

## The crystal structure of barium hydroxide octahydrate $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}^*$

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With 5 figures

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### Auszug

Die Kristalle des Bariumhydroxyd-Oktahydrats gehören der Raumgruppe  $P2_1/n$  an, die Elementarzelle mit  $a = 9,35 \text{ \AA}$ ,  $b = 9,28 \text{ \AA}$ ,  $c = 11,87 \text{ \AA}$  und  $\beta = 99^\circ$  enthält vier Formeleinheiten. Die Struktur wurde mittels zweidimensionaler Fourieranalysen bestimmt. Aus 1020 beobachteten Interferenzen aus acht Zonen ergab sich  $R = 0,124$ . Das Bariumion wird von acht Wasser-Sauerstoffatomen in Abständen zwischen  $2,69 \text{ \AA}$  und  $2,77 \text{ \AA}$  umgeben. Auf Grund von Atomabständen wird die Bindung von Wasserstoffatomen, durch welche die Sauerstoffatome miteinander verknüpft sind, diskutiert.

### Abstract

An x-ray analysis of the crystal structure of barium hydroxide octahydrate has been carried out by two-dimensional Fourier methods. The monoclinic crystals belong to the space group  $P2_1/n$  and have four formula units in a cell of dimensions  $a = 9.35 \text{ \AA}$ ,  $b = 9.28 \text{ \AA}$ ,  $c = 11.87 \text{ \AA}$  with  $\beta = 99^\circ$ . The  $R$  factor for 1020 visually observed reflections in eight zones is 0.124. The barium ion in this structure is found to be coordinated by eight water oxygens in the form of a slightly distorted Archimedean antiprism at distances between  $2.69 \text{ \AA}$  and  $2.77 \text{ \AA}$ . Based on the interatomic distances hydrogen bonds have been proposed, which link the oxygen atoms with one another utilising all the hydrogen atoms in the unit cell.

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### Introduction

The recent discovery<sup>1</sup> of the icosahedral, twelvefold coordination of oxygen atoms round the  $Ba^{2+}$  ion in  $Ba(ClO_4)_2 \cdot 3H_2O$  prompted the authors to undertake a systematic investigation of the geometry of coordination polyhedra in various barium compounds. The structure of  $Ba(OH)_2 \cdot 8H_2O$  was first taken up as it was conjectured that the coordination polyhedron might possibly be the Archimedean anti-prism. This geometrical figure<sup>2</sup> is formed by the eight water molecules<sup>3</sup> around the  $Sr^{2+}$  ion in tetragonal  $Sr(OH)_2 \cdot 8H_2O$  and has not been associated so far with the barium ion. GROTH<sup>4</sup> reports that although  $Ba(OH)_2 \cdot 8H_2O$  exhibits pseudo-tetragonal symmetry, it actually belongs to the monoclinic holohedral class with axial ratios  $a : b : c = 0.9990 : 1 : 1.2799$  and  $\beta = 98^\circ 56'$ . This investigation assumes further interest because, as WELLS<sup>5</sup> points out, very little is known about the structures of highly hydrated salts.

### Experimental

Colourless crystals of the substance were obtained by evaporating, under controlled conditions at ambient temperature, a saturated aqueous solution of  $Ba(OH)_2$  in a desiccator containing sulphuric acid and the crystals after growth were preserved in paraffin oil, these precautions being necessary to prevent the formation of the carbonate by exposure to the atmosphere. Most of the crystals separating out were tabular, but some were in the form of needles parallel to the [100] direction. A crystal of mean radius 0.15 mm was mounted inside a glass capillary along its needle axis and intensity data were recorded on multiple films for the  $Hkl$  zones ( $H = 0$  to 6) using  $CuK\alpha$  radiation. The equi-inclination Weissenberg technique was employed to photograph higher layers. Data were also collected by rotating the crystal about the direction of easy cleavage [110] as it was not possible to cut the crystal along any other prominent crystallographic direction.

<sup>1</sup> N. V. MANI and S. RAMASESHAN, The crystal structure of barium perchlorate trihydrate  $Ba(ClO_4)_2 \cdot 3H_2O$  and the crystal coordination of  $Ba^{++}$  ion. *Z. Kristallogr.* **114** (1960) 200–214.

<sup>2</sup> L. PAULING, The nature of the chemical bond. Cornell University Press, Ithaca, 1960, p. 544.

<sup>3</sup> H. G. SMITH, The crystal structure of strontium hydroxide octahydrate,  $Sr(OH)_2 \cdot 8H_2O$ . *Acta Crystallogr.* **6** (1953) 604–609.

<sup>4</sup> P. v. GROTH, *Chemische Krystallographie* **1** (1917) 119.

<sup>5</sup> A. F. WELLS, *Structural inorganic chemistry*. Clarendon Press, Oxford, 1962, p. 575.

The intensities of all the spots were estimated visually using calibrated intensity strips and were scaled up using WILSON's method, after applying the absorption correction ( $\mu r = 5.3$ ) for a cylindrical specimen and the Lorentz and polarisation factors.

### Crystal data

The cell dimensions of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  obtained from rotation and Weissenberg photographs are  $a = 9.35 \text{ \AA}$ ,  $b = 9.28 \text{ \AA}$  and  $c = 11.87 \text{ \AA}$ . The monoclinic angle computed by the level off-set method<sup>6</sup> is  $99^\circ$ . In addition to the systematic extinctions in the  $0k0$  and  $h0l$  reflections, when  $k$  and  $h+l$  are odd respectively, which indicate the space group to be  $C_{2h}^5 - P2_1/n$  (unique axis  $b$ ), the  $hkl$  spectra with  $h+k = 2n+1$  were also found to be systematically absent. It was further observed that the general  $hkl$  reflections satisfying the conditions

$$h+k+l = 2n, \quad l = 2n+1 \quad \text{and} \quad h+k+l = 2n+1, \quad l = 2n$$

were very weak.

Other crystal data are: Formula weight = 315.51; Melting point =  $78^\circ\text{C}$ ; Volume of the unit cell =  $1017 \text{ \AA}^3$ ; Density (calculated) =  $2.061 \text{ g/cm}^3$ ; Density (measured) =  $2.18 \text{ g/cm}^3$ ; Linear absorption coefficient for  $\text{CuK}\alpha$  radiation =  $35.5 \text{ mm}^{-1}$ ; Number of molecules in the unit cell = 4; Number of electrons per unit cell = 616.

Space group symmetry requires all the atoms to occupy general positions.

### Structure analysis

#### 1. $\rho(yz)$ projection

Out of 143 possible reflections in this zone 91 were of measurable intensity. A Patterson synthesis gave the barium coordinates as  $y = 0.15$  and  $z = 0.25$  in fractions of the cell edges. The signs of 67 amplitudes could be deduced by the heavy-atom method  $\left( \frac{Z_{\text{Ba}}^2}{\sum Z^2_{\text{other atoms}}} = 4.8 \right)$ , all the rest being the weak reflections mentioned earlier, to which barium made no contribution. The first Fourier synthesis showed eight peaks in addition to confirming the position of barium. To minimize the diffraction effects due to the heavy atom, another synthesis was computed using as Fourier coefficients, structure amplitudes from which the temperature-corrected barium contribu-

<sup>6</sup> M. J. BUEGER, X-ray crystallography. (John Wiley, New York, 1942) p. 375-377.

tions were subtracted. A structure-factor calculation putting ten oxygen atoms at the peaks gave an  $R$  value of 0.19 for the observed amplitudes. The atomic scattering factors for neutral barium were

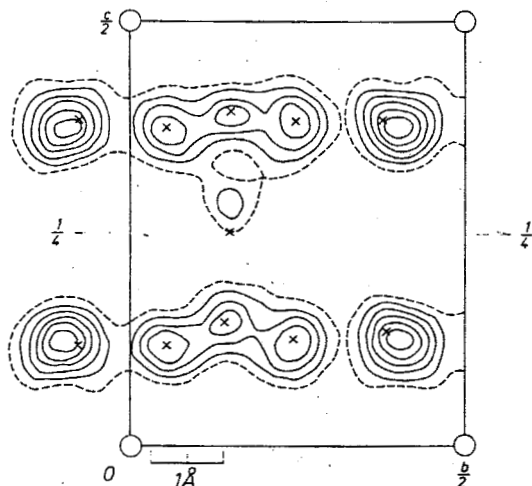


Fig. 1a.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Final barium-removed  $\rho(yz)$  Fourier synthesis with contours drawn at arbitrary intervals. Final atomic positions are indicated by crosses

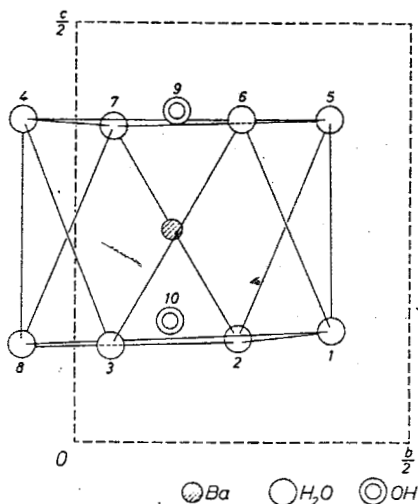


Fig. 1b.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Identification of atoms in the  $\rho(yz)$  projection. The antiprism coordination of water molecules round the barium ion is shown

taken from the paper of THOMAS and UMEDA<sup>7</sup>, while the values of BERGHUIS *et al.*<sup>8</sup> were used for oxygen.

