

# THE CRYSTAL STRUCTURE OF $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ AND THE CRYSTAL CO-ORDINATION OF THE BARIUM ION

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**T**HE investigation of the crystal structure of barium hydroxide octahydrate  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was taken up as part of the programme of the department to study the crystal co-ordination of the  $\text{Ba}^{++}$  ion in various complexes. Additional interest stemmed from the fact that very few structural studies have been conducted on highly hydrated salts in general and hydroxides in particular.

the reflections could be fixed by the 'heavy atom' method. The structure was solved from two-dimensional data by the iterative process of Fourier and difference syntheses. The [100] barium-removed Fourier projection is shown in Fig. 1 (a). The final reliability factors for the [100] and [110] data are 0.11 and 0.12 respectively, the overall R-factor for 1020 visually observed reflections within the  $\text{CuK}\alpha$  sphere of reflection in eight zones being 0.124.

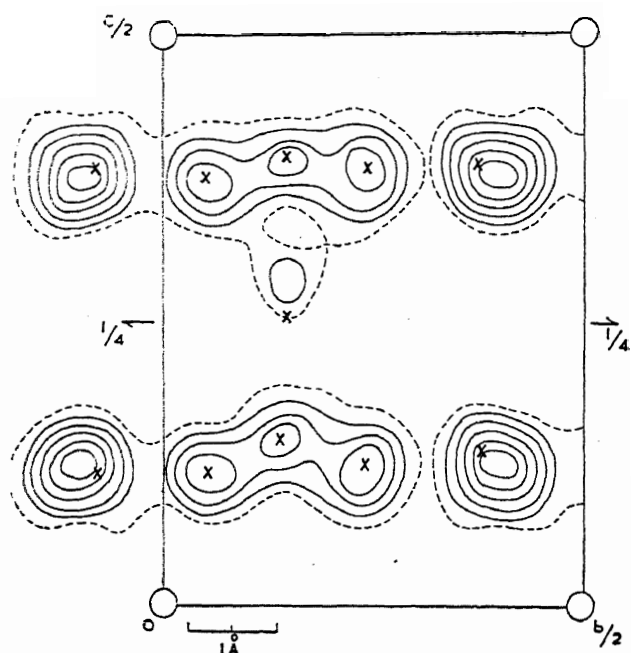


FIG. 1a.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . [100] barium-removed Fourier projection. Contours are drawn at arbitrary intervals.

The substance was crystallised by evaporating a saturated solution of  $\text{Ba}(\text{OH})_2$  at room temperature. Rotation and Weissenberg photographs revealed that the crystal belongs to the monoclinic space group  $C_{2h}^2 - P2_1/n$  with four formula weights in the unit cell of dimensions  $a = 9.35 \text{ \AA}$ , unique axis  $b = 9.28 \text{ \AA}$ ,  $c = 11.87 \text{ \AA}$  and  $\beta = 99^\circ$ . Three-dimensional data were collected about the [100] and [110] axes on multiple films employing the Weissenberg technique. The intensities of the spots were estimated visually by comparison with calibrated intensity strips. The co-ordinates of barium were obtained by computing Patterson syntheses in the two projections and the signs of most of

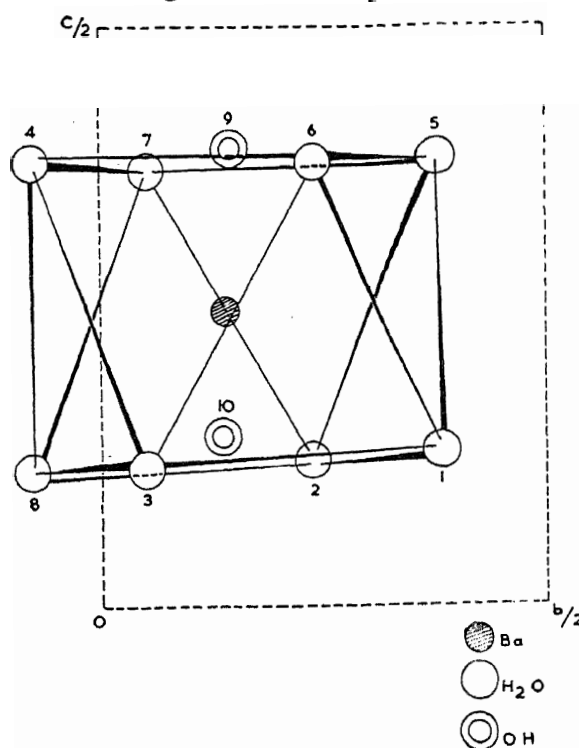


FIG. 1b. Identification of atoms in the [100] projection. The antiprism co-ordination of the barium ion is shown, the axis of the antiprism being parallel to the  $c$ -axis.

