in 4(c):	0.299	3/4	0.469
OH^- :	4 O_7 in 4(c):	0.021	1/4	0.170
	4 O_8 in 4(c):	0.112	3/4	0.271
H_2O :	8 O_9 in 8(d):	0.193	0.982	0.096
	8 O_{10} in 8(d):	0.441	0.974	0.144
	4 O_{11} in 4(c):	0.432	1/4	0.018

From these parameters the structure factors which are listed in Table 4 were calculated assuming the temperature factor $B = 0$ for thallium and $B = 0.1 \text{ \AA}^2$ for the light atoms. For the calculation of the reliability index

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

shown below for different classes of reflections, only observed reflections have been included:

$h0l$:	$R = 0.16$
$h1l$:	$R = 0.13$ (no contribution from the Tl-atoms)
$h3l$:	$R = 0.11$ (» » » » »)
$0kl$:	$R = 0.20$
$1kl$:	$R = 0.12$

DESCRIPTION OF THE STRUCTURE

In the structure proposed each thallium atom is octahedrally surrounded by six oxygen atoms. There seems to be no significant difference between the six Tl—O distances (Table 3). The average value is 2.22 \AA which is close to the value 2.26 \AA found by Zachariassen⁵ for the Tl—O distances in Tl_2O_3 . Of the oxygen atoms in the TlO_6 -octahedron O_1 and O_4 also belong to a sulfate group and each of them is in contact with only one thallium atom. O_7 and O_8 are both in contact with two thallium atoms (Fig. 7) and Pauling's rule for

Table 3. Interatomic distances.

Within a TlO_6 -group:		
$\text{Tl}-\text{O}_1 = 2.21 \text{ \AA}$	$\text{O}_1-\text{O}_7 = 3.18 \text{ \AA}$	$\text{O}_4-\text{O}_9 = 3.21 \text{ \AA}$
$\text{O}_4 = 2.26$	$\text{O}_1-\text{O}_8 = 3.08$	$\text{O}_4-\text{O}_{10} = 3.10$
$\text{O}_7 = 2.19$	$\text{O}_1-\text{O}_9 = 3.39$	$\text{O}_7-\text{O}_9 = 3.17$
$\text{O}_8 = 2.16$	$\text{O}_1-\text{O}_{10} = 3.00$	$\text{O}_7-\text{O}_{10} = 3.33$
$\text{O}_9 = 2.26$	$\text{O}_4-\text{O}_7 = 3.07$	$\text{O}_8-\text{O}_9 = 3.01$
$\text{O}_{10} = 2.22$	$\text{O}_4-\text{O}_8 = 3.17$	$\text{O}_8-\text{O}_{10} = 2.97$
Within the SO_4 -groups:		
$\text{SO}_4(\text{A}):$	$\text{S}_\text{A}-\text{O}_1 = 1.51 \text{ \AA}$	$\text{O}_1-\text{O}_2 = 2.46 \text{ \AA}$
	$-\text{O}_2 = 1.49$	$\text{O}_1-\text{O}_3 = 2.50$
	$-\text{O}_3 = 1.53$	$\text{O}_2-\text{O}_3 = 2.44$
		$(\text{O}_1-\text{O}_1 = 2.43)$
$\text{SO}_4(\text{B}):$	$\text{S}_\text{B}-\text{O}_4 = 1.46 \text{ \AA}$	$\text{O}_4-\text{O}_5 = 2.37 \text{ \AA}$
	$-\text{O}_5 = 1.46$	$\text{O}_4-\text{O}_6 = 2.34$
	$-\text{O}_6 = 1.43$	$\text{O}_5-\text{O}_6 = 2.42$
		$(\text{O}_4-\text{O}_4 = 2.43)$
Short O—O distances:		
	$\text{O}_7-\text{O}_2 = 2.74 \text{ \AA}$	$\text{O}_8-\text{O}_5 = 2.69 \text{ \AA}$
	$\text{O}_9-\text{O}_2 = 2.78 \text{ \AA}$	$\text{O}_{10}-\text{O}_5 = 2.77$
	$\text{O}_9-\text{O}_4 = 2.65 \text{ \AA}$	$\text{O}_{10}-\text{O}_{11} = 2.70$
Other O—O distances less than 3.5 \AA :		
	$\text{O}_1-\text{O}_9 = 3.44 \text{ \AA}$	$\text{O}_4-\text{O}_9 = 3.13 \text{ \AA}$
	$\text{O}_2-\text{O}_4 = 3.19$	$\text{O}_5-\text{O}_9 = 3.31$
	$\text{O}_3-\text{O}_6 = 3.40$	$\text{O}_6-\text{O}_7 = 3.33$
	$\text{O}_3-\text{O}_7 = 3.39, 3.16$	$\text{O}_6-\text{O}_8 = 3.35$
	$\text{O}_3-\text{O}_9 = 2.95$	$\text{O}_6-\text{O}_{11} = 2.94$
	$\text{O}_3-\text{O}_{10} = 3.13$	$\text{O}_8-\text{O}_{11} = 3.07$
	$\text{O}_3-\text{O}_{11} = 3.19$	$\text{O}_9-\text{O}_{10} = 3.14$
	$\text{O}_4-\text{O}_4 = 3.39$	$\text{O}_{10}-\text{O}_{11} = 3.11$