At this stage the arrangement of water molecules and hydroxyl groups round the barium ion was not clear from the Fourier map. The close similarity in cell dimensions, variation in the intensities of spots, chemical properties and the results of Raman effect and infrared studies<sup>9</sup> of this compound and  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , however, suggested that the disposition of atoms might also be similar, even though the two compounds are not isomorphous.  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is tetragonal ( $D_{4h}^8 - P4/ncc$ ) with  $a = 9.00 \text{ \AA}$ ,  $c = 11.58 \text{ \AA}$  and four molecules in the unit cell. Therefore the arrangement of eight water molecules round the central  $\text{Ba}^{2+}$  ion in the form of an Archimedean antiprism appeared very probable. Small movements of oxygen atoms made in accordance with this model fitted the peaks in the Fourier map quite well, the axis of the antiprism being parallel to the  $c$  axis. A structure-factor calculation showed a fall of 0.03 in the  $R$  factor, thus supporting the above assumption.

An  $F_o - F_c$  synthesis was computed on the basis of which eight oxygen atoms were moved. A small movement of barium, which was also indicated, was made by trial so that the heavy atom made a suitable small contribution to the group of weak reflections. Many intense reflections appeared to be affected by secondary extinction and therefore a correction<sup>10</sup> was applied to the observed amplitudes. With these changes, the  $R$  index came down to 0.11. Attempts to refine the oxygen parameters further by the use of difference syntheses did not prove fruitful. The final barium-subtracted  $\rho(yz)$  Fourier synthesis is shown in Fig. 1*a*. The antiprism coordination of waters round barium is seen in Fig. 1*b*.

## 2. Determination of $x$ parameters

The data from the rotation about  $[110]$  was now taken up. This is a projection whose symmetry is  $\bar{1}$  and whose edges are  $(a + b)$  and  $c$ ,

<sup>7</sup> L. H. THOMAS and K. UMEDA, Atomic scattering factors calculated from the TFD atomic model. *J. Chem. Physics* **26** (1957) 293–303.

<sup>8</sup> J. BERGHUIS, IJBERTHA M. HAANAPPEL, M. POTTERS, B. O. LOOPSTRA, CAROLINE H. MACGILLAVRY, and A. N. VEENENDAAL, New calculations of atomic scattering factors. *Acta Crystallogr.* **8** (1955) 478–483.

<sup>9</sup> D. KRISHNAMURTI, Raman and infra-red spectra of some solid hydroxides. *Proc. Indian Acad. Sci.* **50A** (1960) 223.

<sup>10</sup> R. W. JAMES, The optical principles of the diffraction of x-rays. (Bell and Sons, London, 1954) p. 292.

with two formula weights in the asymmetric unit. The fact that  $hk0$  reflections having  $h + k = 2n + 1$  were absent suggested that the  $x$  coordinate of barium might be zero, and this was confirmed by a Patterson synthesis which gave the atomic coordinates of the two bariums in the asymmetric unit. The signs of almost all the 183 observed spots in this zone could be deduced and using these a Fourier synthesis and subsequently a heavy-atom-removed synthesis, shown in Fig. 2, were plotted. The  $(y-x)$  values for all the atoms could be obtained from this map. Knowing the  $y$  coordinates from the  $0kl$  projection and

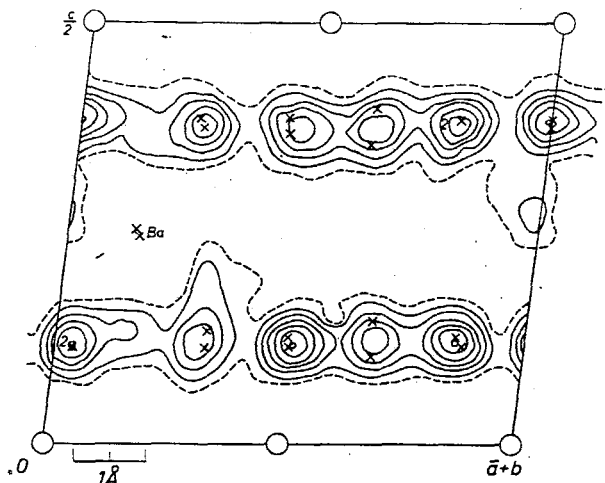


Fig. 2.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Barium-removed Fourier projection using data from rotation about  $[110]$ . Contours are drawn at arbitrary intervals. Final atomic positions are indicated by crosses

Table 1. Atomic coordinates for  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in fractions of the cell edges

Atom	$x$	$y$	$z$
Ba	0	0.148	0.252
$\text{O}_1(\text{H}_2\text{O})$	0.061	0.382	0.133
$\text{O}_2(\text{H}_2\text{O})$	-0.250	0.246	0.125
$\text{O}_3(\text{H}_2\text{O})$	0.196	0.056	0.117
$\text{O}_4(\text{H}_2\text{O})$	0.117	-0.079	0.383
$\text{O}_5(\text{H}_2\text{O})$	-0.061	0.378	0.385
$\text{O}_6(\text{H}_2\text{O})$	0.250	0.246	0.383
$\text{O}_7(\text{H}_2\text{O})$	-0.204	0.054	0.375
$\text{O}_8(\text{H}_2\text{O})$	-0.117	-0.079	0.117
$\text{O}_9(\text{OH})$	0.525	0.150	0.397
$\text{O}_{10}(\text{OH})$	0.476	0.142	0.148

Table 2. Observed and calculated structure factors for the *0kl* projectionThe calculated values are for one formula weight of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

The unobserved reflections are omitted in the table. The structure factors for the unobserved reflections have been computed; the calculated values are in all cases lower than the threshold values.

