

# CRYSTAL CO-ORDINATION OF THE BARIUM ION

BY H. MANOHAR AND S. RAMASESHAN,\* F.A.Sc.

(Department of Physics, Indian Institute of Science, Bangalore-12, India)

Received August 17, 1964

## INTRODUCTION

THE principles governing the structures of complex ionic crystals have been laid down by Pauling<sup>1</sup> in a set of semi-empirical rules which are named after him. According to Pauling's first rule, a co-ordination polyhedron of anions is formed about each cation, the cation-anion distance being the sum of the radii and the co-ordination number (C.N.) or ligancy of the cation being determined by the radius ratio. The values of the minimum radius ratio required for stability of various co-ordination polyhedra have been worked out and are given in Table I. The other rules relate to the sharing of ions between different co-ordination polyhedra. The most important feature of the Goldschmidt-Pauling concept is that approximately the radius of an ion is constant, and that the anion-cation radius ratio plays an important part in determining the final crystal structure.

In the case of barium compounds the ratio of the "univalent" radii of  $Ba^{2+}$  to  $O^{2-}$  is  $1.53/1.76 = 0.87$ , the anions in most of the ionic complexes being oxygen ions.  $Ba^{2+}$ , therefore, should normally exhibit a co-ordination number of nine or ten. However, following the identification of the icosahedral twelve co-ordination of barium in  $Ba(ClO_4)_2 \cdot 3H_2O$  by Mani and Ramaseshan<sup>2</sup> and the eight-fold antiprism co-ordination in  $Ba(OH)_2 \cdot 8H_2O$ <sup>3,4</sup> by the present authors, it was considered worthwhile to undertake a systematic study of the crystal co-ordination of the barium ion to find out whether it displays any other co-ordinations, and if so, to identify the new co-ordination polyhedra and determine their shapes and geometry.

A survey of the structures of barium compounds in the literature revealed that the shapes of the co-ordination polyhedra were identified only when they were of the standard symmetric type such as given in Table I. In cases where the co-ordination numbers were unusual like seven, ten or eleven, beyond giving the numbers and distances of the nearest atoms, no attempts were

\* Present address: Department of Physics, Indian Institute of Technology, Madras 36 (India).

generally made to investigate the shapes of the co-ordination polyhedra. In many cases the nearest neighbours alone at approximately the same distance from the cation were considered for the purpose of crystal co-ordination, the investigators having been reluctant even to give the number of next nearest

TABLE I

*Values of the minimum radius ratio for stability of various co-ordination polyhedra*

Polyhedron	Co-ordination number	Minimum Radius ratio
Cubo-octahedron and disheptahedron ..	12	1.00
Icosahedron .. .. .	12	0.902
<i>a</i> .. .. .	9	0.732
Cube .. .. .	8	0.732
Square antiprism .. .. .	8	0.645
<i>b</i> .. .. .	7	0.592
Octahedron .. .. .	6	0.414
Tetrahedron .. .. .	4	0.225
Triangle .. .. .	3	0.155

(a) This polyhedron with 18 equal faces is obtained by adding 3 atoms at the centres of the vertical faces of a right triangular prism.

(b) This polyhedron is obtained by adding an atom at the centre of a face of an octahedron.

neighbours. In the present study, all the inter-atomic distances were calculated and the positions of atoms co-ordinating barium were plotted in the most suitable projection. The heights of these atoms were represented by metal rods cut to appropriate lengths and a careful study of these models led to the identification of some new co-ordination polyhedra. The results obtained in the investigation are presented in this paper. In the accompanying figures, one example (in a few cases, two) of the actual atomic positions of the co-ordinating atoms is given for each type of co-ordination and

alongside the idealised polyhedron has been drawn. Only ionic compounds have been considered in this review.

OCTAHEDRAL CO-ORDINATION (C.N. 6)

Simple ionic compounds having the formula  $BaX_6$ ,<sup>5</sup> where X is O, S, Se and Te, as also barium imide  $BaNH_6$ ,<sup>6</sup> crystallise in the cubic rocksalt structure with the barium ion exhibiting a six-fold octahedral co-ordination. The co-ordination polyhedron round barium in the oxide is shown in Fig. 1. In the system  $BaCO_3-CaCO_3$ , solid solutions are formed which are reported<sup>7</sup> to show the aragonite structure when the proportion of  $BaCO_3$  varies between 100 per cent to 80 per cent and the calcite structure, for  $BaCO_3$  less than 60 per cent. In the latter case, therefore,  $Ba^{2+}$  is co-ordinated octahedrally by six oxygens. The low temperature forms of barium silicate  $Ba_2SiO_3$  and barium germanate  $Ba_2GeO_3$  belong to the structure type pseudowollastonite  $\alpha-CaSiO_3$  (Hilmer).<sup>8</sup> The structure and symmetry of  $\alpha-CaSiO_3$  have been

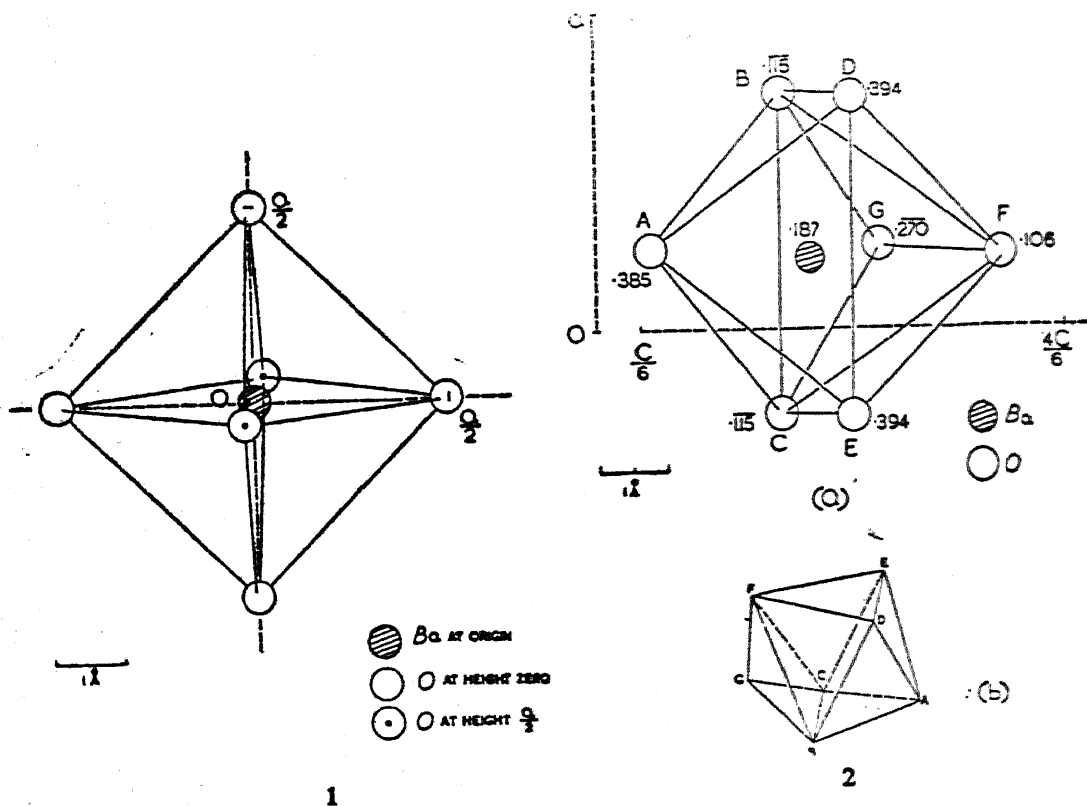


Fig. 1. Octahedral co-ordination around  $Ba^{2+}$  ion in  $BaO$ .

Fig. 2. Co-ordination polyhedron (Octahedron + 1) in the high temperature form of  $BaGeO_3$ . In this and following figures of this paper, the numbers by the side of atoms indicate heights in fractional co-ordinates along the axis of projection.

derived from an X-ray analysis<sup>9</sup> of the isostructural synthetic compound  $\text{SrGeO}_3$ , crystals of which are more easily obtained, where the  $\text{Sr}^{2+}$  ions are found to be at the centres of octahedra of O atoms. Therefore, barium displays an octahedral co-ordination in the above-mentioned two compounds.

A slightly distorted octahedral environment for barium has also been observed in more complex structures—as for example, in the silicate benitoite,<sup>10</sup>  $\text{BaTiSi}_2\text{O}_9$ , in monoclinic barium peroxide monohydroperoxidate  $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ <sup>11</sup> and in the hexagonal meta-antimonate  $\text{BaSb}_2\text{O}_6$ .<sup>12</sup> A number of complex alkaline-earth molybdates, tungstates and uranates<sup>13,14</sup> like  $\text{Ba}_3\text{WO}_6$ ,  $\text{Ba}_3\text{UO}_6$ ,  $\text{Ba}_2\text{CaWO}_6$ ,  $\text{Ba}_2\text{CaMoO}_6$ ,  $\text{Ba}_2\text{SrUO}_6$ ,  $\text{Sr}_2\text{BaUO}_6$  crystallise with the ideal cubic  $(\text{NH}_4)_3\text{AlF}_6$  structure or with slightly distorted variations. This can be referred to as the cryolite structure<sup>15</sup> with the general formula  $\text{A}_3\text{BX}_6$ , where one-third of the A atoms are in octahedral holes in a cubic close-packed  $\text{A}_2\text{X}_6$  assembly. The other two-thirds of the A atoms are surrounded by twelve equidistant X ions.

#### CO-ORDINATION NUMBER SEVEN

Wells<sup>16</sup> describes three arrangements for seven-fold co-ordination of cations. The odd atom G is placed above the centre of one face BCF of an octahedron [Fig. 2 (b)], which is distorted chiefly by separating the atoms at the corners of this face; or beyond the centre of one of the rectangular faces ADCF of a trigonal prism [Fig. 3 (b)] with some consequent distortion. The former arrangement has been found in the high temperature form of  $\text{BaGeO}_3$ <sup>5</sup> [Fig. 2 (a)], while the latter is present for both the non-equivalent barium ions in  $\text{Ba}_2\text{ZnS}_3$ <sup>17</sup>. The arrangement of sulphur atoms round  $\text{Ba}^{2+}$  at 0.326, 0.019, 0.250 (in fractional co-ordinates) is shown in Fig. 3 (a). In the third case, the co-ordinating atoms occupy the vertices of a pentagonal bipyramid. A modified form of this co-ordination polyhedron has been identified in rhombohedral  $\text{NiO} \cdot 3\text{BaO}$ <sup>18</sup> [Fig. 4 (a)]. Here the pentagon is not plane, one atom A having been moved out. The idealised polyhedron is shown in Fig. 4 (b).