the sum of the bond strengths⁶ therefore suggests that one hydrogen atom is probably bound to each of O_7 and O_8 . The remaining two oxygen atoms in the TlO_6 -group, O_9 and O_{10} , are in contact with only one thallium atom and it seems reasonable to assume that each of O_9 and O_{10} is associated with two hydrogen atoms. The oxygen atom, O_{11} , which is not in contact with any of the thallium atoms, must be a water of crystallization. These results of the structure determination show that the formula should probably be written $\text{Tl}_2(\text{OH})_2(\text{H}_2\text{O})_4(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

Chains of TlO_6 -octahedra running parallel to the b -axis can be distinguished in the structure; the thallium atoms within such a chain being joined together by means of O_7 , O_8 and the oxygens of the sulfate groups, O_1 and O_4 (Fig. 7). The shortest distance between two thallium atoms linked together in this way is 4.01 \AA . The different chains have no oxygens or sulfate groups in common. The packing of the atoms is shown in Fig. 8, which is a projection of half the unit cell on the zx -plane.

Water molecules in contact with cations with a high charge usually tend to form hydrogen bonds to surrounding oxygen atoms and it therefore seems reasonable to assume that in this structure the forces that hold the different

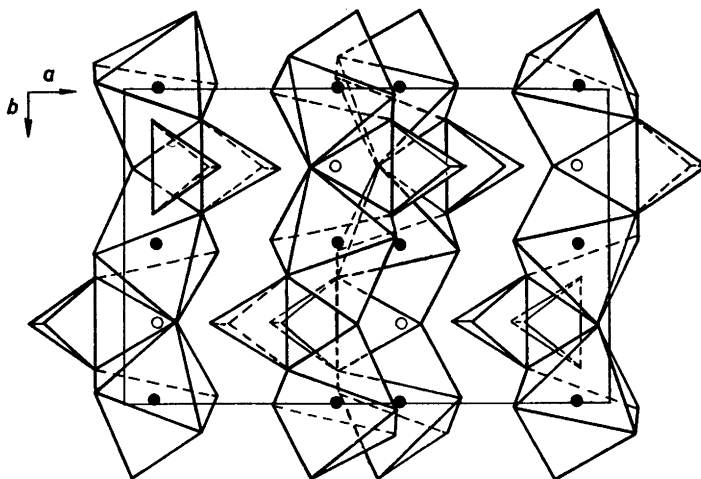


Fig. 7. Projection of the structure along the c -axis showing the chains of TlO_6 -octahedra running parallel to the b -axes. Filled circles indicate Tl-atoms; open circles indicate O_{11} -atoms.