h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>
0 0 2	49.3	-52.0	0 6 8	10.8	8.0	1 1 4	28.6	27.5	1 5 1	29.6	32.7	1 11 0	9.5	- 6.9
4	20.6	- 7.9	9	10.1	8.9	5	33.6	-32.3	2	5.7	- 2.2	1	9.5	8.1
6	39.8	-40.6	10	12.3	-13.9	6	23.0	-21.2	3	33.6	-32.9	2	14.1	11.2
8	46.8	50.9	11	10.2	-11.3	7	22.9	24.8	5	31.3	29.4	3	13.4	-11.9
10	18.4	-17.9	12	11.4	13.2	8	16.6	16.2	6	- 5.6	5.1	4	12.4	-10.8
12	10.1	8.4	13	5.8	8.0	9	19.7	-20.4	7	27.2	-24.5	5	10.3	10.7
14	13.9	-15.1				10	14.9	-11.8	9	20.4	19.6			
			0 7 7	4.4	3.1	11	17.1	15.0	11	14.7	-15.1	2 0 $\overline{12}$	19.2	22.5
-0 1 8	8.4	- 8.2	9	5.0	- 3.0	12	10.2	9.5	13	12.4	12.4	$\overline{10}$	24.9	-25.4
10	3.4	1.9	11	3.8	0.5	13	11.8	-11.5				$\overline{8}$	23.6	28.3
13	3.0	- 1.3				14	8.1	- 8.7	1 6 $\overline{11}$	6.5	2.1	$\overline{6}$	32.3	-35.4
14	3.6	2.2	0 8 0	12.7	11.5				5	6.9	- 2.2	$\overline{4}$	40.5	44.0
15	2.5	0.6	1	23.0	-24.4	1 2 $\overline{12}$	10.1	6.6	11	5.6	3.2	$\overline{2}$	40.7	-49.2
			2	9.7	- 8.9	$\overline{10}$	6.0	3.6	12	4.9	3.3	0	14.5	30.5
-0 2 0	15.9	-12.4	3	16.6	13.8	$\overline{8}$	17.8	9.8				2	49.7	-48.1
1	49.7	-46.9	4	6.6	5.6	4	17.9	- 9.4	1 7 $\overline{12}$	13.0	14.2	4	42.1	42.8
2	14.7	13.9	5	14.8	-13.8	5	5.8	2.0	$\overline{10}$	15.9	-16.1	6	29.8	-32.2
3	44.0	45.4	6	7.0	- 6.1	6	8.1	2.6	$\overline{8}$	15.5	12.8	8	22.0	23.6
4	13.9	-13.0	7	17.0	17.8	7	5.3	1.9	10	6.9	- 5.4	10	20.3	-24.6
5	34.9	-36.9	8	7.1	7.1	8	9.5	- 6.7	$\overline{6}$	22.7	-20.0	12	17.6	22.7
6	10.1	8.8	9	15.3	-13.5	9	4.1	3.0	14	9.8	9.1	14	14.1	-13.4
7	24.6	25.7	10	5.1	- 5.5				$\overline{4}$	32.6	32.6			
8	6.5	- 6.3	11	7.9	8.4	1 3 $\overline{14}$	11.9	11.0	$\overline{2}$	26.8	-25.1	2 1 $\overline{14}$	5.4	- 2.4
9	20.7	-21.6				$\overline{13}$	9.9	9.2	0	17.6	14.1	$\overline{9}$	7.2	- 5.4
10	5.5	6.4	0 9 2	3.9	0.7	$\overline{12}$	14.9	-16.9	1	8.9	- 8.1	$\overline{8}$	11.5	6.7
11	15.4	20.0	7	2.8	- 1.1	$\overline{11}$	4.7	- 3.2	2	26.5	-25.4	$\overline{6}$	10.2	- 0.9
12	5.7	- 5.2	8	4.7	- 3.3	$\overline{10}$	21.9	22.8	3	10.7	9.9	$\overline{5}$	9.2	1.0
13	13.4	-14.3	9	2.2	1.3	$\overline{8}$	20.0	20.0	4	29.4	31.3	4	7.3	2.4
14	3.5	3.0	10	0.9	1.3	$\overline{7}$	16.7	18.4	6	20.2	-19.4	5	8.8	- 1.8
						$\overline{6}$	25.6	26.0	8	15.4	13.1	7	10.3	5.6
-0 3 5	3.9	- 0.2	0 10 0	19.8	-20.3	$\overline{5}$	27.5	28.6	9	6.6	- 5.5	8	11.6	- 7.2
7	6.7	- 5.1	2	15.7	14.7	$\overline{4}$	44.1	49.0	10	17.5	-15.2	10	6.6	2.4
9	6.0	4.4	4	12.2	- 9.7	$\overline{3}$	6.0	2.4	11	4.2	4.4	14	3.5	2.1
11	3.0	- 0.7	6	14.4	13.0	$\overline{2}$	50.1	46.9	12	7.3	13.0			
13	4.0	1.3	7	1.7	1.7	$\overline{1}$	15.6	- 7.4				2 2 $\overline{14}$	4.9	4.2
14	2.1	0.5	8	11.2	-13.2	0	28.6	-22.9	1 8 $\overline{9}$	4.9	- 0.6	$\overline{13}$	14.8	-21.1
						1	40.7	-38.7	10	3.5	1.6	$\overline{12}$	6.2	- 7.2
0 4 0	39.2	-34.1	1 0 $\overline{13}$	6.0	- 2.6	2	34.6	34.0				$\overline{11}$	18.5	-24.4
1	27.4	25.4	$\overline{11}$	7.2	3.8	3	34.0	31.5	1 9 $\overline{10}$	4.0	3.8	$\overline{10}$	8.4	7.1
2	34.5	32.4	$\overline{9}$	8.6	- 2.1	4	44.1	-48.4	$\overline{9}$	13.3	14.2	$\overline{9}$	21.3	20.3
3	17.6	-15.5	$\overline{7}$	9.5	0.8	5	7.0	4.6	$\overline{8}$	9.3	- 8.6	$\overline{8}$	10.2	- 5.8
4	24.0	-21.8	$\overline{5}$	7.3	- 5.1	6	34.0	32.9	$\overline{7}$	14.7	-13.6	$\overline{7}$	28.4	-26.5
5	14.9	15.3	7	5.7	1.1	8	23.6	-18.4	$\overline{6}$	10.7	10.9	$\overline{6}$	11.3	9.4
6	23.2	23.7	9	7.7	- 0.6	9	16.8	-17.3	$\overline{5}$	13.8	12.3	$\overline{5}$	35.1	42.4
7	15.0	-16.1	11	6.0	3.6	10	20.4	17.7	$\overline{4}$	8.8	- 6.4	$\overline{4}$	13.3	-14.6
8	19.4	-21.9	13	5.6	- 3.9	11	9.8	9.6	$\overline{3}$	18.8	17.6	$\overline{3}$	39.0	-45.2
9	10.9	11.1				12	16.7	-17.0	$\overline{2}$	7.5	5.1	$\overline{2}$	15.9	13.3
10	15.7	15.9	1 1 $\overline{14}$	10.0	- 9.7	14	13.4	12.9	$\overline{1}$	20.5	20.2	$\overline{1}$	36.6	38.9
11	8.1	- 8.1	$\overline{13}$	11.7	11.6				0	13.2	-12.0	0	15.1	- 9.9
12	11.4	-12.4	$\overline{12}$	9.7	9.4	1 4 $\overline{14}$	3.2	2.1	1	16.1	-14.6	1	39.7	-44.2
13	6.9	- 7.3	$\overline{11}$	16.6	-16.7	$\overline{13}$	3.6	3.6	2	13.7	13.2	2	15.9	12.4
14	8.7	9.3	$\overline{10}$	12.5	-11.6	$\overline{7}$	5.7	- 2.6	3	13.4	13.0	3	38.5	44.8
			$\overline{9}$	19.7	22.0	9	7.4	3.1	4	9.1	- 5.7	4	12.6	-12.7
0 5 6	4.1	- 1.2	$\overline{8}$	17.2	17.6	11	5.2	- 3.4	5	17.0	-17.3	5	32.7	-34.4
8	9.8	6.2	$\overline{7}$	23.1	-25.2	12	3.5	1.9	6	5.9	4.6	6	11.2	9.0
10	3.7	- 2.4	$\overline{6}$	23.7	-24.2	13	3.9	1.1	7	17.7	15.9	7	29.0	24.5
			$\overline{5}$	33.7	33.8				8	8.8	- 9.0	8	8.8	- 6.4
0 6 0	13.8	11.4	$\overline{4}$	31.3	27.9	1 5 $\overline{13}$	13.1	-12.1	9	11.2	- 9.4	9	25.8	-23.7
1	14.8	14.6	$\overline{3}$	45.0	-41.4	$\overline{11}$	15.0	15.4				10	9.2	6.5
2	24.7	-23.3	$\overline{2}$	28.8	-27.0	$\overline{9}$	18.6	-21.5	1 11 $\overline{6}$	5.7	9.5	11	19.7	22.2
3	25.0	-22.3	$\overline{1}$	27.9	37.6	$\overline{7}$	25.0	25.8	$\overline{5}$	10.2	-11.9	12	5.4	- 5.8
4	32.0	30.0	0	23.1	25.7	$\overline{5}$	33.6	-29.4	$\overline{4}$	12.1	-11.4	13	12.9	-15.6
5	20.0	18.9	1	34.7	-38.6	$\overline{3}$	33.5	33.1	$\overline{3}$	13.5	12.7	14	3.9	3.8
6	18.2	-15.8	2	32.9	-29.6	$\overline{2}$	8.8	5.1	$\overline{2}$	8.7	7.8			
7	11.6	- 9.5	3	45.8	40.1	$\overline{1}$	29.9	33.7	$\overline{1}$	10.1	- 8.2	2 3 $\overline{13}$	4.3	1.0

Table 2 (Continued)