#### CO-ORDINATION NUMBER EIGHT

The cubic co-ordination of eight fluorines round the barium ion manifests itself in barium fluoride,<sup>19</sup>  $\text{BaF}_2$ , which is isotypic with cubic fluorite. Recently, the structure and dielectric properties of a series of tetragonal compounds having the general formula  $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ , where  $x$  could be varied over a wide range between 0.67 and 1.14, have been described.<sup>20</sup>

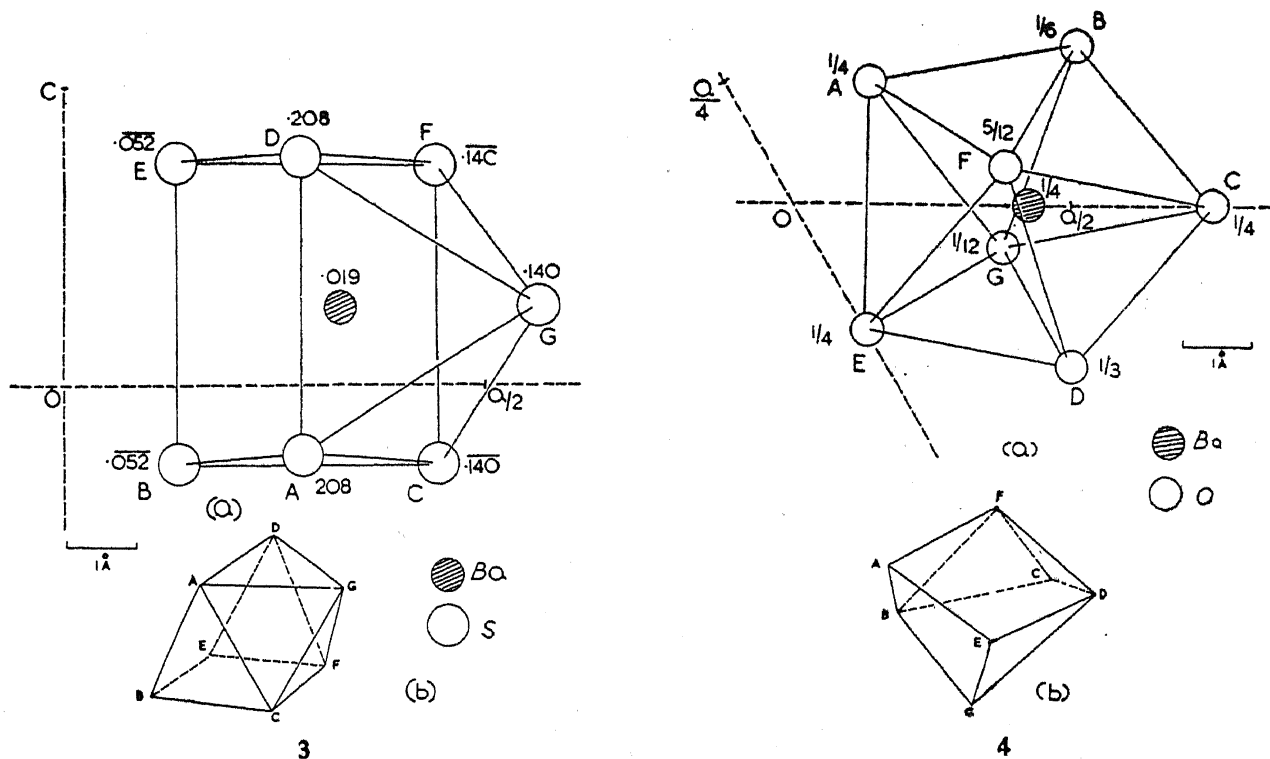


FIG. 3. Co-ordination polyhedron of sulphurs (Trigonal prism one face-centred) round  $Ba^{++}$  ion in  $Ba_3ZnS_3$ .

FIG. 4. Co-ordination polyhedron (Modified pentagonal pyramid) in  $NiO \cdot 3BaO$ .

The barium ions are reported to be surrounded by eight oxygens at the corners of a highly distorted cube. The co-ordination polyhedron (Fig. 5) when drawn was actually found to be a square prism with sides  $3.7 \text{ \AA}$ ,  $3.7 \text{ \AA}$  and  $3.0 \text{ \AA}$ .

Eight-fold co-ordination polyhedra which are more satisfactory than the cube from the point of stereochemistry are reported<sup>21</sup> to be the dodecahedron with triangular faces, the square Archimedean antiprism and the triangular prism with two of its rectangular faces centred. The Archimedean antiprism<sup>22</sup> is obtained when the top square face of a cube is rotated with respect to its bottom face by  $45^\circ$ . The resulting figure is bounded by eight triangular and two square faces and all the sixteen edges are equal. It has a maximum symmetry of  $\bar{8}2m$ . The antiprism arrangement of oxygens in a slightly distorted form is present in barium hydroxide octahydrate  $Ba(OH)_2 \cdot 8H_2O$ , whose crystal structure has recently been solved<sup>3,4</sup>. It has also been subsequently identified by the present writers for one of the two non-equivalent barium ions in the hydrated barium silicate  $BaO \cdot SiO_2 \cdot 6H_2O$ .<sup>23</sup> In this structure, the waters and oxygen atoms are

indistinguishable. The co-ordination polyhedra for the two compounds are shown in Figs. 6 and 7 respectively. As Mani and Ramaseshan<sup>2</sup> have

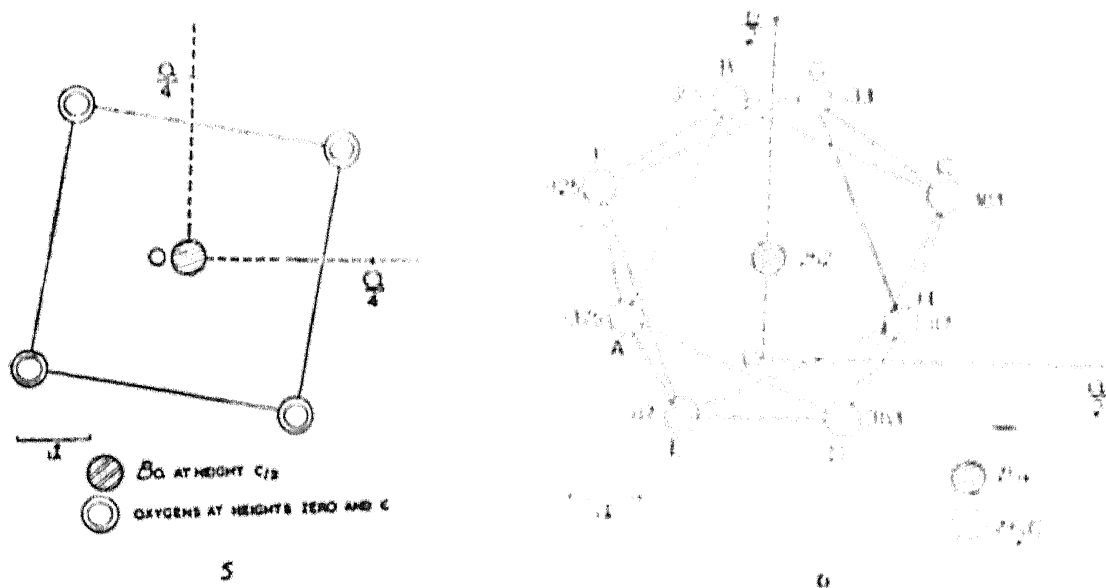


FIG. 5. Square prismatic co-ordination of barium in  $\text{Ba}_2(\text{Ti}_{0.2}\text{Mg}_{0.8})\text{O}_{10}$ .

FIG. 6. Co-ordination polyhedron (Square antiprism) in  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

pointed out, the trigonal prism with two faces centred [Fig. 8 (b) and (d)] can be considered as a highly distorted antiprism [Fig. 8 (a) and (c)]. The distortion consists in converting the square face ABCD of the antiprism into a rhombus and bending it along the diagonal BD to form two triangles ABD and BDC. The vertices A and C now centre the rectangular faces BDEF and BDHG of the triangular prism BDLFGH.

The triangular dodecahedron, also called the bisdisphenoid, is shown in Fig. 9 (c). This figure can be derived from a cube by stretching the top and bottom square faces ABCD and EFGH along perpendicular face diagonals BD and EG to obtain two rhombuses. The shorter diagonals AC and FH are now moved away from the centre of gravity of the solid so that each rhombus gives rise to two equilateral triangles which are not in the same plane. The resulting solid is bounded by twelve equilateral triangles. The structure of the silicate Gillespite  $\text{BaFeSi}_4\text{O}_{10}$ <sup>24</sup> consists of tetragonal zig-zag layers of  $\text{SiO}_4$  tetrahedra sharing corners. The barium atoms are reported to lie between the layers with a distorted cubic co-ordination. However, when the co-ordinating oxygen atoms were plotted, as shown in Fig. 9 (a) and (b), they were found to occupy the corners of a dodecahedron. Barium molybdate  $\text{BaMoO}_4$  and tungstate  $\text{BaWO}_4$  are both isotypes of tetragonal scheelite  $\text{CaWO}_4$ .<sup>25</sup> The co-ordination polyhedron of eight

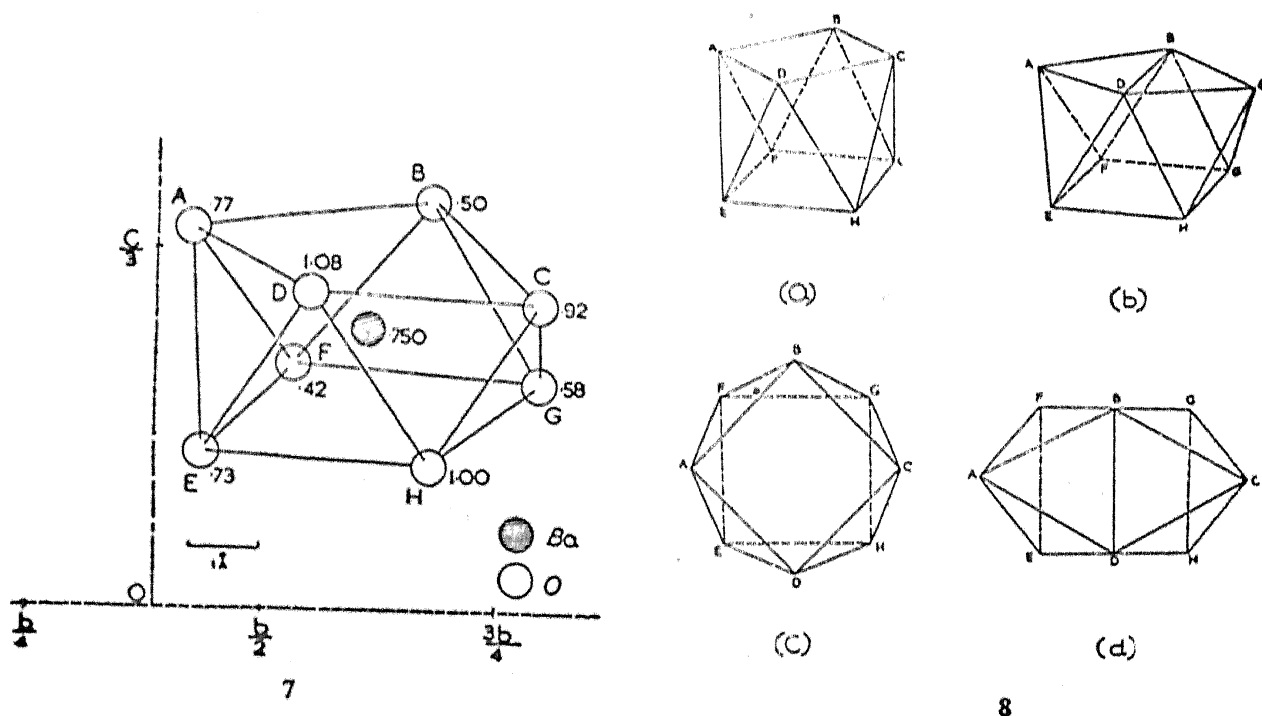


FIG. 7. Square antiprism co-ordination round one of the barium ions in  $\text{BaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O}$ .