chains together are hydroxyl bonds from the water molecules with O_9 and O_{10} and perhaps also from the oxygen atoms O_7 and O_8 . Among the interatomic distances listed in Table 3 there are also some short O—O-distances of about the length expected for a hydroxyl bond. The accuracy of the parameter values is probably not high enough definitely to distinguish these as being significantly shorter than a normal O—O-distance. However, each of O_7 and O_8 is involved in one and each of O_9 and O_{10} in two such short bonds, which is the same as

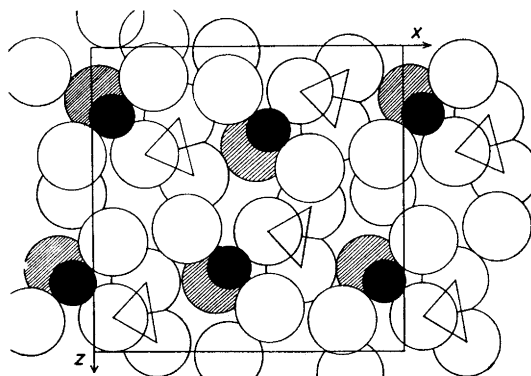


Fig. 8. Projection of half the unit cell on the xz -plane. Small circles represent thallium atoms and large circles oxygen atoms. Large shaded circles represent O_7 or O_8 .

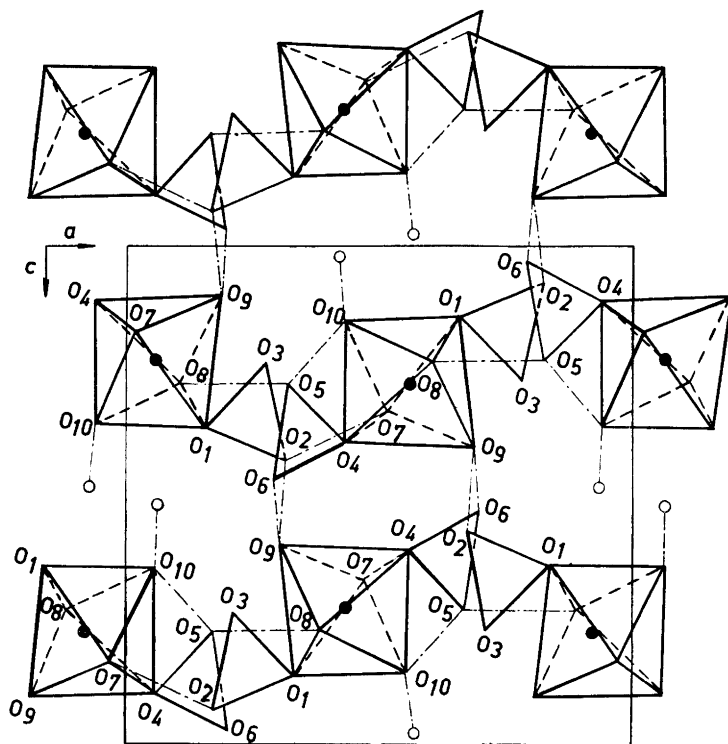


Fig. 9. Projection of the unit cell along the b -axis. The projection shows how the sulfate groups (represented as triangles) and the TiO_6 -octahedra are linked together. Lines marked -.-.-, between oxygen atoms represent short O—O distances which may indicate the presence of hydrogen bonds. Filled circles indicate Ti-atoms; open circles indicate O_{11} -atoms.

the number of hydrogen atoms that can be assumed to be associated with these oxygens. If hydroxyl bonds were present the arrangement around these oxygen atoms could be expected to be approximately tetrahedral. Except for O_{10} the deviations from an approximate tetrahedral arrangement do not seem so large as to make the assumption of hydrogen bonds unlikely and even if small parameter changes are assumed no other way of forming the hydrogen bonds seems to give a more plausible arrangement. The water molecule O_{11} is in contact with two O_{10} atoms at a distance of 2.70 Å. The angle $\text{O}_{11}-\text{O}_{10}-\text{O}_{11}$ is 110° , which is close to the tetrahedral angle 109° and therefore supports the assumption of a hydrogen bond between O_{10} and O_{11} . The other short distance in which O_{10} is involved is O_5-O_{10} but the angle $\text{O}_{11}-\text{O}_{10}-\text{O}_5$ is as large as 147° .