k	k l	F <sub>o</sub>	F <sub>c</sub>	k	k l	F <sub>o</sub>	F <sub>c</sub>	k	k l	F <sub>o</sub>	F <sub>c</sub>	k	k l	F <sub>o</sub>	F <sub>c</sub>	
2	3 9	7.9	6.1	2	8 10	6.5	-5.3	3	1 9	23.5	-24.4	3	7 2	23.3	-20.0	
7	8.8	-5.7		9	17.4	17.4		10	10.7	-8.2		1	9.8	9.5		
13	5.1	2.2		7	6.9	8.1		11	15.3	17.0		0	23.4	24.8		
				7	17.7	-18.9		12	12.1	14.4		2	27.9	-27.2		
2	4 14	11.5	13.8	8	10.0	-9.8		13	9.9	-8.9		4	22.9	20.8		
13	5.7	-5.2		5	17.0	16.3		14	6.8	-9.9		5	13.6	-12.7		
12	9.8	-11.9		4	9.6	6.8		6	18.6	-18.6		2	11.3	14.4		
11	8.7	-9.7		3	21.9	-19.9		3	2 14	4.5	-2.7	7	4.4	5.5		
10	16.7	17.4		2	8.3	-7.1		12	7.7	5.5		8	20.7	19.3		
9	17.9	-20.1		1	24.2	26.0						10	16.0	-14.8		
8	27.9	-32.6		0	11.7	12.7		3	3 14	14.2	13.7		7	31.7	35.6	
7	17.0	16.4		1	21.6	-23.1		12	16.0	-16.5		3	9 9	11.2	11.0	
6	23.7	26.5		2	13.2	-12.0		11	7.6	-6.5		8	7.6	-5.5		
4	13.0	-10.2		3	18.1	17.0		10	19.5	20.6		7	15.3	-14.3		
3	18.3	19.3		4	8.8	5.6		9	10.9	7.9		6	7.8	7.2		
2	31.8	32.1		5	21.3	-19.1		8	23.7	-24.1		5	19.0	19.2		
1	34.9	-38.5		6	7.8	5.6		7	10.7	-10.5		4	12.8	-11.2		
0	48.2	-56.1		7	17.0	18.6		6	29.4	30.7		3	18.0	-17.2		
1	20.6	18.5		8	9.1	8.7		5	11.8	12.6		2	9.2	9.8		
2	25.4	29.9		9	14.7	-14.2		4	34.6	-38.0		1	13.4	12.8		
3	8.8	-4.9		10	6.6	-7.5		3	13.5	-12.2		0	8.0	-6.7		
4	14.5	-11.2						2	50.1	34.5		1	17.1	-16.6		
5	19.5	20.1		2	9 9	4.3	1.8	1	11.3	11.7		4	4 14	10.6	13.4	
6	29.4	25.5		8	4.6	-2.8		0	26.5	-31.4		13	5.2	-0.5		
7	25.5	-21.9		9	4.7	2.0		1	11.4	-15.3		3	18.0	20.4		
8	29.0	-28.6						2	32.0	37.0		4	11.2	-11.0		
9	13.0	9.0		2	10 8	10.3	-10.7	3	15.6	12.8		5	18.1	-15.3		
10	14.9	16.6		8	17.4	16.3		4	33.1	-34.9		6	8.0	7.5		
11	8.0	-7.0		4	20.1	-20.4		5	15.9	-10.8		7	13.1	10.7		
12	11.5	-11.3		2	15.7	17.5		6	27.8	26.6		8	6.5	-5.1		
13	8.8	10.5		2	15.7	-15.4		7	11.4	9.4						
				2	17.1	18.9		8	23.7	-22.0		3	11.5	8.5	-11.9	
2	5 8	7.7	-6.8	4	18.4	-19.4		9	5.3	-4.3		4	10.8	-11.5		
8	6.6	6.1		5	4.3	-5.7		10	20.3	18.4		3	11.6	11.3		
10	5.4	-2.8		6	14.8	14.1		12	15.9	-14.3		2	11.0	9.3		
				7	2.7	2.9		13	6.3	-5.0		1	11.9	-8.5		
2	6 13	5.9	-7.1									0	11.0	-7.9		
12	9.5	11.0		3	0 13	7.8	-6.6	3	4 14	4.7	1.7	1	11.8	10.3		
11	8.7	12.3		11	5.1	0.9		12	6.0	-3.0		2	11.8	10.2		
10	11.4	-12.3		9	5.8	2.7		11	7.8	-4.0		3	11.1	-12.1		
9	16.0	-17.3		7	5.8	4.9						4	6.5	-10.9		
8	20.3	20.9		5	10.2	-8.9		3	5 13	10.9	-12.2	4	0 12	15.8	17.8	
7	15.4	13.3		3	9.1	5.8		11	17.3	16.9		10	24.2	-25.8		
6	24.5	-22.5		11	8.9	5.7		9	22.4	-23.1		8	32.8	33.7		
5	11.9	-9.5						7	25.5	25.8		6	28.2	-29.0		
4	16.3	14.2		3	1 14	6.4	-4.5	8	5.8	-5.8		4	26.5	27.9		
3	21.4	21.6		13	14.6	16.8		5	31.4	-28.0		2	28.3	-47.8		
2	21.1	-20.7		12	13.0	13.3		4	5.8	-6.5		0	31.3	53.3		
1	30.4	-29.7		11	14.5	-14.0		3	33.5	31.0		2	28.3	-32.7		
0	32.2	34.1		10	19.0	-22.0		2	12.8	11.6		4	28.8	27.7		
1	17.3	16.7		9	13.3	-13.8		1	27.4	-31.4		6	34.2	-31.9		
2	22.5	-24.3		8	9.0	9.8		1	28.1	30.8		8	27.3	27.0		
3	12.4	-9.9		7	29.0	-32.4		3	30.3	-30.6		10	16.2	-20.4		
4	12.3	11.9		5	37.3	45.4		5	30.0	27.3		12	13.0	17.7		
5	19.2	19.6		4	32.2	40.4		7	24.7	-23.0						
6	19.4	-19.4		3	18.3	-22.7		9	18.4	18.9		4	1 14	5.9	-3.1	
7	19.3	-19.0		2	27.2	-44.4		11	17.6	-14.5		9	7.1	-5.1		
8	20.6	21.6		1	12.1	15.7						8	8.1	6.2		
9	13.2	10.0		1	31.9	-48.6		3	7 12	11.4	12.3		6	21.7	-20.0	
10	15.3	-13.8		2	6.2	-9.6		11	7.0	-7.8		4	2 14	6.8	7.5	
11	9.0	-8.4		3	33.6	46.9		10	16.4	-13.8		13	12.3	14.7		
12	8.0	8.5		4	32.5	39.5		9	5.7	7.4		11	17.0	-19.7		
				5	17.9	-17.9		8	19.9	19.5		9	29.9	31.4		
2	7 11	4.3	1.8	6	26.7	-27.0		6	25.8	-24.8		8	13.7	-13.3		
				7	18.7	16.5		4	25.2	23.0		7	28.0	-29.1		
2	8 11	11.4	-12.9	8	5.7	5.6		3	17.8	-20.0		6	13.2	15.1		



Table 2 (Continued)