FIG. 8. Relationship between the square antiprism [(a) and (c)] and the trigonal prism with two prism faces centred [(b) and (d)].

oxygens in the scheelite type can be described as a distorted dodecahedron. In the structure of  $\text{B}_2\text{ZnO}_2$ ,<sup>26</sup> the barium ion is reported to be surrounded by four oxygens at relatively short distances ( $2 \times 2.64 \text{ \AA}$ ,  $2 \times 2.68 \text{ \AA}$ ) in the form of a distorted bisphenoid,<sup>27</sup> which is a closed four-faced wedge-like solid resembling the tetrahedron but possessing no planes of symmetry. If two more at a larger distance of  $2.97 \text{ \AA}$  are considered, the six are reported to form a *strongly distorted* octahedron. It was, however, felt that the barium ion should have a more symmetric co-ordination. When the two next nearest neighbours  $3.36 \text{ \AA}$  away were also included and the eight co-ordinating atoms plotted, a *slightly distorted* bisdisphenoidal arrangement could be identified. The reported<sup>28</sup> similarity in the powder diagrams of  $\text{BaMnO}_2$ ,  $\text{B}_2\text{CoO}_2$  and  $\text{B}_2\text{ZnO}_2$  leads one to expect the same co-ordination polyhedron for  $\text{Ba}^{2+}$  in the first two substances as well.

A new eight co-ordination, shown in Fig. 10 (a), has been identified in barium uranate,  $\text{BaUO}_4$ .<sup>29</sup> The idealised polyhedron [Fig. 10 (b)] can be described in terms of a plane pentagon MLSTN whose vertices are joined to a point R on one side and two others O and P on the other, the line OP being parallel to the plane of the pentagon. It is interesting to observe that

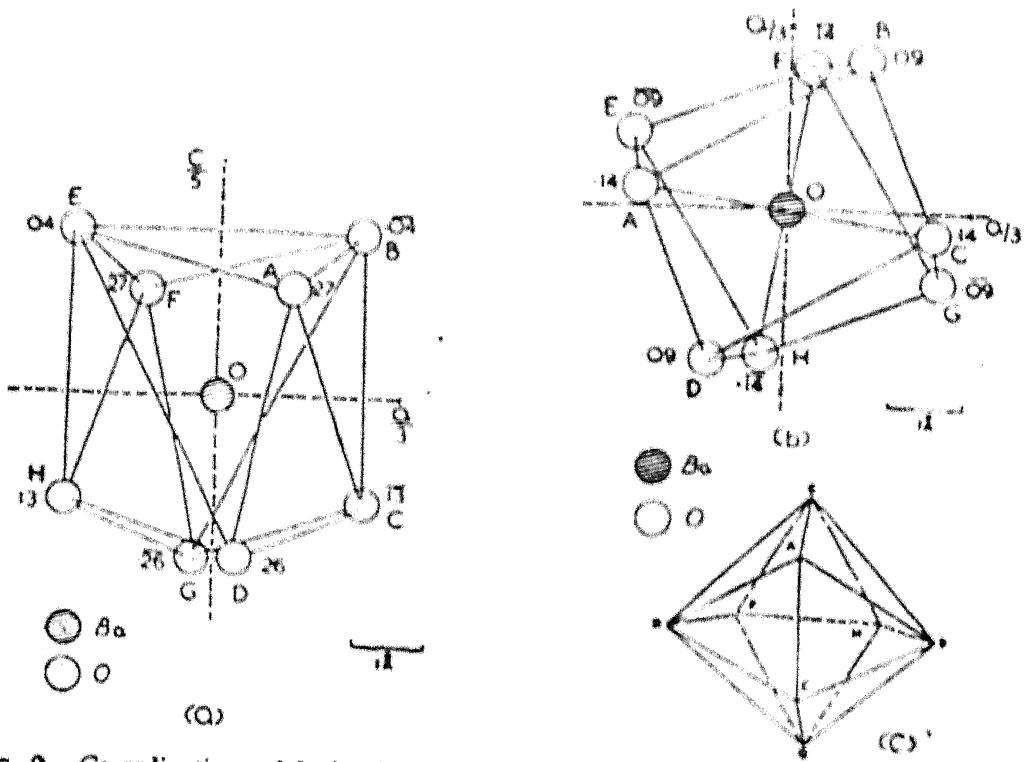


FIG. 9. Co-ordination polyhedron<sub>7</sub> (Triangular dodecahedron) round barium in  $BaFeSi_4O_{16}$ .

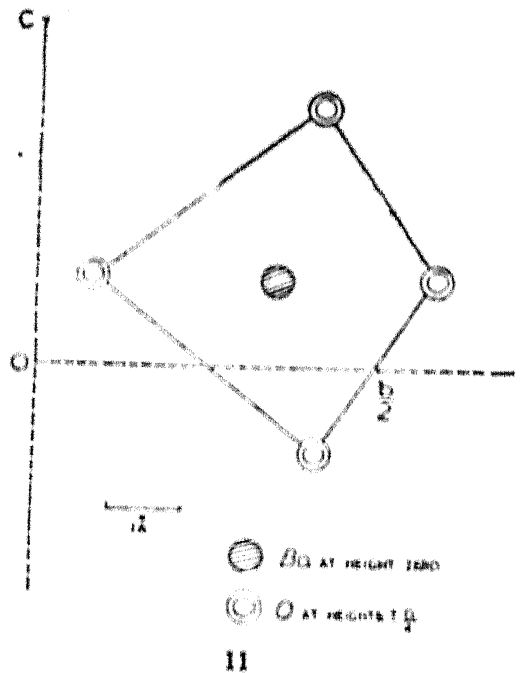
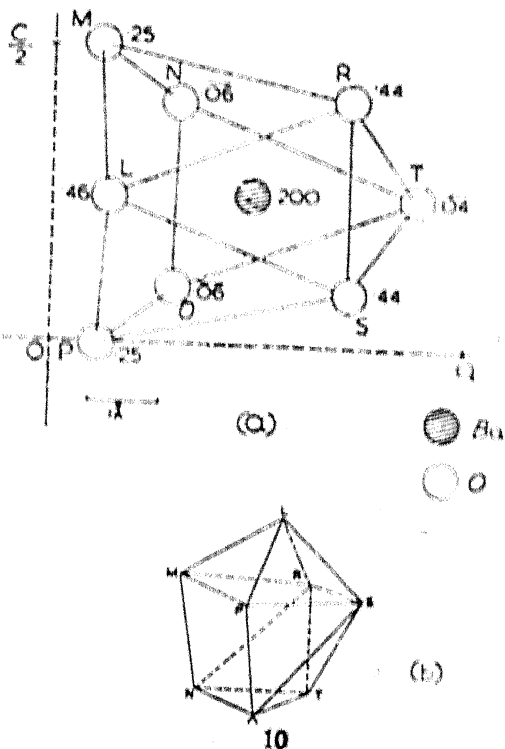


FIG. 10. New eight-fold co-ordination of  $Ba^{2+}$  in  $BaUO_6$  (see text).

FIG. 11. Co-ordination polyhedron (Quadrilateral prism) in  $NiO \cdot BaO$ .



the points OPLRT also form a plane pentagon approximately perpendicular to the first.

In barium permanganate  $\text{Ba}(\text{MnO}_4)_2$ <sup>30</sup> the eight oxygens co-ordinating the barium form an orthorhombic prism while in  $\text{NiO}\cdot\text{BaO}$ ,<sup>18</sup> they form a quadrilateral prism as shown in Fig. 11.

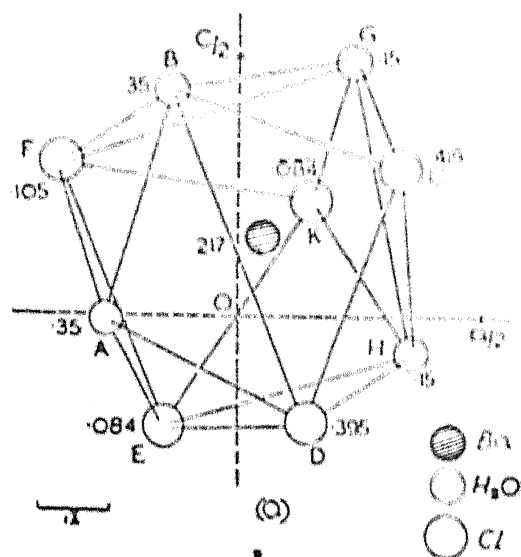
#### NINE-FOLD CO-ORDINATION

The halides of barium,  $\text{BaX}_2$ <sup>31</sup> ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) crystallise in the structure of  $\text{PbCl}_2$ . Here each barium is surrounded by nine halogen ions, six at the apices of a trigonal prism and the remaining three beyond the centres of the three prism faces [Fig. 12 (b)]. This appears to be the most common arrangement for nine-fold co-ordination. It is identified in barium orthoplumbate  $\text{Ba}_2\text{PbO}_4$  and orthostannate  $\text{Ba}_2\text{SnO}_4$ ,<sup>32</sup> which are isomorphous with  $\text{K}_2\text{NiF}_4$  and also in  $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$ <sup>33</sup> with which  $\text{BaI}\cdot 6\text{H}_2\text{O}$ <sup>34</sup> is isotypic. In the latter compounds nine waters make up the co-ordination polyhedron. On the other hand, in  $\text{BaCl}_2\cdot \text{H}_2\text{O}$ <sup>35</sup> and  $\text{BaBr}_2\cdot \text{H}_2\text{O}$ <sup>36</sup> which are isomorphous, six halogen ions are at the corners of the triangular prism while two waters and one halogen form the face centres. The same co-ordination polyhedron is formed by six oxygens and three waters in the orthorhombic form of barium pentathionate dihydrate  $\text{BaS}(\text{S}_2\text{O}_3)_2\cdot 2\text{H}_2\text{O}$ ,<sup>37</sup> in barium selenopentathionate dihydrate  $\text{BaSe}(\text{S}_2\text{O}_3)_2\cdot 2\text{H}_2\text{O}$ <sup>38</sup> and in barium tetrathionate dihydrate  $\text{BaS}_4\text{O}_6\cdot 2\text{HO}$ .<sup>39</sup>

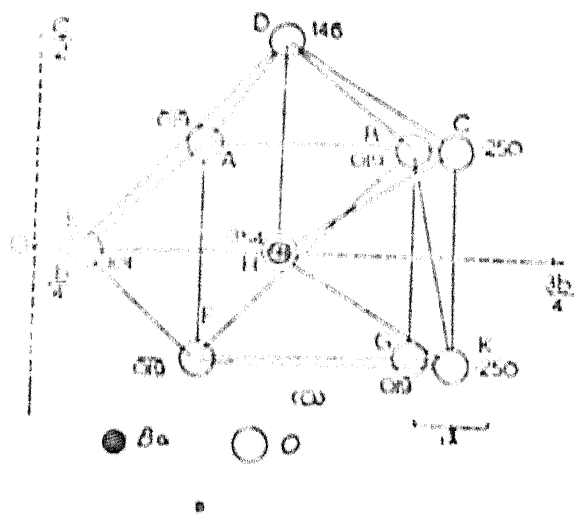
The structure of  $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ <sup>40</sup> consists of identical puckered  $(\text{BaCl}_2\cdot 2\text{H}_2\text{O})_n$  layers parallel to the  $a$ - $c$  plane. Each barium is reported to be surrounded by four chlorine ions at distances between 3.11 Å and 3.27 Å and four waters at distances between 2.78 Å and 2.82 Å in a distorted cubic configuration. In plotting the neighbours of barium [Fig. 12 (a)], however, it was found that the co-ordination number was nine and not eight as reported. This was because only the atoms within a layer had been considered, the chlorine K in the next layer at a distance 3.38 Å from  $\text{Ba}^{2+}$  having been overlooked. When this is also taken into account, the same co-ordination polyhedron discussed before is found to result.