With the possible exception of O_5-O_{10} it therefore seems reasonable to assume that the short O—O distances listed in Table 3 and shown in the projection in Fig. 9

Table 4. Observed and calculated structure factors. The F_c and F_o -values are listed in groups in the following order: $h0l$, $0kl$, $1kl$, $h1l$, $h3l$. Structure factors belonging to more than one group are listed only once.

$h0l$	F_o	F_c	$h0l$	F_o	F_c
002	167	-312	3013	82	66
4	133	148	14	162	-146
6	172	-159	15	47	-43
8	169	134			
10	42	-26	400	127	-173
12	51	-43	1	203	-241
14	81	88	2	-	6
			3	230	310
101	37	65	4	12	-5
2	21	24	5	213	-242
3	93	-123	6	31	31
4	41	48	7	94	89
5	117	127	8	35	-25
6	97	-91	9	50	-29
7	229	-216	10	30	-15
8	129	105	11	-	-7
9	242	207	12	45	25
10	82	-61	13	71	67
11	179	-152			
12	64	50	501	20	6
13	140	122	2	96	-99
14	65	-60	3	72	69
15	119	-130	4	123	141
			5	59	-57
200	147	179	6	143	-164
1	144	-198	7	55	57
2	130	-190	8	179	168
3	148	214	9	101	-87
4	96	149	10	204	-194
5	104	-125	11	102	88
6	88	-90	12	185	166
7	82	73	13	61	-57
8	83	57	14	107	-120
9	36	-22			
10	30	6	600	184	-187
11	-	9	1	133	-156
12	50	-36	2	135	177
13	51	47	3	119	127
14	58	49	4	129	-145
15	78	-87	5	78	-83
			6	83	84
301	22	-14	7	78	75
2	74	-79	8	69	-65
3	85	-76	9	34	-13
4	117	166	10	-	14
5	78	83	11	-	-11
6	129	-190	12	30	27
7	55	-51	13	41	37
8	145	126	14	53	-61
9	63	57			
10	187	-168	701	37	-30
11	94	-74	2	51	-46
12	209	181	3	70	77
			4	63	58

Table 4. (Continued)

$h\ 0$	F_o	F_c	$h\ 0\ l$	F_o	F_c
7 0 5	126	-121	11 0 7	36	40
6	39	- 36	8	138	-144
7	172	187	9	60	- 62
8	45	53	10	139	173
9	181	-181	11	39	43
10	75	- 56			
11	164	148	12 0 0	-	12
12	57	50	1	163	167
13	128	-129	2	34	- 23
			3	160	-167
8 0 0	225	-265	4	29	20
1	28	19	5	135	123
2	172	190	6	-	3
3	-	- 14	7	64	- 66
4	177	-174	8	-	- 4
5	22	14	9	36	39
6	157	141			
7	-	- 14	13 0 1	23	- 20
8	73	- 69	2	40	49
9	-	- 6	3	-	- 19
10	-	1	4	76	- 95
11	-	- 6	5	65	70
12	38	35	6	86	120
			7	72	- 91
9 0 1	27	- 20	8	108	-124
2	50	55			
3	71	79	14 0 0	92	128
4	52	- 54	1	63	70
5	142	-128	2	90	-120
6	51	46	3	86	-113
7	163	180	4	75	112
8	85	- 81	5	71	108
9	155	-155	6	53	- 74
10	89	87			
11	140	140	15 0 1	53	43
12	51	- 73	2	-	0
			3	65	- 88
10 0 0	138	-143			
1	138	143	0 $k\ l$		
2	129	127	0 2 0	232	217
3	132	-130	2	293	-252
4	76	- 75	4	141	168
5	102	105	6	145	-159
6	51	51	8	73	71
7	88	- 90	10	-	4
8	57	- 51	12	46	- 41
9	37	27	14	67	88
10	33	20			
11	37	32	0 4 0	376	359
			2	347	-247
11 0 1	-	2	4	190	193
2	45	39	6	99	-133
3	-	15	8	73	85
4	84	- 93	10	34	- 25
5	34	- 26	12	47	- 31
6	144	141	14	50	86