h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>
4 6 2	22.2	20.7	5 1 $\bar{10}$	14.1	-16.6	5 5 $\bar{17}$	20.4	-27.7	6 0 2	38.1	-43.8	6 5 $\bar{12}$	4.6	-1.5
3 17.6	-15.2	$\bar{9}$	24.2	25.5	$\bar{11}$	21.6	25.1	4	35.2	33.9	4	75.2	33.9	
4 18.4	17.6	$\bar{8}$	17.2	18.3	$\bar{9}$	18.1	-15.3	6	23.4	-16.8	6 6 $\bar{12}$	11.2	4.1	
5 16.0	16.1	$\bar{7}$	24.2	-27.0	$\bar{7}$	28.9	25.6	8	22.5	20.4	$\bar{11}$	14.8	13.4	
6 17.1	-17.0	$\bar{6}$	23.3	-20.9	$\bar{5}$	42.3	-45.7	10	26.2	-27.6	$\bar{10}$	18.0	-18.0	
7 14.7	-13.3	$\bar{5}$	24.1	27.1	$\bar{3}$	35.0	31.8	6 2 $\bar{13}$	17.9	17.9	$\bar{9}$	76.9	-17.5	
8 16.4	15.3	$\bar{4}$	15.5	21.6	$\bar{1}$	14.9	11.6	$\bar{12}$	7.1	-6.9	$\bar{8}$	20.6	22.8	
9 10.9	11.0	$\bar{3}$	23.0	-30.2	-1	33.3	31.8	$\bar{11}$	19.2	-19.6	$\bar{7}$	15.8	12.0	
10 13.4	-12.8	$\bar{2}$	9.0	-21.2	3	44.0	-46.8	$\bar{10}$	11.7	11.5	$\bar{6}$	15.3	-12.6	
11 9.8	-10.4	$\bar{1}$	12.7	31.2	5	28.9	25.6	$\bar{9}$	28.4	29.7	$\bar{5}$	10.0	-8.6	
4 7 $\bar{11}$	5.4	2.3	0	14.6	22.6	7	20.9	-14.3	$\bar{8}$	25.7	-27.6	$\bar{4}$	16.2	12.0
$\bar{9}$	7.8	-3.8	1	17.3	-29.5	9	21.6	25.2	$\bar{7}$	25.7	-27.6	$\bar{3}$	20.6	19.3
7	7.1	4.8	2	20.9	-22.8	11	19.9	-26.6	$\bar{5}$	17.0	17.3	$\bar{2}$	29.7	-28.0
4 8 $\bar{10}$	4.0	1.7	3	24.1	27.9	4	18.3	19.0	$\bar{4}$	9.1	-12.9	$\bar{1}$	23.6	-24.8
$\bar{9}$	19.0	16.1	4	18.3	19.0	5 7 $\bar{10}$	22.1	-21.9	$\bar{3}$	18.7	-30.5	0	25.6	27.3
$\bar{8}$	8.0	9.8	5	29.6	-27.5	$\bar{8}$	24.1	23.4	$\bar{2}$	10.9	18.7	1	17.8	13.3
$\bar{7}$	15.6	-15.7	6	17.2	-17.3	$\bar{6}$	27.7	-24.1	$\bar{1}$	23.8	46.3	2	14.3	-10.8
$\bar{6}$	11.5	-13.5	7	25.8	24.3	$\bar{4}$	29.8	26.4	0	5.6	-3.6	3	12.1	-8.4
$\bar{5}$	18.0	17.4	8	18.1	17.2	$\bar{2}$	30.6	-27.0	1	21.3	-29.9	4	19.2	13.4
$\bar{3}$	21.7	-21.9	9	16.7	-18.6	0	28.3	27.7	3	20.0	16.7	5	20.1	16.6
$\bar{1}$	23.5	22.0	10	14.3	-14.2	1	11.5	-9.2	4	14.3	-13.5	6	22.9	-22.9
0	14.2	15.0	11	15.0	16.1	2	23.8	-25.4	5	29.8	-27.0	7	17.3	-17.3
1	19.9	-18.1	12	12.2	10.5	4	28.6	23.7	7	29.8	30.6	8	20.1	17.0
2	13.0	-13.9	5 2 12	6.0	-5.5	6	25.3	-24.5	9	18.9	-19.7	9	12.5	10.0
3	19.0	18.3	8	21.2	22.3	8	21.2	22.3	11	17.5	13.0	6 7 9	4.2	5.6
5	19.3	-19.4	9	8.7	-7.3	9	8.7	-7.3	6 4 $\bar{13}$	9.1	-10.6	6 8 9	15.3	14.7
6	6.0	-3.6	5 3 $\bar{13}$	8.8	8.1	12	18.5	-22.0	$\bar{12}$	13.8	-16.3	$\bar{8}$	7.5	4.3
7	14.7	15.4	13	21.7	26.2	5 9 8	11.7	-10.4	$\bar{11}$	10.4	13.2	$\bar{7}$	23.2	-19.6
8	8.9	10.5	10	21.7	26.2	$\bar{7}$	17.3	-16.3	$\bar{10}$	18.1	16.4	$\bar{6}$	21.7	20.3
9	11.2	-12.3	9	11.6	7.7	$\bar{6}$	11.7	14.6	9	13.4	-11.4	$\bar{5}$	16.1	12.6
4 9 8	4.4	3.5	8	21.0	-24.4	$\bar{5}$	22.3	23.7	$\bar{8}$	22.4	-21.3	$\bar{4}$	18.6	-18.1
4 10 6	14.3	13.0	7	17.3	-21.9	$\bar{4}$	12.7	-10.7	$\bar{7}$	14.8	10.8	$\bar{3}$	13.6	-12.9
$\bar{4}$	14.4	-11.6	6	29.8	28.0	$\bar{3}$	23.0	-23.2	$\bar{6}$	21.0	24.5	$\bar{2}$	19.2	19.9
$\bar{2}$	20.8	21.0	5	13.3	13.2	$\bar{2}$	8.6	6.5	$\bar{5}$	14.9	-15.5	0	6.0	4.4
0	21.3	-22.7	4	34.2	-37.2	$\bar{1}$	17.4	15.8	$\bar{4}$	23.2	-21.6	3	23.1	-21.6
2	15.6	12.9	3	27.3	34.1	0	13.6	-12.0	$\bar{3}$	20.5	19.2	1	25.3	19.3
4	12.2	-11.4	2	9.1	10.5	1	18.7	-18.4	$\bar{2}$	22.6	23.1	4	13.5	12.4
5 0 $\bar{13}$	13.2	-8.0	0	22.4	-27.1	2	16.1	15.7	$\bar{1}$	17.4	-15.7	5	20.5	-15.8
$\bar{11}$	7.5	3.4	1	18.9	-26.0	3	22.3	24.8	0	24.9	-28.2	6	11.8	-9.4
$\bar{5}$	13.0	-7.9	2	31.0	31.6	4	9.6	-9.5	2	23.4	25.1	7	13.9	15.5
3	9.4	5.8	4	36.4	-34.4	5	19.9	-20.7	3	16.6	-15.3	4	23.4	-19.3
5 1 $\bar{13}$	13.0	15.0	6	32.1	27.9	6	9.2	6.2	4	23.4	-19.3	6 10 $\bar{4}$	15.2	-17.6
$\bar{12}$	12.5	13.1	7	14.3	10.5	6 0 $\bar{12}$	20.9	27.0	5	17.7	15.4	$\bar{2}$	21.8	18.9
$\bar{11}$	19.8	-19.1	8	23.0	-21.9	$\bar{10}$	19.7	-17.0	6	25.9	18.6	0	21.5	-18.5
			9	12.0	-12.9	$\bar{8}$	21.1	18.5	7	15.8	-11.2	2	15.8	16.9
			10	18.5	20.5	$\bar{6}$	33.0	-39.4	8	21.3	-19.9			
			12	16.9	-19.8	$\bar{4}$	24.5	41.2	9	10.7	9.9			
			5 4 $\bar{13}$	10.5	8.0	$\bar{2}$	7.4	-22.0	10	15.4	17.5			
			11	9.4	-6.5	0	12.3	28.4						

making use of the antiprism model, the  $x$  coordinates of the atoms could be deduced. However, these were not very accurate due to the overlap of two atoms at each peak in the electron-density map. A difference synthesis which was made proved difficult to interpret for the same reason. The  $R$  factor for the observed reflections in this zone at this stage was 0.14.

A Fourier synthesis using  $F(hk0)$  coefficients was made utilizing 31 coefficients picked out from the general  $hkl$  data. Small movements of oxygen atoms, mainly the  $x$  parameters, were made

Table 3. Observed and calculated structure factors for the projection down [110]  
 The calculated values are for two formula weights of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  which are contained in the  
 asymmetric unit in this projection.