The nine-fold co-ordination polyhedron [Fig. 12 (b)] consisting of a trigonal prism BDEFGH with the three prism faces centred by atoms A, C and K can also be looked at from a different point of view. It can be considered as a pentagonal pyramid D-ABCHE, D being the apex, placed over a triangle FGK in such a way that the vertices of the triangle F, G and K lie midway below AB, BC and EH respectively. A slightly modified form of the latter description has been identified in barium platinum titanium

oxide  $\text{Ba}_4\text{Ti}_2\text{PtO}_{10}$ .<sup>41</sup> The unit cell contains two groups of non-equivalent barium atoms, and the arrangement of oxygens round barium at 0.146, 0.473, O is shown in Fig. 13 (a). Here the atoms F, G, K at the vertices of the triangle lie directly below the vertices A, B, C respectively of the pentagon. The idealised polyhedron is shown in Fig. 13 (b).



12



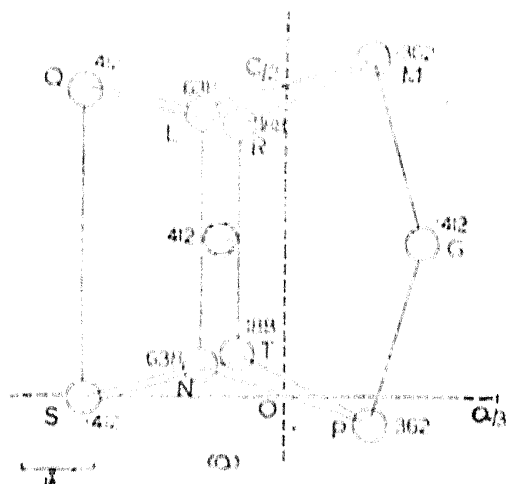
13

FIG. 12. Co-ordination polyhedron (Trigonal prism with three faces centred) in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

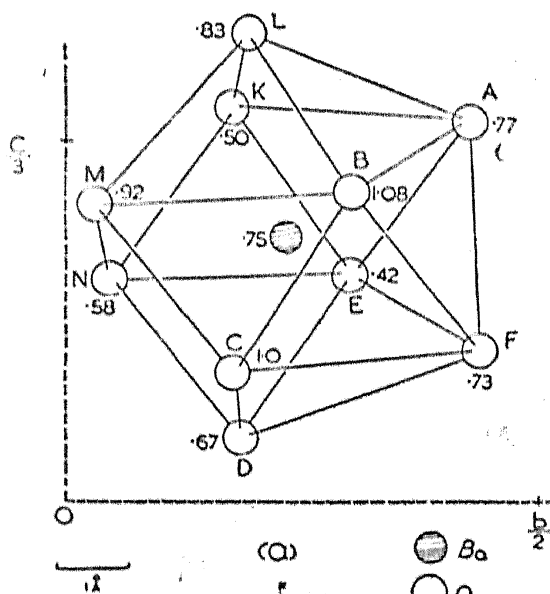
FIG. 13. Co-ordination of oxygens round one of the barium ions in  $\text{Ba}_4\text{Ti}_2\text{PtO}_{10}$  (see text).

A new nine-fold co-ordination, shown in Fig. 14 (a), has been identified in the mineral paracelecin  $\text{BaAl}_2\text{Si}_2\text{O}_8$ .<sup>42</sup> The polyhedron, idealised in Fig. 14 (b), can be described as a cube whose one edge MP has been elongated to make room for one more atom G situated beyond MP to co-ordinate the metal ion at the centre. The other polymorphic modification, barium feldspar or celecin, having the same formula, in which the configuration of oxygens is reported to be exactly similar has presumably the same co-ordination polyhedron of oxygen atoms round barium. Solid solutions of  $\text{BaCO}_3$  and  $\text{CaCO}_3$  crystallise, as mentioned already, in the structure of aragonite when the content of  $\text{BaCO}_3$  varies between 80 per cent and 100 per cent.<sup>44</sup> In this structure<sup>45</sup> as also in the silicate sanbornite  $\text{BaSi}_2\text{O}_8$ <sup>46</sup> the

above-mentioned polyhedron has been observed. It may be noted in passing that an investigation<sup>47</sup> of the high temperature phases of alkaline-earth carbonates reveals the interesting fact that  $\text{BaCO}_3$  changes from the orthorhombic aragonite type to the hexagonal calcite type at  $803^\circ\text{C}$ . and the cubic sodium chloride type of structure at  $976^\circ\text{C}$ . The transitions are related to the rotational activity of the carbonate ions.



14



15

FIG. 14. Nine-fold co-ordination of barium in paracelestin,  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (see text).

FIG. 15. Ten-fold co-ordination around the second barium ion in  $\text{BaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O}$  (see text).

### CO-ORDINATION NUMBER TEN

Wells<sup>48</sup> has pointed out that co-ordination polyhedra less symmetrical than those commonly known are found in some crystals and has cited the example of  $\text{LaF}_3$  for eleven-fold co-ordination. However, the shapes of the polyhedra do not appear to have been investigated hitherto. In the hydrated silicate  $\text{BaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ,<sup>23</sup> there are two non-equivalent barium ions in the unit cell, one of which, as mentioned earlier, exhibits an eight-fold co-ordination. The other barium, however, is co-ordinated by ten oxygens (either hydroxyl groups or waters). The polyhedron (Fig. 15), is made up of

two regular pentagonal pyramids E-AFDNK and B-AFCML sharing an edge AF. The solid has two other pentagonal pyramids with apices at A and F and two square faces KLMN and MNDC. The figure can also be described as consisting of a pentagonal pyramid F-ABCDE placed over a square KLMN. This co-ordination polyhedron has also been found in a slightly distorted form for all three non-equivalent barium ions in barium hydrogen orthophosphate  $\text{BaHPO}_4$ <sup>49</sup> and also in the silicate harmotone  $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ .<sup>50</sup>

The cations in rhombohedral normal orthophosphate of barium  $\text{Ba}_3(\text{PO}_4)_2$ <sup>51</sup> have two kinds of environment. Barium ions of one kind, e.g., that at 0, 0, 0.208 (in hexagonal indexing) are co-ordinated by ten oxygens as shown in Fig. 16 (a). The co-ordination polyhedron consists of a hexagonal pyramid placed over a triangle. Other compounds crystallising in this structure can be indicated by the formula  $\text{Ba}_3(\text{XO}_4)_2$ <sup>52</sup> where X = As, V, Cr, Mn.

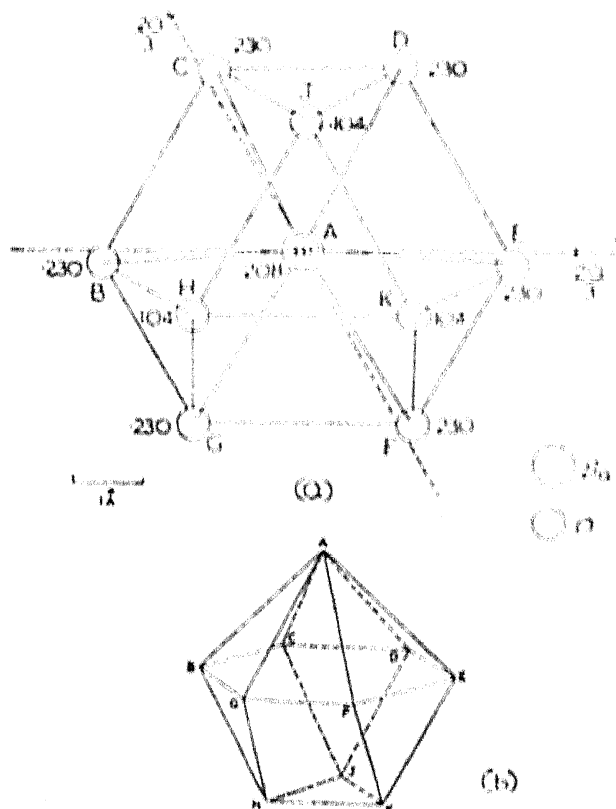


FIG. 16. Co-ordination polyhedron round  $\text{Ba}^{2+}$  in  $\text{Ba}_3(\text{PO}_4)_2$  (see text).

The structure of barium peroxide  $\text{BaO}_2$ <sup>53</sup> can be regarded from the geometrical point of view as derived from the rocksalt structure by replacing the  $\text{Na}^+$  and  $\text{Cl}^-$  by barium and peroxide ions respectively. Therefore, the

barium ion is octahedrally co-ordinated by six peroxide groups. The C.N. is, however, ten. The co-ordination polyhedron [Fig. 17 (a)] consists of eight oxygens belonging to four peroxide groups which form a flat square prism of sides  $3.81 \text{ \AA}$  and height  $1.49 \text{ \AA}$ , which is the O-O distance in the peroxide group, and two more which lie beyond the square faces. Barium carbide  $\text{BaC}_2^{54}$  also displays the same atomic arrangement.

In barium tetratitanate  $\text{BaTi}_4\text{O}_9^{55}$  it has been pointed out by the investigators of the structure that the metal ion has ten co-ordinating oxygens at the corners of a pentagonal prism. The co-ordination polyhedron for this compound is shown in Fig. 18 (a).

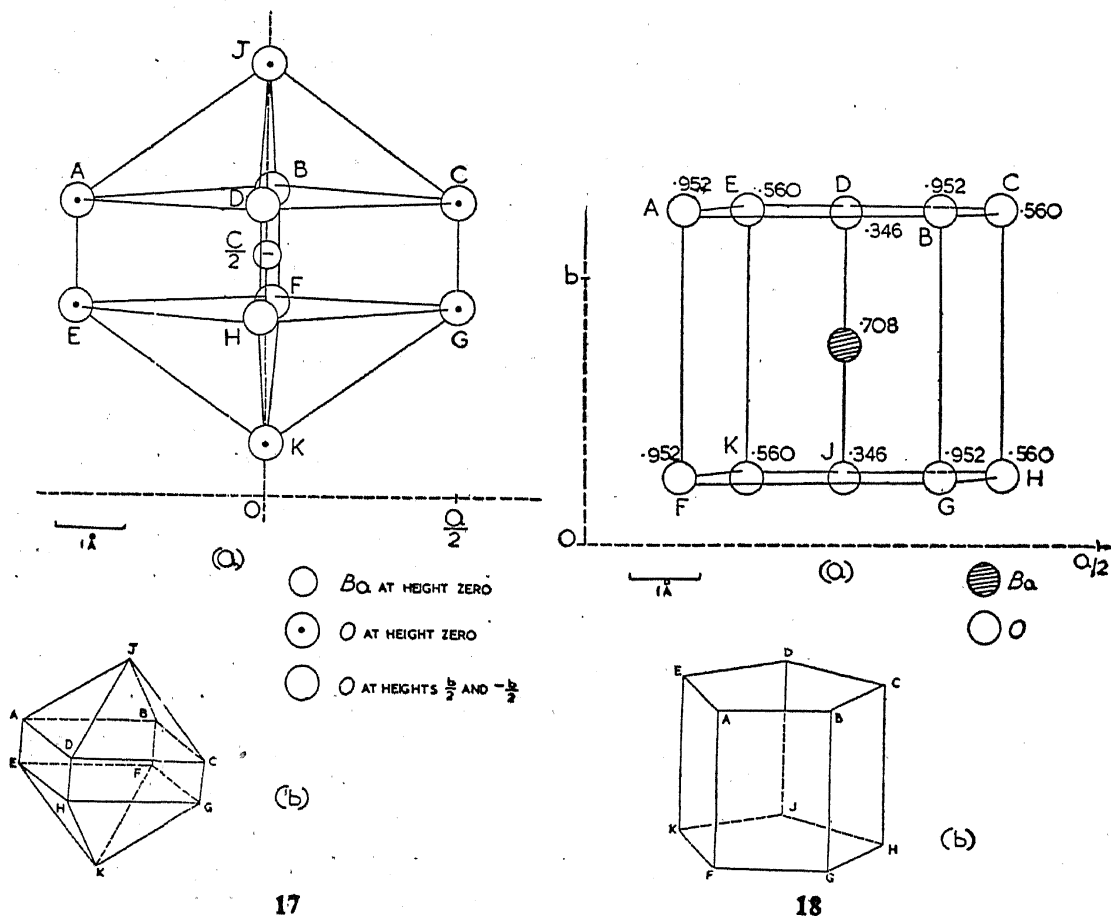


FIG. 17. Co-ordination polyhedron in  $\text{BaO}_2$ .

