

other bromobismuthates(III) with BiBr_6^{3-} groups linked to polyanions. For example, in potassium decabromodibismuthate(III) tetrahydrate (Lazarini, 1977a) with binuclear $\text{Bi}_2\text{Br}_{10}^{4-}$ anions, the Bi—Br(terminal) distances range from 2.749 to 2.878 Å, the Bi—Br(bridging) distances are 2.979 and 3.006 Å; in tetraphenylphosphonium enneabromodibismuthate(III) (Lazarini, 1977c) with binuclear $\text{Bi}_2\text{Br}_9^{3-}$ anions, the Bi—Br(terminal) distances range from 2.704 to 2.766 Å and the Bi—Br(bridging) distances from 2.987 to 3.109 Å; while in caesium enneabromodibismuthate(III) (Lazarini, 1977d), with BiBr_6^{3-} octahedra sharing three *cis*-vertices with three other octahedra forming corrugated layers, the Bi—Br(terminal) distances are 2.713 and the Bi—Br(bridging) distances 2.979 Å. It is obvious that the Bi—Br distances in isolated BiBr_6^{3-} anions are slightly longer than the Bi—Br(terminal) distances and considerably shorter than the Bi—Br(bridging) distances, in structures with BiBr_6^{3-} groups linked to polynuclear anions.

The Rb—Br contacts are in agreement with expected values (ionic radii: Rb^+ 1.49, Br^- 1.95 Å; Wells, 1975). Contacts between Br atoms of different anions shorter than 3.90 Å are not present.

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Barium Chloride Dihydrate by Neutron Diffraction*

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Abstract. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, monoclinic, $P2_1/n$, $Z = 4$, $a = 6.7215$ (2), $b = 10.9080$ (3), $c = 7.1316$ (2) Å, $\beta = 91.104$ (3)° from room-temperature X-ray measurements, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å. Ferroelastic species: $mmmF2/m$. Each Ba^{2+} ion is linked to four others in a flat square pyramidal arrangement forming puckered layers parallel to (010). Each link consists of one bridging Cl^- ion and one bridging water molecule. The latter is oriented so that two Ba^{2+} neighbors and two H atoms are arranged approximately tetrahedrally about the O atom.

Introduction. The neutron-diffraction data collection and preliminary results have been described previously

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(Padmanabhan, Busing & Levy, 1963). We have recently made a final least-squares refinement assuming anisotropic extinction of type 1 (Coppens & Hamilton, 1970). Intense reflections omitted in the earlier work are now included. Ten reflections judged to be affected

Table 1. *Fractional coordinates* ($\times 10^4$) for $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

Standard errors are given in parentheses. The equipoints for $P2_1/n$ are $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

| | x | y | z |
|-------|----------|----------|-----------|
| Ba | 5410 (2) | 2831 (1) | 6461 (2) |
| Cl(1) | 8625 (1) | 811 (1) | 7946 (1) |
| Cl(2) | 6419 (1) | 1049 (1) | 3020 (1) |
| O(1) | 3777 (2) | 1404 (1) | 9409 (2) |
| O(2) | 2007 (2) | 1474 (1) | 5060 (2) |
| H(11) | 3534 (5) | 621 (2) | 8837 (4) |
| H(12) | 4755 (5) | 1252 (3) | 10405 (4) |
| H(21) | 984 (5) | 1374 (3) | 5969 (4) |
| H(22) | 2471 (5) | 656 (3) | 4891 (5) |

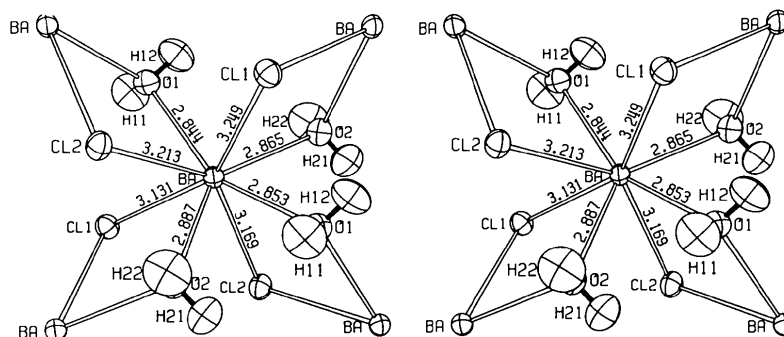


Fig. 1. Stereoscopic view down the b axis of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ showing the bridging between Ba^{2+} ions to form a layer. Interatomic distances are given in Å; their standard errors are about 0.002 Å.