$$h' = h + k = 0, \quad k' = -h + k, \quad l' = l$$

$k' l'$	$ F_o $	$F_c$	$k' l'$	$ F_o $	$F_c$	$k' l'$	$ F_o $	$F_c$	$k' l'$	$ F_o $	$F_c$	$k' l'$	$ F_o $	$F_c$
0 2	90.4	- 97.1	2 $\overline{12}$	9.4	- 9.6	3 $\overline{2}$	62.4	70.6	4 10	28.1	28.1	6 0	37.2	41.6
4*	45.0	- 15.9	$\overline{11}$	35.6	- 37.4	$\overline{1}$	25.9	27.1	11	17.9	- 19.4	1	35.5	39.2
6	75.6	- 81.7	$\overline{10}$	16.3	11.4	0	60.1	- 61.6	12	22.9	- 29.5	2	37.2	- 43.6
8	97.7	102.3	$\overline{9}$	49.8	41.6	1	22.9	- 23.0	13	15.0	17.1	3	24.8	- 30.5
10	39.8	- 36.3	$\overline{8}$	14.1	- 11.7	2	55.6	65.8	14	13.6	19.6	4	16.9	18.2
12	21.9	17.1	$\overline{7}$	52.9	- 45.4	3	21.5	23.5	5 $\overline{11}$	23.3	28.8	5	15.5	13.3
14	29.6	- 30.1	$\overline{6}$	18.7	17.5	4*	50.1	- 72.8	$\overline{10}$	< 3.8	- 1.6	6	15.7	- 18.0
1 $\overline{14}$	14.7	- 15.5	$\overline{5}$	60.3	64.5	5	18.8	- 24.8	$\overline{9}$	29.8	- 30.7	7	15.0	- 18.0
$\overline{13}$	22.4	21.3	$\overline{4}$	24.5	- 25.2	6	43.5	57.7	$\overline{8}$	< 5.6	- 1.1	8	24.8	32.3
$\overline{12}$	18.4	17.9	$\overline{3}$ *	64.6	- 85.6	7	18.7	19.7	$\overline{7}$	27.8	19.1	9	19.5	25.0
$\overline{11}$	33.4	- 28.3	$\overline{2}$	25.2	23.9	8	44.6	- 44.5	$\overline{6}$	< 5.0	2.9	10	22.0	- 24.0
$\overline{10}$	28.8	- 22.5	$\overline{1}$	81.8	- 82.5	9	17.5	- 14.8	$\overline{5}$	39.4	- 37.2	11	15.1	- 17.6
$\overline{9}$	34.3	39.2	0	28.5	- 20.5	10	35.4	37.2	$\overline{4}$	< 7.7	- 4.9	7 $\overline{6}$	26.2	- 26.7
$\overline{8}$	31.7	30.9	1	78.5	- 76.3	11	15.2	12.0	$\overline{3}$	58.8	71.9	$\overline{5}$	5.5	6.0
$\overline{7}$	38.7	- 48.5	2	28.9	25.8	12	24.2	- 28.7	$\overline{2}$	< 8.0	2.0	$\overline{4}$	24.6	26.5
$\overline{6}$	40.0	- 42.4	3	86.5	91.5	13	8.1	- 9.0	$\overline{1}$	51.3	- 50.7	$\overline{3}$	7.2	- 4.0
$\overline{5}$	61.5	63.0	4	25.1	- 28.8	14	21.0	22.1	0	< 8.2	- 0.2	$\overline{2}$	25.7	- 26.9
$\overline{4}$	54.3	54.4	5*	59.6	- 81.7	4 $\overline{12}$	21.8	- 23.3	1	25.1	18.8	$\overline{1}$	7.9	6.5
$\overline{3}$	63.8	- 79.8	6	18.9	19.1	$\overline{11}$	18.8	19.5	2	< 9.4	5.1	0	26.8	31.9
$\overline{2}$	58.2	- 57.1	7	56.7	49.6	$\overline{10}$	26.6	30.7	3	46.0	- 51.1	1	5.8	- 10.4
$\overline{1}$	71.5	71.9	8	18.2	- 10.6	$\overline{9}$	18.6	- 18.8	4	< 8.0	- 5.8	2	28.3	- 35.4
0	62.9	53.3	9	45.5	- 36.4	$\overline{8}$	28.8	- 25.6	5*	47.7	70.3	3	5.7	8.3
1	84.4	- 73.7	10	15.5	12.4	$\overline{7}$	20.2	14.1	6	< 7.7	0.8	4	23.0	27.9
2	65.5	- 53.8	11	37.2	42.0	$\overline{6}$	35.9	30.4	7	28.8	- 37.3	5	5.3	- 4.0
3	73.9	81.5	12	12.5	- 12.7	$\overline{5}$	33.7	- 25.6	8	< 7.0	- 0.6	6	21.0	- 23.7
4	63.8	56.8	13	25.7	- 34.5	$\overline{4}$	48.6	- 51.8	9	22.8	20.9	7	4.5	4.6
5	72.5	- 66.2	14	6.5	7.0	$\overline{3}$	39.8	40.6	10	< 5.6	3.8	8	23.9	28.0
6	56.9	- 48.5	15	16.5	16.9	$\overline{2}$	57.3	58.7	11	22.9	- 30.9	8 $\overline{5}$	16.6	- 18.4
7	52.3	49.3	3 $\overline{13}$	10.6	8.4	$\overline{1}$	32.8	- 32.4	12	< 3.8	- 2.8	$\overline{2}$	8.4	- 9.0
8	38.1	34.8	$\overline{12}$	27.8	- 23.5	0	36.6	- 43.9	13	20.2	27.8	$\overline{1}$	22.9	20.6
9	43.2	- 41.8	$\overline{11}$	10.9	- 9.2	1	23.1	22.8	6 $\overline{9}$	14.0	- 12.6	0	11.3	10.9
10	25.0	- 21.7	$\overline{10}$	36.7	42.2	2	37.2	47.1	$\overline{8}$	25.1	22.5	1	24.1	- 24.5
11	34.9	31.0	$\overline{9}$	14.5	12.8	3	30.4	- 34.6	$\overline{7}$	21.2	23.6	2	10.0	- 10.2
12	19.8	25.0	$\overline{8}$	44.6	- 39.8	4	47.1	- 58.7	$\overline{6}$	30.3	- 31.8	3	20.1	23.3
13	22.0	- 21.6	$\overline{7}$	19.6	- 17.1	5	31.7	39.1	$\overline{5}$	23.8	- 24.1	4	8.5	9.2
14	15.2	- 17.6	$\overline{6}$	49.7	49.0	6	34.5	46.9	$\overline{4}$	22.7	26.5	5	16.8	- 20.2
15	14.2	18.2	$\overline{5}$	27.8	20.3	7	20.0	- 23.0	$\overline{3}$	17.5	12.8	6	7.0	- 9.5
2 $\overline{14}$	6.7	5.5	$\overline{4}$	53.6	- 65.2	8	26.6	- 28.3	$\overline{2}$	20.1	- 16.3			
$\overline{13}$	24.2	24.0	$\overline{3}$	23.9	- 25.0	9	16.6	15.6	$\overline{1}$	24.2	- 20.8			

so as to satisfy the electron-density map as well as standard interatomic distances. The  $F_c$ 's were calculated at each stage to verify the appropriateness of the movements.

Further refinement of the structure was not undertaken in any projection for lack of suitable computational facilities. The final atomic coordinates for  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  are given<sup>11</sup> in Table 1. It may be noted that the value of zero for the  $x$  coordinate of barium does not arise out of the symmetry requirements of the space group. The observed and calculated structure factors for the zero-layer data are tabulated in Tables 2 and 3. The reflections marked with an asterisk, which show large discrepancies, have been omitted in estimating the  $R$  values.

<sup>11</sup> In this and the following tables, the symbols  $O_1$  to  $O_8$  denote water oxygens,  $O_9$  and  $O_{10}$  hydroxyl oxygens. The same notation is used in the figures.

## 3. Three-dimensional data

Higher-layer data  $Hkl$  ( $H = 1$  to 6) were next taken up and structure factors computed. These are given in Table 2.

Table 4. Numbers of reflections in the various zones, isotropic temperature factors and  $R$  values

Zone	Number of reflections recorded	Number of reflections visually observed	Isotropic temperature factor ( $B$ )	$R$ value for observed reflections
$0kl$	143	91	2.1	0.110
$1kl$	283	154	1.8	0.127
$2kl$	278	150	1.4	0.128
$3kl$	273	127	1.5	0.125
$4kl$	255	122	1.3	0.120
$5kl$	232	95	1.0	0.132
$6kl$	217	98	0.9	0.135
Data from rotation about $[110]$	193	183	2.0	0.120

The hydrogen atoms are not included in the structure-factor calculations as their positions have not been fixed. Table 4 gives the number of reflections,  $R$  values indices and isotropic temperature factors for different zones. The progressive decrease in  $B$  values is presumably due to inaccuracies in the absorption factors resulting from the non-uniformity of crystal dimensions.

## Accuracy

The standard deviations of electron density<sup>1</sup>  $\sigma(\rho_0)$  and atomic coordinates  $\sigma(x)$  have been evaluated using CRUICKSHANK'S relations<sup>12,13</sup> for a centrosymmetric structure, the central curvatures of the atoms  $\frac{\partial^2 \rho_0}{\partial x^2}$  being obtained by BOOTH'S method<sup>14</sup>. The calculations were made in the best resolved  $\sigma(yz)$  projection using the  $F_o - F_c$ .

<sup>12</sup> D. W. J. CRUICKSHANK, The accuracy of electron density maps in x-ray analysis with special reference to dibenzyl. *Acta Crystallogr.* **2** (1949) 65–82.

<sup>13</sup> D. W. J. CRUICKSHANK and A. P. ROBERTSON, The comparison of theoretical and experimental determinations of molecular structures, with applications to naphthalene and anthracene. *Acta Crystallogr.* **6** (1953) 698–705.

<sup>14</sup> A. D. BOOTH, The accuracy of atomic coordinates derived from Fourier series in x-ray structure analysis. *Proc. Roy. Soc. [London] A* **188** (1946) 77–92.

values obtained in the final structure-factor calculation. The following results were obtained

$\sigma(\rho_0) = 0.208 e \cdot \text{\AA}^{-2}$ ;  $\sigma(z_{\text{Ba}}) = 0.0016 \text{\AA}$ ; Mean  $\sigma(z_{\text{oxy}}) = 0.031 \text{\AA}$ .  
Mean standard deviation of the O—O bond =  $0.044 \text{\AA}$ ; Mean standard deviation of the Ba—O bond =  $0.0311 \text{\AA}$ .

### Structure

The unit cell of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  contains 4 barium ions, 32 water oxygens and 8 hydroxyl oxygens (excluding the hydrogens) all of them situated in general positions. The water oxygens lie in layers at four different heights of approximately  $\frac{1}{3}$ ,  $\frac{2}{3}$ ,  $\frac{1}{3}$  and  $\frac{2}{3}$  along the  $c$  axis. In the layers they are arranged in groups of four in the form of squares. The barium ions are situated at heights approximately  $\frac{1}{4}$  and  $\frac{3}{4}$  along the  $c$  axis, in between the layers of oxygen atoms, such that each barium is coordinated by eight water oxygens which form a slightly distorted Archimedean antiprism, the Ba—O distances varying between  $2.69 \text{\AA}$  and  $2.77 \text{\AA}$ . This is perhaps the first time that this coordination polyhedron has been explicitly reported for the  $\text{Ba}^{2+}$  ion. The O—O contacts within the antiprism range from  $3.16 \text{\AA}$  to  $3.59 \text{\AA}$ . The interatomic distances within the antiprism are given in Table 5.