FIG. 18. Co-ordination polyhedron (Pentagonal prism) in  $\text{BaTi}_4\text{O}_9$ .

ELEVEN-FOLD CO-ORDINATION

An interesting geometric figure [Fig. 19 (a)] has been identified as the co-ordination polyhedron around barium in barium thiosulphate mono-

hydrate  $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .<sup>56</sup> In this structure barium has eleven nearest neighbours consisting of nine oxygens and two sulphurs. The idealised solid [Fig. 19 (b)] consists of a plane pentagon ABCDE, with two triangles FGH and KLM oriented in the same manner, placed symmetrically above and below it, and is bounded by eighteen triangular faces.

Wells<sup>57</sup> reports that the 'tysonite' structure of  $\text{LaF}_3$  is adopted among others by certain complex fluorides of barium like  $\text{BaThF}_6$  and  $\text{BaUF}_6$ . In tysonite, the  $\text{La}^{3+}$  ion is reported to have five equidistant nearest neighbours at a distance 2.36 Å, at the apices of trigonal bipyramid. The next nearest neighbours are six more fluorines at the corners of a trigonal prism at a distance of 2.70 Å. All the eleven atoms, when taken together, are found to form the above-mentioned polyhedron. In fact, in Fig. 19 (b), it is easy to see that the triangular faces of the prism are FEK and GDL and the vertices of the bipyramid A-BHM-C.

In barium chlorate monohydrate  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ <sup>58</sup> and the isomorphous  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ <sup>59</sup> the co-ordination polyhedron (Fig. 20) of ten oxygens and one water can be described as a square placed over a hexagonal pyramid, the hexagon being puckered.

#### CO-ORDINATION NUMBER TWELVE

Twelve-fold co-ordination is exhibited in a variety of ways in barium compounds. A large number of compounds crystallise with the cubic perovskite structure  $\text{XYO}_3$ <sup>60</sup> or with slightly distorted variants of lower symmetry. These departures from the symmetric form are of great interest because of the dielectric and magnetic properties of these compounds. In the 'ideal' perovskite structure, which is cubic, the X ions and the O ions of nearly equal size, form a close-packed arrangement with the smaller Y ions in some of the interstices. The sequence of layers in cubic close-packing is ABCABC... with the usual convention adopted in close-packing arrangements. The X ions are thus co-ordinated by twelve oxygen ions, the co-ordination polyhedron being the cubo-octahedron [Fig. 21 (b)]. The most common example of this structure is barium titanate  $\text{BaTiO}_3$  in which the co-ordinating atoms around barium are shown in Fig. 21 (a).  $\text{BaTiO}_3$  is remarkable in having five crystalline forms. The simple cubic form is present between 120° C. and 1460° C. There is a high temperature form above 1460° C. which is hexagonal. Between 120° C. and 5° C., the substance is tetragonal, between 5° C. and -80° C. it is orthorhombic and below -80° C., it has a rhombohedral structure. The three forms below 120° C., the Curie temperature, are ferroelectric. The changes in cell parameters, however, and the displacements

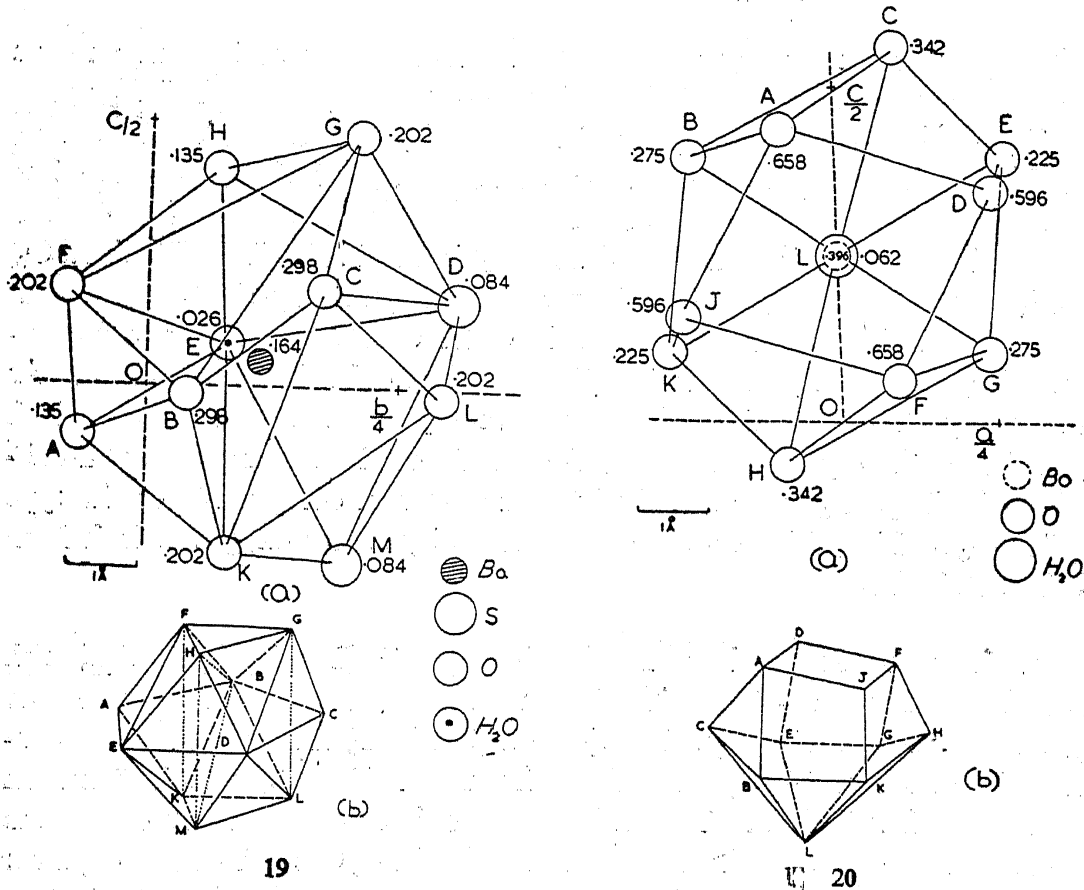


FIG. 19. Eleven-fold co-ordination of  $Ba^{2+}$  in  $BaS_2O_8 \cdot H_2O$  (see text).

FIG. 20. Co-ordination polyhedron in  $Ba(ClO_3)_3 \cdot H_2O$ .

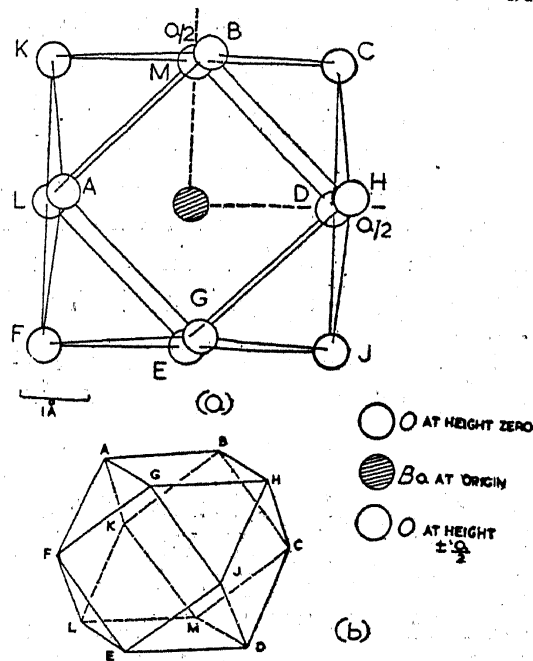


FIG. 21. Co-ordination polyhedron (Cubo-octahedron) in  $BaTiO_3$ .

of the atoms are extremely small and the environment of barium remains the same. Other examples of the cubic perovskite type are  $\text{BaYO}_3$  where  $\text{Y} = \text{Zr}$ ,  $\text{Sn}$ ,  $\text{Ce}$ ,  $\text{Hf}$ , (Wells<sup>61</sup>),  $\text{Pr}$ ,  $\text{Th}$  (Wells<sup>62</sup>) and  $\text{U}$ .<sup>63</sup> A barium-iron oxide having the stoichiometric composition  $\text{BaFeO}_3$  with the cubic perovskite structure has also been reported,<sup>64</sup> Fe being in valence state 4+. Certain substituted perovskites<sup>65</sup> such as  $\text{Ba}_3\text{NiTa}_2\text{O}_9$ ,  $\text{BaKTiNbO}_6$ ,  $\text{BaLaKTiAlNbO}_9$ ,  $\text{BaLiF}_3$  having ideal cubic or slightly distorted symmetry also crystallise in this structure. The barium atoms in  $\text{Ba}_3\text{O} \cdot 2\text{TiO}_2$  are reported<sup>66</sup> to be surrounded by twelve oxygens of the type found in cubic barium titanate. As seen already, in pseudocubic alkaline-earth molybdates and tungstates, which crystallise in the cryolite structure, two-thirds of the barium atoms in substances like  $\text{Ba}_3\text{WO}_6$  and both the barium atoms in compounds of the type  $\text{Ba}_2\text{CaWO}_6$  and  $\text{Ba}_2\text{CaMoO}_6$  are co-ordinated by twelve oxygens which form a cubo-octahedron.

In the structure of the mineral psilomelane<sup>67</sup>  $(\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ , with the ratio of  $\text{Ba}:\text{H}_2\text{O} = 1:2$  (the barium ions and water molecules are crystallographically indistinguishable), each  $(\text{Ba}, \text{H}_2\text{O})$  is reported to be situated at the centre of 14 oxygen atoms, shown in Fig. 22, which form an irregular tetrahexahedron. The author reports that it is more convenient to ignore the more distant ( $> 3.0 \text{ \AA}$ ) four atoms P, C, Q, F which are coplanar with the central atom and describes the co-ordination in terms of a polyhedron formed by a prism and pyramid sharing one edge with adjacent members. However, it is seen that the Ba-O distances increase progressively from  $2.78 \text{ \AA}$  to  $3.16 \text{ \AA}$  after which there is a gap, the two largest distances being  $3.62 \text{ \AA}$  and  $3.76 \text{ \AA}$ . Therefore, it appears very reasonable to ignore the atoms P and Q at these distances, in which case we find the co-ordination polyhedron consisting of eight oxygens A, G, B, H, M, D, F, C and four waters K, J, L, E to be a cubo-octahedron. The naming of atoms belonging to the cubo-octahedron is the same as in Fig. 21 (b). An error in the co-ordinates of  $\text{O}_1$  (Table I, page 435 of the original paper) which should be  $0.168, 0, 0.572$  instead of  $0.168, 0, \overline{0.072}$ , as reported, should be pointed out here. The same co-ordination polyhedron is also present in the mineral hollandite,  $\text{BaMn}_8\text{O}_{16}$ .<sup>68</sup>