Table 2. Distances and angles involving water molecules and hydrogen bonds in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

| | | Distances (Å) | | | Angles (°) | |
|------|------------------------------|---------------|------------------------|------------------------|------------------------|-----------|
| | | O—H | H...Cl | O...Cl | O—H...Cl | H—O—H |
| O(1) | H(11)...Cl(2) | 0.959 (3) | 2.253 (3) | 3.189 (2) | 165.0 (3) | 105.4 (3) |
| | H(12)...Cl(2) | 0.972 (4) | 2.168 (3) | 3.124 (2) | 167.4 (3) | |
| O(2) | H(21)...Cl(1) | 0.960 (3) | 2.228 (3) | 3.179 (2) | 170.4 (3) | 102.6 (3) |
| | H(22) ... Cl(1) ... Cl(2) | 0.953 (3) | 2.672 (4) 2.488 (3) | 3.310 (2) 3.242 (2) | 124.7 (3) 136.0 (3) | |

by instrument errors were omitted, leaving a total of 1029 observations. The final discrepancy index $R(F^2)$ is 4.6%. Neutron scattering lengths used were: $b(\text{Ba}) = 0.512$, $b(\text{Cl}) = 0.9580$, $b(\text{O}) = 0.5803$, and $b(\text{H}) = -0.3740$, all in units of 10^{-12} cm (Koester, 1972). Refined coordinates are given in Table 1; some interatomic distances and angles are listed in Fig. 1 and in Table 2.*

The computer programs used in this work were those listed by Lisensky, Johnson & Levy (1976).

Discussion. The coordinates of the non-hydrogen atoms are in qualitative agreement with those from the X-ray study by Jensen (1945). They are also consistent with the coordinates from an electron diffraction study by Padmanabhan, Jakkal & Shankar (1963). The hydrogen positions from the present work do not agree, however, with those proposed by Silvidi & McGrath

(1960) on the basis of NMR studies. This discrepancy was explained by El Saffar (1966) who showed that Silvidi and McGrath had probably mistaken the [101] and [011] directions, respectively, for the a and c axes defined by Jensen.

Fig. 1 shows how Ba^{2+} is coordinated to four H_2O molecules and four Cl^- ions to form puckered layers parallel to (010). In addition each Ba makes a contact of 3.340 (2) Å with a Cl(1) ion in an adjacent layer. This can be seen in Fig. 2 which shows the contents of a unit cell viewed parallel to the layers. The coordination about Ba^{2+} can be described approximately as a square antiprism with one square face enlarged to accommodate the fifth Cl^- ion.

Distances and angles involving the hydrogen atoms are given in Table 2. Within a layer H(12) and H(21) form hydrogen bonds to Cl(2) and Cl(1), respectively, and H(11) is bonded to Cl(2) of an adjacent layer. H(22) is more loosely coordinated to two ions, Cl(1) and Cl(2), also in an adjacent layer. This arrangement is consistent with the IR results of Schiffer & Hornig (1969) on a 5% deuterated sample. They noted that three of the four observed OD stretching frequencies correspond to strong hydrogen bonding. Brink (1972) has reported similar IR studies in more detail.

A remarkable property of this material, noted by

* Lists of structure factor squares and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33491 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

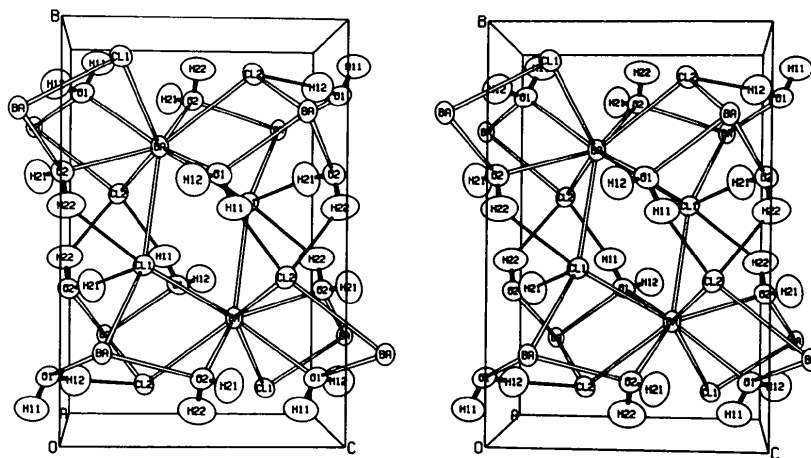


Fig. 2. Stereoscopic drawing of a unit cell of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The direction of view is parallel to the layers of Fig. 1 and interlayer contacts are shown.

Mügge (1890), is the ease with which it twins under mechanical stress. This property is now recognized as ferroelasticity (Aizu, 1969, 1970). Careful examination of the mechanical deformation and the change in the optical properties of the crystal when stress is applied shows that the twinning occurs because the β angle, which is slightly greater than 90° , changes to its supplement, $180^\circ - \beta$. Consideration of the crystal structure reveals that this transformation involves an interchange in the roles of Cl(1) and Cl(2), O(1) and O(2), H(11) and H(22), and H(12) and H(21). No changes occur in the interatomic contacts within a layer, but the puckering of each layer reverses, the layers move with respect to one another, and different atoms become involved in the Ba-Cl contacts and $\text{H} \cdots \text{Cl}$ bonds between layers. Using the terms defined by Aizu, the ferroelastic species is $mmmF2/m$, the space group of the prototype structure is $Pcnb$, and the spontaneous strain is 0.01362 (4) at room temperature. The latter is obtained from the β angle as $(\sqrt{2}/2)(\beta - \pi/2)$.

The ferroelastic effect in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ has been discussed in more detail by Wadhawan (1978). The authors thank him for his helpful comments.

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