Table 5. *Interatomic distances within an antiprism*

Distance		Distance		Distance	
Ba—O <sub>1</sub>	2.69 Å	O <sub>1</sub> —O <sub>2</sub>	3.16 Å	O <sub>1</sub> —O <sub>5</sub>	3.37 Å
Ba—O <sub>2</sub>	2.73	O <sub>2</sub> —O <sub>8</sub>	3.27	O <sub>5</sub> —O <sub>2</sub>	3.54
Ba—O <sub>3</sub>	2.75	O <sub>8</sub> —O <sub>3</sub>	3.18	O <sub>2</sub> —O <sub>7</sub>	3.43
Ba—O <sub>4</sub>	2.76	O <sub>3</sub> —O <sub>1</sub>	3.30	O <sub>7</sub> —O <sub>8</sub>	3.52
Ba—O <sub>5</sub>	2.77	O <sub>5</sub> —O <sub>6</sub>	3.16	O <sub>8</sub> —O <sub>4</sub>	3.55
Ba—O <sub>6</sub>	2.73	O <sub>6</sub> —O <sub>4</sub>	3.26	O <sub>4</sub> —O <sub>3</sub>	3.59
Ba—O <sub>7</sub>	2.72	O <sub>4</sub> —O <sub>7</sub>	3.23	O <sub>3</sub> —O <sub>6</sub>	3.59
Ba—O <sub>8</sub>	2.77	O <sub>7</sub> —O <sub>3</sub>	3.28	O <sub>6</sub> —O <sub>1</sub>	3.45

The antiprisms do not share atoms with one another. The hydroxyl oxygens are situated at heights approximately  $\pm$  (0.10, 0.15, 0.35 and 0.40) along the  $c$  axis and are too far away ( $4.76$  and  $5.13 \text{\AA}$ ) from the barium ion to take part in its coordination.

It should be mentioned that it has not been possible to distinguish between the water oxygens and the hydroxyl oxygens in this structure and the positions have been assigned solely by analogy with  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . This assignment, however, appears quite reasonable, for

it is highly improbable that out of eight water molecules which are in no way different from one another, only some should coordinate the metal ion in an eight-fold coordination. A three-dimensional view of the unit cell of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is shown in Fig. 3, while Fig. 4 shows the projection of the unit cell on a plane perpendicular to the  $c$  axis. In the figures, four antiprisms marked  $A, B, C$  and  $D$  corresponding

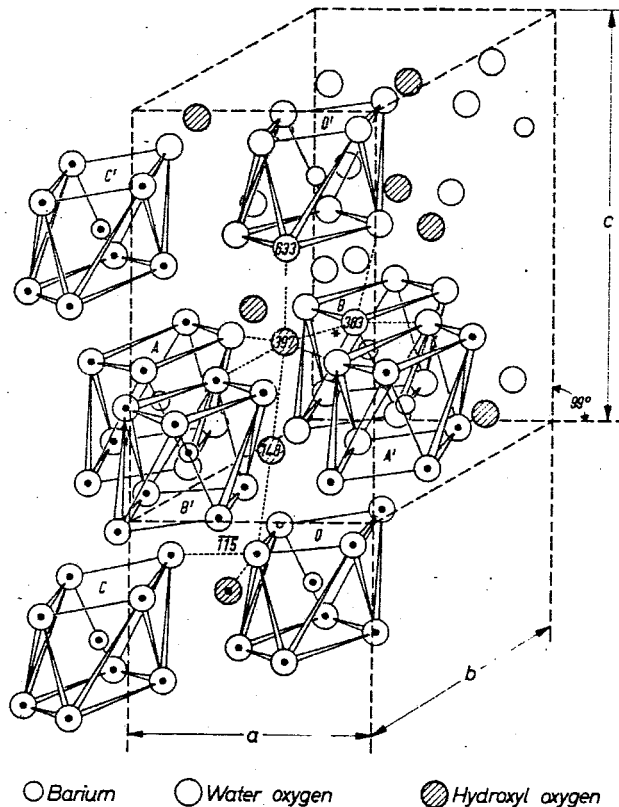


Fig. 3.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . A three-dimensional view of the unit cell. Circles with dots at the centre indicate atoms outside the unit cell. Numbers denote heights along the  $c$  axis in fractional coordinates, decimal points being omitted. Hydrogen bonds formed by the hydroxyl oxygen at  $c = 0.397$  and water oxygens at  $0.383$  marked\* and  $-0.115$  are indicated by dotted lines

to the four asymmetric units of the cell and the rest indicated by primed letters, related to the former by unit translations, are shown.

It may be observed in the figures that the water oxygens which coordinate the barium ion can be divided into two groups. Atoms of one kind (e.g. that at  $z = 0.383$  marked \*) are surrounded nearly

tetrahedrally by one barium ion, *one hydroxyl oxygen* and *two water oxygens*, while waters of the second kind (e.g. that at  $z = -0.115$ ) also have an approximately tetrahedral environment, but the coordinating atoms consist of one barium, *two hydroxyl oxygens* and *one water oxygen*. Out of eight non-equivalent water oxygens in the unit cell,  $O_1$  and  $O_5$  alone belong to the latter category. Each hydroxyl oxygen, on the other hand, (e.g. that at  $z = 0.397$ ) is surrounded by five waters and one hydroxyl group which form a distorted octahedron.

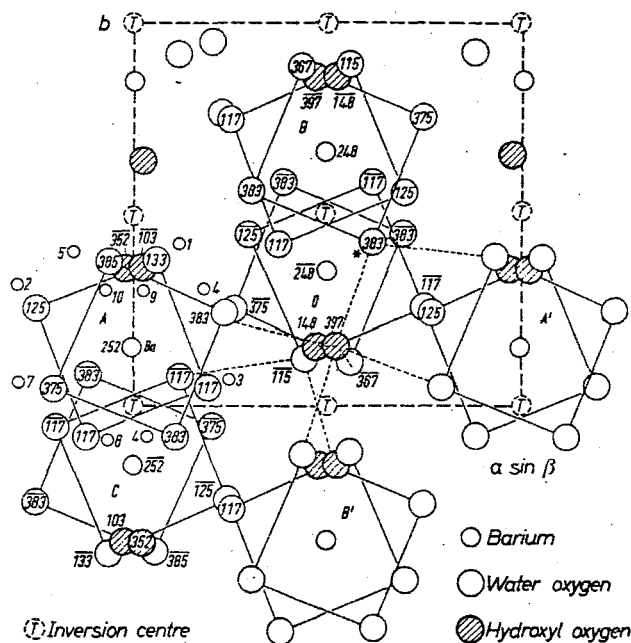


Fig. 4.  $Ba(OH)_2 \cdot 8H_2O$ . Projection of the unit cell perpendicular to the  $c$  axis. Numbers indicate heights along the  $c$  axis in fractional coordinates. Decimal points are omitted. Hydrogen bonds formed by the hydroxyl oxygen at  $c = 0.397$  and water oxygens at  $0.383$  marked \* and  $-0.115$  are shown by dotted lines

The O—O contacts in all these cases range between  $2.62 \text{ \AA}$  and  $3.09 \text{ \AA}$ . These closest distances for all the waters and hydroxyl groups are given in Table 6.

It is interesting, at this stage, to compare the crystal structures of  $Ba(OH)_2 \cdot 8H_2O$  and  $Sr(OH)_2 \cdot 8H_2O$  in both of which the metal ions are surrounded by water molecules in an identical manner. The  $c$ -axis projection of the unit cell of  $Sr(OH)_2 \cdot 8H_2O$  is shown in Fig. 5. It is seen that in this structure also, the antiprisms round the strontium

ion are situated in two layers in the  $ab$  plane, but are stacked one exactly above the other along the  $c$  axis. The hydroxyl groups form continuous chains parallel to the  $c$  axis with a separation of  $\frac{1}{4}c$ . Therefore each hydroxyl oxygen is surrounded octahedrally by four water molecules having the same  $z$  coordinates and two hydroxyl groups, one above and the other below. Every water oxygen is surrounded approximately tetrahedrally by one  $\text{Sr}^{2+}$  ion, one hydroxyl group and

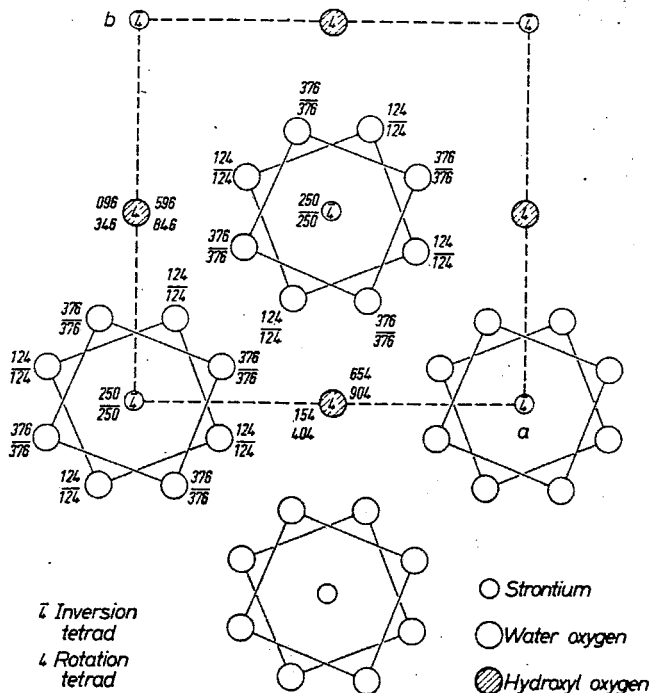


Fig. 5.  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Projection of the unit cell perpendicular to the  $c$  axis. Numbers indicate heights along the  $c$  axis in fractional coordinates, decimal points having been omitted.