The other type of close-packing, hexagonal close-packing, in which the sequence of close-packed layers is ABAB... is displayed in hexagonal  $\text{BaNiO}_3$ <sup>18</sup> [(Fig. 23 (a))]. Here again the co-ordination number of barium is twelve, the polyhedron [Fig. 23 (b)] being known as the disheptahedron.  $\text{BaMnO}_6$ <sup>69</sup> also has the hexagonal close-packed arrangement of barium and



oxygens at low temperatures. At high temperatures, however, the arrangement is close-packed but the sequence of layers is ABAC.... The high

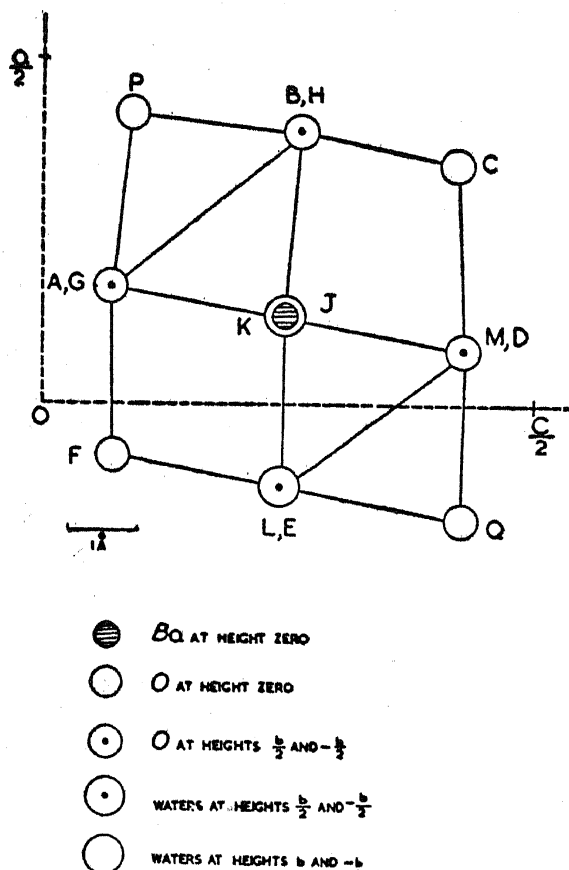


FIG. 22. Co-ordinating atoms round  $Ba^{2+}$  in  $(Ba, H_2O)_2Mn_5O_{10}$  (Cubo-octahedron).

temperature form of  $BaTiO_3$ <sup>70</sup> which exists at temperatures above 1460° C. is closely related to the perovskite structure, the arrangement of close-packed  $BaO_3$  layers being ABCACB.... In cases such as the last two mentioned, the cubic as well as hexagonal close-packing arrangements exist, depending on the layer in which the barium considered is present.

The structure of the isomorphous compounds<sup>71</sup>  $Ba_5Nb_4O_{15}$  and  $Ba_5Ta_4O_{15}$  have been described as a five layer (ABCBC) repeat, closest packing of oxygens with a barium replacing an oxygen in each layer in the unit cell. The crystal structures of a number of new ferromagnetic compounds of barium belonging to the trigonal and hexagonal systems such as  $BaFe_{18}O_{27}$ ,  $Ba_2Zn_2Fe_{12}O_{22}$ , etc., have been published.<sup>72, 73</sup> The structure of these compounds is related to the magnetoplumbite structure. In these structures, the oxygen and barium atoms together are reported to form a slightly expanded close-packed arrangement with Ba atoms in certain selected positions

and smaller ions in certain of the holes. In  $\text{BaFe}_{12}\text{O}_{19}$  which is isomorphous with magnetoplumbite, the oxygen ions form a hexagonal close-packed lattice, some sites of which are occupied by barium. From powder diffraction studies and permittivity measurements at different temperatures over the entire range of composition, a tetragonal perovskite structure has been deduced for  $(\text{Pb}, \text{Ba})\text{TiO}_3$ .<sup>74</sup>

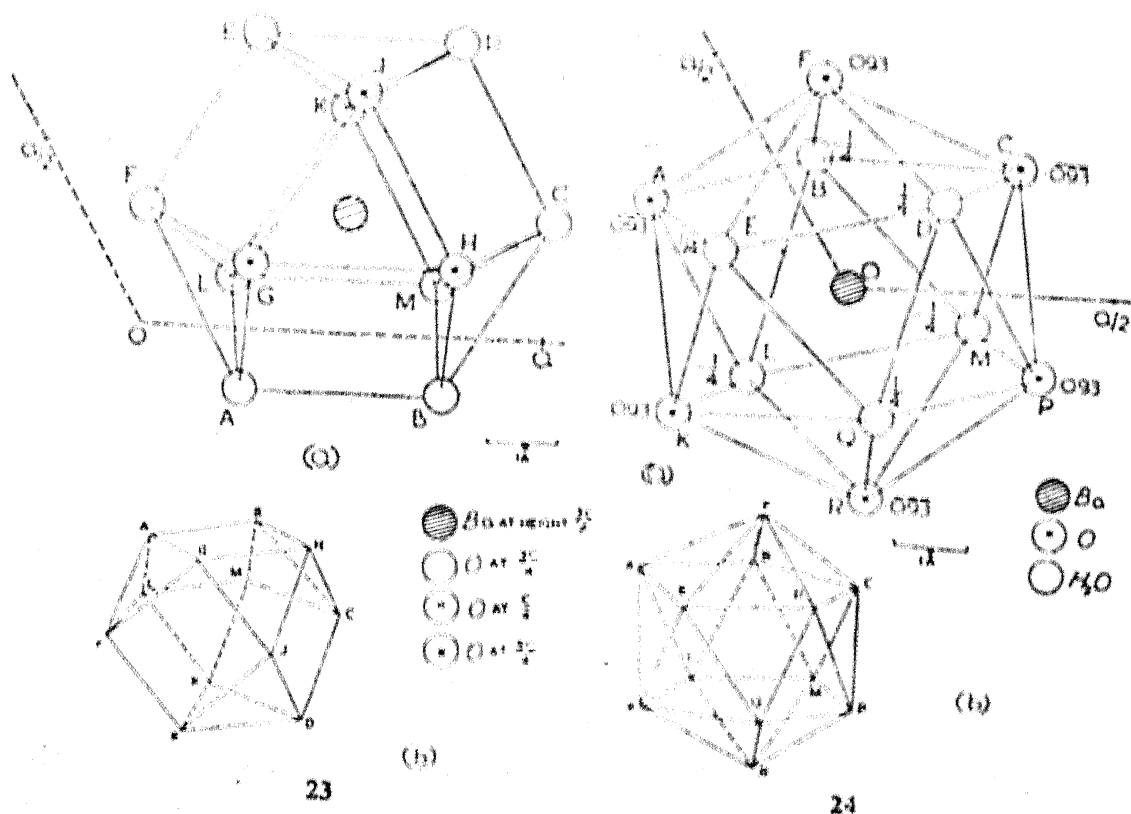
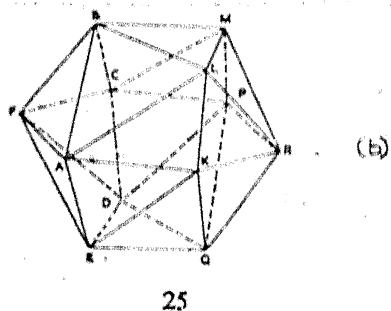
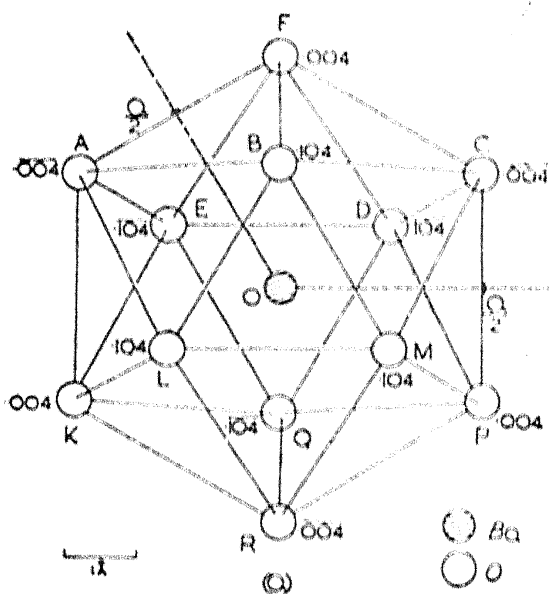


FIG. 23. Co-ordination polyhedron (Disheptahedron) in  $\text{BaNiO}_6$ .  
 FIG. 24. Icosahedral co-ordination of barium in  $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ .

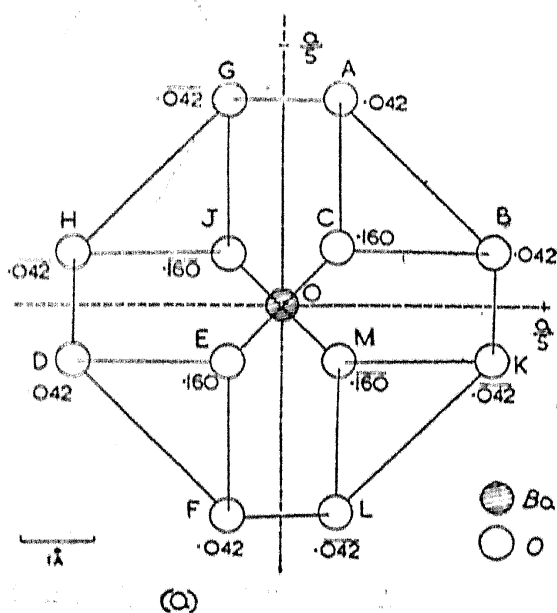
The arrangement of six perchlorate oxygens and six waters round barium in the form of an icosahedron has been reported by Mani and Ramaseshan<sup>3</sup> in barium perchlorate trihydrate  $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ . The figure of the icosahedron is obtained by placing six spheres F-ABCDE in a pentagonal pyramidal arrangement in contact with a similar group R-KLMPQ but with a rotation of  $36^\circ$ . The solid [Fig. 24 (b)] is bounded by twenty equilateral triangles and has six five-fold axes and ten three-fold axes. The icosahedron is one of the five regular solids<sup>75</sup>, the most symmetrical polyhedra having all their faces regular and alike and all the vertices surrounded in the same manner. The others are the tetrahedron, octahedron, cube and the pentagonal dodecahedron. A deformed icosahedral arrangement of oxygens round  $\text{Ba}^{2+}$  has

been identified by the above authors in cubic  $\text{Ba}(\text{NO}_3)_2$ <sup>76</sup> and also in the isomorphous complex fluorides,  $\text{BaXF}_6$ ,<sup>77</sup> where  $\text{X} = \text{Si}, \text{Ge}$  and  $\text{Ti}$ . In the latter structures, the co-ordination polyhedron is made up of twelve fluorine ions. A highly distorted arrangement has been found by the present writers in barium peroxide dihydro-peroxidate  $\alpha\text{-BaO}_2 \cdot 2\text{H}_2\text{O}_2$ .<sup>78</sup>

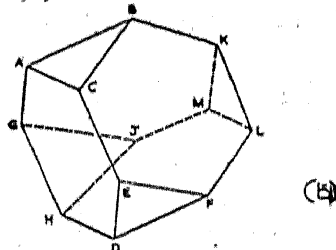
The icosahedron can also be described in terms of a chair-shaped hexagon AFCPRK [Fig. 24 (b)] with two triangles EDQ and BLM which are crossed with respect to each other placed symmetrically above and below it. On the other hand, in  $\text{Ba}_3(\text{PO}_4)_2$ ,<sup>51</sup> where barium ions of the second kind are surrounded by twelve oxygens as shown in Fig. 25 (a), the hexagon is practically planar, the maximum difference in heights between the atoms in the plane being 0.17 Å; whereas in  $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  the difference in heights between the atoms F, K or P and A, C or R of the puckered hexagon is 1.8 Å. Therefore, the co-ordination polyhedron in the present case can be considered as a deformed icosahedron. The idealised solid is seen in Fig. 25 (b). In



25



(a)



26

FIG. 25. Twelve-fold co-ordination of  $\text{Ba}_{11}^{2+}$  in  $\text{Ba}_3(\text{PO}_4)_2$  (see text).