Table 4. (Continued)

$0kl$	F_o	F_c	$1kl$	F_o	F_c
0 5 1	—	9	1 4 10	73	— 08
3	—	10	11	168	— 156
5	—	6	12	64	54
7	24	— 31	13	131	132
9	—	4			
11	47	30	1 5 1	—	3
13	—	— 8	2	—	0
			3	—	— 14
0 6 0	177	131	4	—	15
2	211	— 188	5	—	— 15
4	201	178	6	—	4
6	98	— 125	7	—	12
8	41	40	8	—	— 7
10	—	2	9	32	— 30
12	33	— 33			
			1 6 1	—	15
0 7 1	—	17	2	90	— 80
3	—	7	3	74	— 65
5	24	— 25	4	51	43
7	—	24	5	133	141
9	—	10	6	39	— 36
11	35	— 37	7	134	— 152
			8	53	60
0 8 0	220	248	9	144	151
2	178	— 174	10	76	— 76
4	88	125	11	134	— 153
6	68	— 103	12	60	70
8	51	78			
			1 7 1	—	10
0 10 0	68	132	2	—	— 27
			3	—	8
1 kl			4	—	— 3
			5	—	— 3
1 2 1	41	22	6	—	22
2	137	— 107	7	—	— 16
3	61	— 69	8	—	— 5
4	47	47	9	33	33
5	138	169	10	26	— 24
6	55	— 60			
7	174	— 205	1 8 1	33	33
8	76	81	2	—	3
9	195	197	3	77	— 79
10	87	— 81	4	31	33
11	162	— 158	5	79	94
12	81	72	6	59	— 59
13	166	147	7	113	— 135
14	71	— 66	8	62	71
15	106	— 125	9	114	150
1 4 1	54	36			
2	30	— 25	h 1 l		
3	119	— 105	0 1 1	—	— 5
4	58	46	3	—	4
5	131	134	5	24	27
6	60	— 56	7	48	— 43
7	129	— 171	9	—	— 5
8	79	86	11	55	42
9	164	168			

Table 4. (Continued)

hkl	F_o	F_c	hkl	F_o	F_c
13	—	— 2	5 1 1	14	— 12
15	31	— 26	2	—	— 5
			3	20	— 21
1 1 1	—	— 4	4	16	— 17
2	22	— 29	5	—	— 2
3	18	— 23	6	19	20
4	17	— 20	7	12	8
5	17	— 19	8	—	3
6	25	— 20	9	—	0
7	24	— 23	10	—	11
8	—	— 5	11	13	— 13
9	44	— 42	12	24	— 20
10	27	— 27	13	—	5
11	—	— 8	14	21	17
12	—	— 14			
13	24	— 21	6 1 0	—	— 8
			1	—	— 2
2 1 0	40	— 41	2	10	8
1	30	— 32	3	18	— 17
2	—	— 4	4	—	— 4
3	12	— 12	5	—	— 5
4	51	— 54	6	17	— 17
5	17	— 23	7	—	— 11
6	—	— 11	8	14	— 13
7	20	— 19	9	14	— 12
8	25	— 23	10	14	— 13
9	—	— 7	11	—	— 1
10	—	— 1	12	15	— 11
11	27	— 18			
12	24	— 18	7 1 1	—	— 3
13	—	— 10	2	—	— 10
14	—	— 9	3	—	— 3
			4	—	— 1
3 1 1	51	— 46	5	23	— 22
2	38	— 42	6	17	— 19
3	24	— 33	7	—	— 8
4	22	— 28	8	13	— 11
5	—	— 14	9	17	— 16
6	9	— 13	10	—	— 3
7	22	— 21	11	—	— 4
8	15	— 13	12	—	— 0
9	—	— 7	13	15	— 10
10	26	— 20			
			8 1 0	16	— 15
4 1 0	9	— 10	1	—	— 2
1	58	— 56	2	21	— 21
2	—	— 4	3	—	— 5
3	10	— 9	4	—	— 11
4	19	— 24	5	—	— 11
5	19	— 19	6	13	— 9
6	22	— 26	7	15	— 16
7	12	— 12	8	—	— 9
8	9	— 11	9	—	— 0
9	15	— 14	10	—	— 3
10	13	— 11	11	17	— 15