two water molecules, there being only one species from the point of view of environment. The  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  structure can be obtained from that of  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  by displacing the top layer, consisting of the metal ions at  $z = \frac{3}{4}$  with their coordinating antiprisms of water molecules and the hydroxyl groups at heights  $\sim 0.60, 0.65, 0.85$  and  $0.90c$ , with respect to the bottom layer, consisting of the metal ions at  $z = \frac{1}{4}$  with their coordinating water molecules and hydroxyl groups at heights  $\sim 0.10, 0.15, 0.35$  and  $0.40c$ , through

Table 6. *Closest neighbours of water molecules and hydroxyl groups*

Distance		Distance	
O <sub>1</sub> <sup>I</sup> —O <sub>9</sub> <sup>IV</sup>	2.78 Å	O <sub>4</sub> <sup>I</sup> —O <sub>7</sub> <sup>II</sup>	2.87 Å
—O <sub>9</sub> <sup>III</sup>	2.62	—O <sub>1</sub> <sup>III</sup>	3.07
—O <sub>4</sub> <sup>III</sup>	3.07	—O <sub>10</sub> <sup>III</sup>	2.79
—Ba <sup>I</sup>	2.69	—Ba <sup>I</sup>	2.76
O <sub>2</sub> <sup>I</sup> —O <sub>6</sub> <sup>IV</sup>	2.87	O <sub>5</sub> <sup>I</sup> —O <sub>10</sub> <sup>IV</sup>	3.09
—O <sub>7</sub> <sup>III</sup>	2.89	—O <sub>10</sub> <sup>III</sup>	2.60
—O <sub>10</sub> <sup>I</sup>	2.79	—O <sub>8</sub> <sup>III</sup>	3.03
—Ba <sup>I</sup>	2.73	—Ba <sup>I</sup>	2.77
O <sub>3</sub> <sup>I</sup> —O <sub>8</sub> <sup>II</sup>	2.77	O <sub>8</sub> <sup>I</sup> —O <sub>2</sub> <sup>IV</sup>	2.87
—O <sub>6</sub> <sup>III</sup>	2.92	—O <sub>9</sub> <sup>I</sup>	2.82
—O <sub>10</sub> <sup>I</sup>	2.71	—O <sub>3</sub> <sup>III</sup>	2.92
—Ba <sup>I</sup>	2.75	—Ba <sup>I</sup>	2.73
O <sub>8</sub> <sup>I</sup> —O <sub>3</sub> <sup>II</sup>	2.77	O <sub>7</sub> <sup>I</sup> —O <sub>4</sub> <sup>II</sup>	2.87
—O <sub>5</sub> <sup>III</sup>	3.03	—O <sub>2</sub> <sup>III</sup>	2.89
—O <sub>9</sub> <sup>III</sup>	2.67	—O <sub>9</sub> <sup>I</sup>	2.74
—Ba <sup>I</sup>	2.77	—Ba <sup>I</sup>	2.72
O <sub>9</sub> <sup>I</sup> —O <sub>1</sub> <sup>IV</sup>	2.78	O <sub>10</sub> <sup>I</sup> —O <sub>5</sub> <sup>IV</sup>	3.09
—O <sub>10</sub> <sup>I</sup>	2.92	—O <sub>9</sub> <sup>I</sup>	2.92
—O <sub>1</sub> <sup>III</sup>	2.62	—O <sub>3</sub> <sup>I</sup>	2.71
—O <sub>7</sub> <sup>I</sup>	2.74	—O <sub>4</sub> <sup>III</sup>	2.75
—O <sub>8</sub> <sup>III</sup>	2.67	—O <sub>2</sub> <sup>I</sup>	2.79
—O <sub>6</sub> <sup>I</sup>	2.70	—O <sub>5</sub> <sup>III</sup>	2.60

I  $x, y, z$  of Table 1.II  $\bar{x}, \bar{y}, \bar{z}$ III  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ IV  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

a distance of 2.75 Å along the  $b$  axis. As a result, one of the water oxygens of the antiprism comes almost above a hydroxyl group in the lower layer displacing an OH group, so that the first mentioned OH is now coordinated by five water molecules and one OH. By this shearing, as it were, the environment of water oxygens is also altered correspondingly and since this movement is asymmetric, two species of water oxygens with different environments are generated.

### Hydrogen bonding

In an excessively hydrated crystal like  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  it is reasonable to expect hydrogen bonds between oxygen atoms, particularly in view of the short distances found. It must be mentioned that the accuracy of the oxygen parameters and consequently the O—O bond distances in the present structure is not very high, as evidenced from the values of the standard deviations. However, it is sufficient for some general conclusions to be drawn. Hydrogen bonds between



water molecules in the same antiprism are ruled out, since in that case, the hydrogen atoms would lie on the side facing the cation, which is extremely improbable. This deduction is also borne out by the O—O distances within the antiprism which are all greater than 3.16 Å.

The properties of water and ice, as also a study of the structures of many crystalline hydrates, reveal that the water molecule generally behaves as if there were a tetrahedral distribution of two positive and two negative charges, and in many cases the arrangement of the nearest neighbours is consistent with this tetrahedral character (WELLS<sup>15</sup>). Thus we find that in crystals containing monovalent metal ions, the water molecule is generally attached to two oxygen atoms of an oxy-ion and to two monovalent positive ions on the side of its positive and negative charges respectively. The neighbours of the water molecule may well be other waters suitably oriented so that oppositely charged regions are adjacent. Examples of these arrangements<sup>16,17</sup> are found in  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .

When the water molecule has a divalent metal ion as one of its neighbours, it makes three external contacts and the bonds to the metal ion and two oxygen atoms are coplanar or nearly so — as for example<sup>18,19</sup> in  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  or  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . However, there are also instances where the water molecule makes four external contacts, three to oxygen atoms and the fourth to a divalent metal ion, these four bonds being tetrahedral.  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  can be quoted as an example of this arrangement<sup>20</sup>. Similarly in  $\text{Ba}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$  each water molecule is reported to be tetrahedrally coordinated by one barium, two waters and one sulphur<sup>21</sup>. Thus the criterion regarding the environment of a water molecule, when multivalent metal ions are present, appears to be by no means unique.

<sup>15</sup> A. F. WELLS<sup>5</sup>, p. 575—576.

<sup>16</sup> J. P. HARPER, Crystal structure of sodium carbonate monohydrate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . Z. Kristallogr. **95** (1936) 266—273.

<sup>17</sup> A. C. LARSON and L. HELMHOLZ, Redetermination of the crystal structure of lithium sulphate monohydrate  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . J. Chem. Physics **22** (1954) 2049.

<sup>18</sup> C. A. BEEVERS and H. LIPSON, The crystal structure of beryllium sulphate tetrahydrate  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ . Z. Kristallogr. **82** (1932) 297—308.

<sup>19</sup> C. D. WEST, Crystal structures of hydrated compounds. II. Structure type  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Z. Kristallogr. **91** (1935) 480—493.

<sup>20</sup> C. A. BEEVERS and C. M. SCHWARTZ, The crystal structure of nickel sulphate heptahydrate  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . Z. Kristallogr. **91** (1935) 157—169.

<sup>21</sup> M. NARDELLI and G. FAVA, The crystal structure of barium thiosulphate monohydrate. Acta Crystallogr. **15** (1962) 477—484.

As mentioned already, the water molecule in the present structure, with a tetrahedral environment of three oxygens and one barium, belongs to the latter category mentioned above and the three short O—O distances suggest the formation of hydrogen bonds. In the case of the hydroxyl group, the six nearest octahedrally arranged oxygen atoms also appear to be hydrogen bonded to the central oxygen judging from distances alone. Nevertheless, it must be remarked that, to the knowledge of the writers, there appear to be no instances in literature, apart from  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , where a hydroxyl oxygen forms hydrogen bonds in this manner. The hydrogen bonds formed in three typical cases (by the hydroxyl oxygen at  $z = 0.397$ , and the water oxygens at 0.383 marked \* and at  $-0.115$ ) are shown in Figs. 3 and 4 by dotted lines. The rest of the bonds have been omitted for the sake of clarity of the diagram.

On the basis of the above postulation, we find that all the anti-prisms and the hydroxyl groups are linked up with one another by a continuous network of hydrogen bonds which utilizes all the 72 hydrogen atoms in the unit cell.

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