FIG. 26. Co-ordination polyhedron (Truncated tetrahedron) in  $\text{BaCa}_3(\text{C}_2\text{H}_3\text{O}_2)_6$ .

cubic close-packing also (Fig. 21) there is a 3-6-3 arrangement of atoms round the cation, but the orientation of the triangles GHJ and KLM with respect to the plane hexagon ABCDEF is different. It has in fact been pointed out that the cubic close-packing arrangement can be converted into the icosahedral arrangement by the application of a force along a triad axis.

In barium dicalcium propionate  $\text{Ba}_2\text{Ca}_2(\text{C}_3\text{H}_5\text{O}_2)_6$ ,<sup>79</sup> the co-ordination polyhedron when plotted [Fig. 26 (a)], is found to be a truncated tetrahedron. This solid, with four hexagonal and four triangular faces and twelve vertices, is shown in Fig. 26 (b).

An unusual co-ordination polyhedron is the hexagonal prism which is present in hexagonal high temperature barium feldspar  $\text{BaAl}_2\text{Si}_2\text{O}_8$ <sup>80</sup> (Fig. 27).

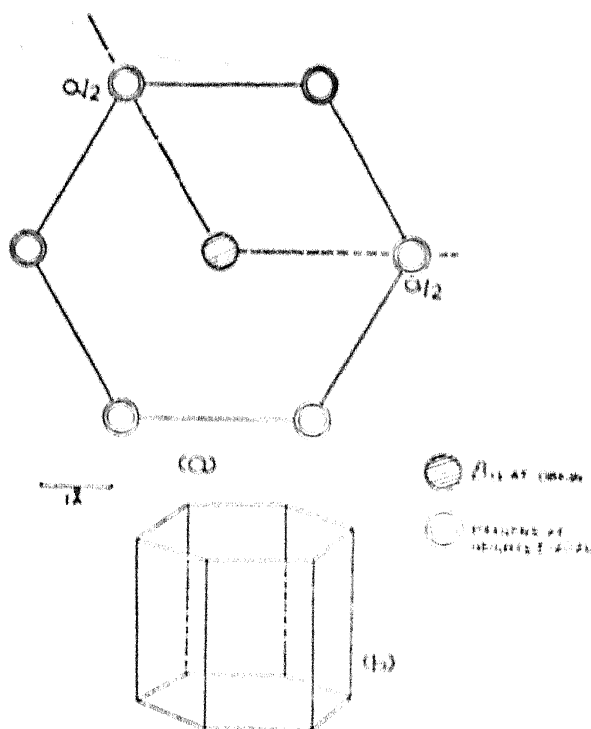


FIG. 27. Co-ordination polyhedron (Hexagonal prism) round  $\text{Ba}^{2+}$  in high temperature barium feldspar ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ).

In orthorhombic barite  $\text{BaSO}_4$ ,<sup>81, 82</sup> the barium ion is co-ordinated by twelve oxygens at distances between 2.69 Å and 3.32 Å, as seen in Fig. 28 (a). These oxygen atoms form a new type of co-ordination polyhedron [Fig. 28 (b)] which can be described in terms of two boat-shaped hexagons ABCDEF and ABGHJK sharing a common edge AB. The two lower edges ED and JH parallel to the common edge form a square. The hexagons are now centred on the outer side by atoms L and M such that

these two along with F, K, C and G form a plane hexagon. The polyhedron thus resembles a basket with AB as the handle. Mani and Ramaseshan,<sup>2</sup> in discussing the co-ordination of  $Ba^{2+}$  earlier, had reported the co-ordination number to be eight. The co-ordination polyhedron viewed down the  $b$ -axis as represented by these authors is shown in Fig. 28 (c). The atoms which had not been taken into account are F, C, G and K and therefore, the polyhedron was reported to be a trigonal prism with its two vertical faces centred. A large number of substances crystallising in the  $BaSO_4$  structure like  $KMnO_4$ ,  $KClO_4$ ,  $NH_4ClO_4$ ,  $PbSO_4$ ,  $SiSO_4$  (Wyckoff<sup>83</sup>), as also barium compounds like  $BaBeF_4$ ,<sup>84</sup>  $BaFeO_4$ ,<sup>85</sup>  $BaBOF_3$ ,<sup>86</sup>  $BaBeF_3OH$ ,<sup>87</sup>  $BaFPO_3$ ,<sup>88</sup> etc., should display the same type of co-ordination of the metal ion, the co-ordinating atoms being oxygens, fluorines, hydroxyl groups or a combination of these as the case may be.

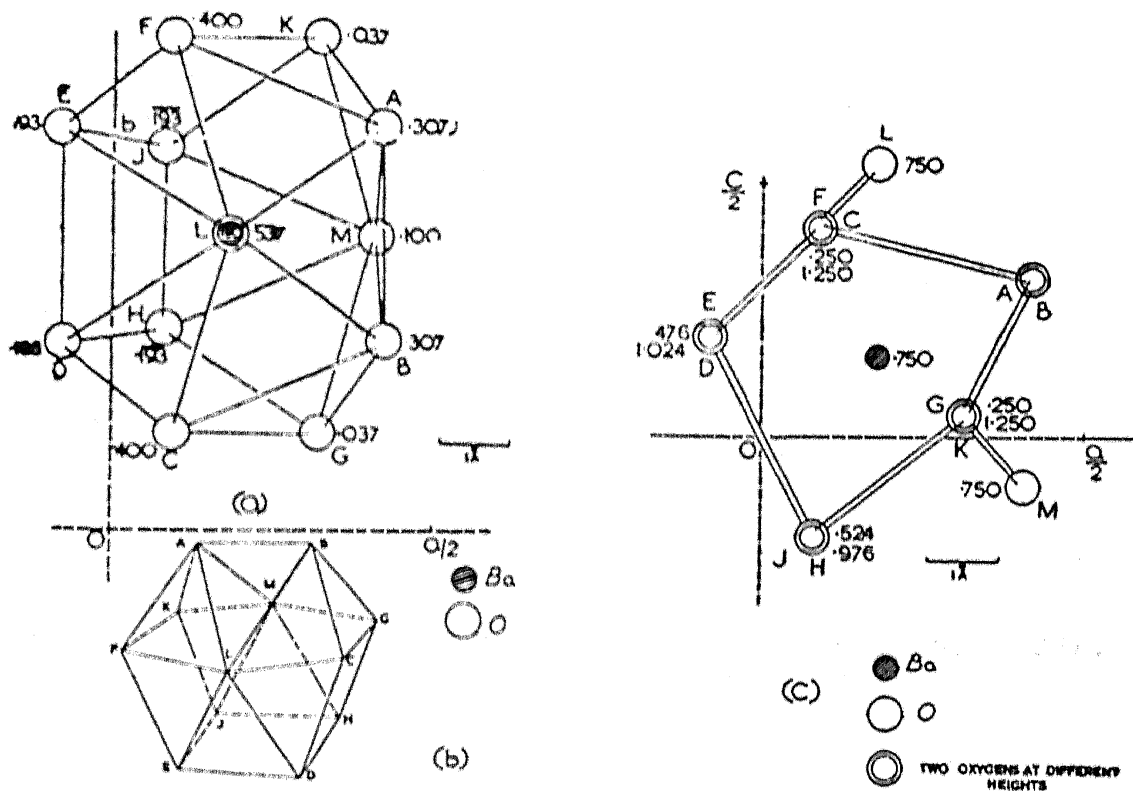


FIG. 28. New twelve-fold co-ordination of  $Ba^{2+}$  in  $BaSO_4$  (see text).

Table II gives the space group, cell dimensions, distances of co-ordinating atoms, C.N. and co-ordination polyhedra for most of the barium compounds that have been discussed.

TABLE II  
*Distances of co-ordinating atoms, co-ordination numbers and polyhedra in barium compounds*

Compound	Space group and cell dimensions (Å)	Ba-O distances (Å)		C.N.	Co-ordination polyhedron
BaO	Fm3m $a=5.50$	2.75		6	Octahedron, Fig. 1
BaTiSi <sub>2</sub> O <sub>6</sub>	P6̄c2 $a_{\text{cell}}=6.60$ $c=9.71$	2.74		6	Distorted octahedron
BaGeO <sub>3</sub> (High temperature)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> $a=4.58$ $b=5.68$ $c=12.76$	1×2.62 1×2.64 1×2.67 1×2.79	1×2.84 1×2.94 1×2.99	7	Octahedron + 1, Fig. 2
Ba <sub>2</sub> ZnS <sub>3</sub>	Pnam $a=12.05$ $b=12.65$ $c=4.21$	Ba <sub>1</sub> -S 1×3.19 2×3.22 2×3.24 2×3.26	Ba <sub>2</sub> -S 2×3.15 2×3.20 2×3.20 1×3.22	7	Trigonal prism, one face-centred, Fig. 3
NiO.3BaO	R3̄c Hexagonal axes: $a=7.85$ $c=16.50$	2.73-2.88		7	Modified pentagonal bipyramid, Fig. 4
BaF <sub>2</sub>	Fm3m $a=6.187$	Ba-F 2.69		8	Cube
Ba <sub>2</sub> (Ti <sub>2-3</sub> Mg <sub>3</sub> )O <sub>16</sub>	14/m $a=10.11$ $c=2.936$	3.01		8	Square prism, Fig. 5
Ba(OH) <sub>2</sub> .8H <sub>2</sub> O	P2 <sub>1</sub> /n $a=9.35$ $b=9.28$ $c=11.87$ $\beta=99^\circ$	1×2.69 1×2.72 2×2.73	1×2.75 1×2.76 2×2.77	8	Archimedean antiprism, Fig. 6
BaO.SiO <sub>2</sub> .6H <sub>2</sub> O	P2 <sub>1</sub> cn $a=8.43$ $b=12.96$ $c=15.01$	Ba-O 2.83-2.90		8	Archimedean antiprism, Fig. 7

TABLE II (Contd.)

Compound	Space group and cell dimensions (Å)	Ba-O distances (Å)		C.N.	Co-ordination polyhedron
BaFeSi <sub>4</sub> O <sub>10</sub>	P4/ncc a= 7.51 c=16.08	4×2.73 4×2.98		8	Triangular dodecahedron, Fig. 9
BaZnO <sub>4</sub>	P3 <sub>1</sub> 21 a= 5.886 c= 6.734	2×2.64 2×2.68	2×2.97 2×3.36	8	do.
BaUO <sub>4</sub>	Pbcn a= 5.75 b= 8.14 c= 8.23	4×2.71 1×2.90	2×2.97 1×2.99	8	See Text, Fig. 10
Ba(MnO <sub>4</sub> ) <sub>2</sub>	Fddd a=14.71 b=11.86 c= 7.39	4×2.4 4×2.6		8	Orthorhombic prism
NiO.BaO	Cmcm a= 5.73 b= 9.20 c= 4.73	4×2.80 4×2.84		8	Quadrilateral prism, Fig. 11
BaCl <sub>2</sub> .H <sub>2</sub> O	Pmcn a= 4.51 b= 9.02 c=11.28	Ba-Cl 2×3.14 2×3.21 1×3.32 1×3.34 1×3.38	Ba-H <sub>2</sub> O 2×2.76	9	Trigonal prism three faces centred, Fig. 12 (b)
BaBr <sub>2</sub> .H <sub>2</sub> O	Pmcn a= 4.59 b= 9.41 c=11.59	Ba-Br 2×3.22 2×3.33 1×3.42 1×3.47 1×3.49	Ba-H <sub>2</sub> O 2×2.81	9	do.
BaS(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> .2H <sub>2</sub> O	Pnma a= 5.00 b=10.30 c=21.78	Ba-O 2×2.72 2×2.79 2×2.91	Ba-H <sub>2</sub> O 1×2.65 1×2.69 1×2.84	9	do.