Table 4. (Continued)

hkl	F_o	F_c	hkl	F_o	F_c
9 1 1	—	3	1 3 12	—	— 1
2	13	10	13	18	— 12
3	—	7			
4	—	3	2 3 0	22	— 24
5	14	17	1	—	6
6	11	— 11	2	—	1
7	—	7	3	—	15
8	—	9	4	—	— 1
9	—	— 5	5	—	— 4
10	11	— 6	6	—	0
10 1 0	25	— 21	7	—	3
1	—	6	8	—	— 2
2	14	— 17	9	—	6
3	—	4	10	—	9
4	28	25	11	25	22
5	—	— 4	12	—	— 8
6	16	— 17	13	—	4
7	—	11	14	17	— 15
8	—	1	3 3 1	20	19
9	11	13	2	—	4
11 1 1	16	— 17	3	28	— 27
2	26	— 24	4	11	— 11
3	25	24	5	11	11
4	—	1	6	—	6
5	—	2	7	36	29
6	14	13	8	—	— 5
12 1 0	16	12	9	14	— 12
1	14	— 16	10	14	12
2	—	— 5	11	14	— 12
3	— 28	26	12	15	12
4	17	— 19	13	15	14
			4 3 0	36	— 34
hkl			1	55	62
0 3 1	19	16	2	13	— 14
3	30	24	3	—	5
5	17	— 13	4	—	— 2
7	16	15	5	32	— 31
9	19	— 14	6	—	— 1
11	32	— 26	7	17	— 15
13	25	21	8	17	— 14
			9	21	22
1 3 1	23	24	10	16	— 11
2	15	15	5 3 1	23	— 23
3	—	— 6	2	20	18
4	—	— 2	3	45	40
5	—	8	4	10	12
6	—	— 4	5	22	26
7	—	— 1	6	24	— 25
8	—	— 12	7	13	— 17
9	38	35	8	—	2
10	21	— 16	9	19	— 17
11	22	— 20	10	—	— 8

Table 4. (Continued)

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
5 3 11	16	13	8 3 4	25	31
12	16	13	5	—	7
6 3 0	18	— 14	6	—	14
1	27	— 30	7	31	33
2	—	— 8	8	—	4
3	—	— 9	9	—	6
4	22	20	10	—	10
5	25	24	11	28	— 24
6	18	18	9 3 1	—	— 3
7	—	1	2	32	— 38
8	21	— 22	3	—	— 8
9	29	— 29	4	—	— 7
10	19	— 16	5	14	— 15
11	—	— 1	6	25	30
12	16	14	10 3 0	43	43
7 3 1	—	7	1	—	— 9
2	—	7	2	—	13
3	17	— 18	3	—	— 9
4	17	— 19	4	43	— 44
5	18	20	5	—	4
6	18	16	6	19	20
7	21	22	7	—	— 4
8	27	33	8	13	12
9	28	— 21	11 3 1	16	16
10	—	0	2	25	26
11	—	— 8	3	16	— 13
12	19	— 21	4	—	— 6
8 3 0	12	— 13	5	—	— 10
1	—	— 14	6	—	— 14
2	13	— 16	7	—	— 6
3	31	— 27	8	13	11

indicate hydrogen bonds. However, the standard deviations of the parameters are too large for a definite conclusion in this respect.

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