In this structure, the barium ion is co-ordinated by eight water molecules which form a slightly distorted Archimedean antiprism,<sup>1</sup> the Ba-O distances varying between 2.69  $\text{\AA}$  and 2.77  $\text{\AA}$ . This is perhaps the first instance where this co-ordination polyhedron has been explicitly reported for the  $\text{Ba}^{++}$  ion. The antiprisms do not share atoms with one another. Each hydroxyl oxygen has close contacts with five waters and one hydroxyl group which form a distorted octahedron. The water molecules have an approximately tetrahedral environment, six out of the eight non-equivalent waters in the unit cell having one barium, one hydroxyl oxygen and

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two water oxygens and the rest, one barium, two hydroxyl oxygens and one water oxygen as nearest neighbours. The structure is thus a slightly distorted version of tetragonal  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .<sup>2</sup> Based on the short interatomic distances in the structure, a network of hydrogen bonds is proposed which links the antiprisms and hydroxyl groups with one another utilising all the hydrogen atoms in the unit cell.

Since the ratio of the univalent radii of  $\text{Ba}^{++}$  to  $\text{O}^{--}$  is 0.87, the barium ion should normally exhibit a co-ordination number of nine. In  $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,<sup>3</sup> however, the number of oxygens surrounding barium has been found to be twelve and the co-ordination polyhedron is the icosahedron, while in  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  the co-ordination number is eight. A systematic survey was therefore made in the literature, of barium compounds whose structures had been solved to find out whether barium shows any other crystal co-ordination number. It was noticed that for the purpose of determining the crystal co-ordination in ionic crystals, the nearest neighbours alone at approximately the same distance from the cation were usually considered, atoms which were only slightly farther away being ignored. Further the shapes of the co-ordination polyhedra were identified only when they were of the standard symmetrical type such as octahedron, cube, etc., which are enumerated in

text-books. In cases where the co-ordination numbers were unusual, like seven, ten or eleven, beyond giving the number and distances of the nearest atoms, no attempt was generally made to investigate the nature and geometry of the polyhedra. In all these cases, the interatomic distances were calculated and the positions of atoms co-ordinating the barium ion were plotted in the most suitable projection, the heights being represented by metal rods cut to appropriate lengths. A study of the models led to the identification of some new geometrical figures for the co-ordination polyhedra. The present investigations reveal that the barium ion displays a range of co-ordination numbers from six right up to twelve.

Details of these investigations are being reported elsewhere. The writers wish to acknowledge the help given by Dr. G. Aravamudan of the Chemistry Department, Indian Institute of Technology, Madras, in growing the crystals of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Thanks are due to Professor R. S. Krishnan for his keen interest in the problem.

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## REVIEW OF RECENT RESULTS ON INTERNAL CONVERSION \*

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UNTIL a few years ago it was believed that all was well with the theory of internal conversion as originally developed by Rose<sup>1</sup> and his collaborators. This theory was based on the rather simplifying assumption that the nucleus can be treated as point charge. There was so much faith in this theory that experimentalists interpreted all their data on this and assigned multipolarities for gamma transitions. Experiments on some M1 transitions soon revealed discrepancies between theory and experiment in spite of the rather moderate precision with which the  $\alpha_{\kappa}$ 's were determined. Sliv<sup>2</sup> recalculated the  $\alpha_{\kappa}$  on a more realistic model, namely, the one in which the charge on the nucleus is distributed uniformly on a sphere of radius R. The inclusion of this

effect (static approximation) removed the anomalies observed in the case of M1 transitions. In general, the new calculations differed from Rose's especially for heavy nuclei, and predicted values which were a good deal larger than the point nucleus values. It must be pointed out that the  $\alpha(E2)$  was unaffected by these calculations.

Church and Weneser<sup>3</sup> made an important contribution to the theory of internal conversion when they pointed out the importance of the so-called penetration effect or dynamic effect. This effect which arises from the penetration of the atomic electron into the nuclear volume introduces new matrix elements into the conversion electron ejection different from that due to gamma-ray emission. This had the interesting consequence that when the gamma-ray matrix element was vanishingly small due to some selection rule, the new matrix element would in-

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