TABLE II (Contd.)

Compound	Space group and cell dimensions (Å)	Ba-O distances (Å)		C.N.	Co-ordination polyhedron
BaSc(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Pnma a= 4.98 b= 10.36 c= 22.20	Ba-O 2×2.74 2×2.81 2×2.86	Ba-H <sub>2</sub> O 1×2.51 1×2.65 1×2.74	9	Trigonal prism three faces centred, Fig. 12 (b)
BaS <sub>4</sub> O <sub>6</sub> ·2H <sub>2</sub> O	P2 <sub>1</sub> /c a= 5.17 b= 9.46 c= 19.07 β=96°	2.73-2.90		9	do.
BaCl <sub>2</sub> ·2H <sub>2</sub> O	P2 <sub>1</sub> /n a= 6.74 b= 10.86 c= 7.14 β=90° 57'	Ba-Cl 1×3.11 1×3.16 1×3.24 1×3.27 1×3.38	Ba-H <sub>2</sub> O 1×2.78 1×2.80 1×2.81 1×2.82	9	do. Fig. 12 (a)
Ba <sub>4</sub> Ti <sub>2</sub> PtO <sub>10</sub>	Abam a= 13.09 b= 13.33 c= 5.77	Ba <sub>1</sub> -O 1×2.71 1×2.72 2×2.79 2×3.02		9	See Text Fig. 13
BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (Paracelcian)	P2 <sub>1</sub> /n a=9.076 b=9.583 c=8.578 β≈90°	2×2.69 2×2.79 1×2.82 2×2.85 2×3.33		9	Cube + 1, Fig. 14
BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (Celcian)	I2/c a= 8.627 b= 13.045 c= 14.408 β=115° 13'	1×2.667 1×2.902 1×2.939 1×3.135 2×2.850 1×2.909 1×3.112 1×2.927		9	Cube + 1 Fig. 14 (b)
BaCO <sub>3</sub>	Pnma a= 5.28 b= 8.83 c= 6.39	2×2.76 3×2.80 4×2.84		9	do.
BaSi <sub>2</sub> O <sub>6</sub> (Sanbornite)	Pcmm a= 4.63 b= 7.69 c= 13.53	7×(2.74-2.94) 2×3.14		9	do.



TABLE II (Contd.)

Compound	Space group and cell dimensions (Å)	Ba-O distances (Å)		C.N.	Co-ordination polyhedron
BaO · SiO <sub>2</sub> · 6H <sub>2</sub> O	P2 <sub>1</sub> cn a = 8.43 b = 12.96 c = 15.01	Ba <sub>II</sub> -O 2.83-2.90		10	See Text, Fig. 15
BaHPO <sub>4</sub>	Pn2 <sub>1</sub> a a = 14.12 b = 17.15 c = 4.59	2.6-3.5		10	do.
Ba <sub>2</sub> Al <sub>4</sub> Si <sub>12</sub> O <sub>32</sub> · 12H <sub>2</sub> O (Harmotone)	P2 <sub>1</sub> a = 9.87 b = 14.14 c = 8.72 β = 124° 15'	Ba-O 1 × 3.02 1 × 3.04 2 × 3.08 2 × 3.26	Ba-H <sub>2</sub> O 1 × 2.77 1 × 2.80 1 × 2.92 1 × 2.99	10	do.
Ba <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub>	R $\bar{3}$ m (Hexagonal axes) a = 5.60 c = 20.97	Ba <sub>I</sub> -O 1 × 2.71 3 × 2.80 6 × 2.83		10	See Text, Fig. 16
BaO <sub>2</sub>	F4/mmm <sub>c</sub> a = 5.384 c = 6.841	8 × 2.79 2 × 2.68		10	See Text, Fig. 17
BaTi <sub>4</sub> O <sub>9</sub>	Pmmn a = 14.53 b = 3.79 c = 6.29	4 × 2.81 2 × 2.96 4 × 3.09		10	Pentagonal prism, Fig. 18
BaS <sub>2</sub> O <sub>8</sub> · H <sub>2</sub> O	Pbcn a = 20.07 b = 7.19 c = 7.37	Ba-O 2 × 2.78 1 × 2.79 1 × 2.83 1 × 2.90 2 × 3.00 1 × 3.55	Ba-H <sub>2</sub> O 1 × 2.83 Ba-S 1 × 3.44 1 × 3.66	11	See Text, Fig. 19
Ba(ClO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O	I2/c a = 8.86 b = 7.80 c = 9.35 β = 93° 30'	Ba-O 10 × (~2.87)	Ba-H <sub>2</sub> O 1 × (~2.60)	11	See Text, Fig. 20

TABLE II (Contd.)

Compound	Space group and cell dimensions (Å)	Ba-O distances (Å)		C.N.	Co-ordination polyhedron
BaTiO <sub>3</sub> (Cubic perovskite)	Pm3m $a = 3.986$	2.82		12	Cubo-octahedron, Fig. 21
(Ba, H <sub>2</sub> O) <sub>2</sub> Mn <sub>5</sub> O <sub>10</sub> (Psilomelane)	A2/m $a = 9.56$ $b = 2.88$ $c = 13.85$ $\beta = 92^\circ 30'$	Ba-O 2 × 2.85 2 × 2.91 2 × 2.96 1 × 3.00 1 × 3.16	Ba-H <sub>2</sub> O 2 × 2.78 2 × 2.88	12	do. Fig. 22
BaMn <sub>2</sub> O <sub>14</sub> (Hollandite)	I4/m $a = 9.96$ $c = 2.86$	8 × 2.74 4 × 3.31		12	Cubo-octahedron, Fig. 21
BaNiO <sub>3</sub>	C6mc $a = 5.58$ $c = 4.832$	6 × 2.79 6 × 2.90		12	Disheptahedron, Fig. 23
BaMnO <sub>3</sub> (low temperature)	P6 <sub>3</sub> mc $a = 5.67$ $c = 4.71$	6 × 2.84 6 × 2.86		12	do.
BaMnO <sub>3</sub> (High temperature)	P6 <sub>3</sub> /mmc $a = 5.67$ $c = 9.38$	6 × 2.83 6 × 2.86		12	See Text.
BaTiO <sub>3</sub> (non-ferroelectric)	C6 <sub>3</sub> /mmc $a = 5.735$ $c = 14.05$	Ba <sub>1</sub> -O 6 × 2.89 6 × 2.94	Ba <sub>11</sub> -O 6 × 2.88 3 × 2.78 3 × 2.96	12	See Text.
Ba <sub>2</sub> Ta <sub>4</sub> O <sub>18</sub>	P3̄ml $a = 5.79$ $c = 11.75$	2.7-3.0		12	See Text.
Ba <sub>2</sub> Zn <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub>	R3̄m (Hexagonal axes) $a = 5.876$ $c = 43.558$	3 × 2.80 6 × 2.94 3 × 3.19		12	See Text.
Ba(ClO <sub>4</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	P6 <sub>3</sub> or P6 <sub>3</sub> /m $a = 7.278$ $c = 9.64$	Ba-O 3 × 2.96 3 × 3.18	Ba-H <sub>2</sub> O 6 × 3.03	12	Icosahedron, Fig. 24

TABLE II—Contd.

Compound	Space group and cell dimensions (Å)	Ba-O distances (Å)	C.N.	Co-ordination polyhedron
Ba(NO <sub>3</sub> ) <sub>2</sub>	Pa3 a= 8·11	6×2·82 6×3·00	12	Icosohedron Fig. 24
BaSiF <sub>6</sub>	R $\bar{3}$ m a= 4·75 a=97° 58'	Ba-F 6×2·75 6×2·88	12	do.
BaGeF <sub>6</sub>	R $\bar{3}$ m a= 4·83 a=98° 1'	Ba-F 6×2·77 6×2·92	12	do.
$\alpha$ -BaO <sub>2</sub> ·2H <sub>2</sub> O <sub>2</sub>	C2/c a= 8·454 b= 6·398 c= 8·084 $\beta$ =96° 32'	2×2·68 2×2·74 2×2·78 2×2·86 2×2·93 2×2·97	12	do.
Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	R $\bar{3}$ m (Hexagonal axes) a= 5·60 c=20·97	Ba <sub>n</sub> -O 6×3·23 6×2·80	12	See Text, Fig. 25
BaCa <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>6</sub>	Fd3m a=18·20	3·10	12	Truncated tetrahedron, Fig. 26
BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (High temperature barium feldspar)	6/mmm a= 5·25 c= 7·84	3·05	12	Hexagonal prism, Fig. 27
BaSO <sub>4</sub>	Pnma a= 8·85 b= 5·43 c= 7·13	1×2·69 1×2·76 2×2·77 2×2·80	2×2·94 2×3·10 2×3·32	12 See Text, Fig. 28

## DISCUSSION

Table III (Pauling<sup>88</sup>) shows the co-ordination for representative cations to be expected on the basis of radius-ratios. These have generally been

verified to be true in actual structures. Potassium, however, is seen to display several different types of co-ordination. As the present survey shows the barium ion also exhibits a rich variety of co-ordination.

TABLE III  
*Values of the ligancy for cations with oxygen ion*  
 (After Pauling)

Ion	Radius ratio	Predicted ligancy	Observed ligancy
B <sup>2+</sup>	0.20	3 or 4	3, 4
Be <sup>2+</sup>	0.25	4	4
Li <sup>+</sup>	0.34	4	4
Si <sup>4+</sup>	0.37	4	4, 6
Al <sup>3+</sup>	0.41	4 or 6	4, 5, 6
Ge <sup>4+</sup>	0.43	4 or 6	4, 6
Mg <sup>2+</sup>	0.47	6	6
Na <sup>+</sup>	0.54	6	6, 8
Ti <sup>4+</sup>	0.55	6	6
Sc <sup>3+</sup>	0.60	6	6
Zr <sup>4+</sup>	0.62	6 or 8	6, 8
Ca <sup>2+</sup>	0.67	8	7, 8, 9
Ce <sup>4+</sup>	0.72	8	8
K <sup>+</sup>	0.75	9	6, 7, 8, 9, 10, 12
Cs <sup>+</sup>	0.96	12	12

The values in antique are those usually found for the cation.

The other values are observed only in a few crystals.

In the earlier work of Goldschmidt<sup>89</sup> and Pauling,<sup>1</sup> only closed polyhedra formed by the nearest neighbours were considered. However, to obtain closed polyhedra in more complex crystals, it is necessary to take into account not merely the atoms which are the nearest neighbours, but also those which are next nearest ones. The question naturally arises as to the limit to the cation-anion distance one should go. Such limits have been set uptil now purely by convenience and not because they are dictated by any physical considerations.

The question why an ion sometimes prefers a higher co-ordination than usual still remains to be satisfactorily answered. The radius-ratios for the alkali halides (Wells<sup>90</sup>) and for the alkaline-earth metals in relation to O, S, Se and Te are shown in Tables IV and V respectively. The salts which are expected to crystallise in the rocksalt structure are enclosed in full lines.

TABLE IV  
*Values of radius ratio for the alkali halides*  
(After Wells)

	Li	Na	K	Rb	Cs
F	0.44	0.70	0.98	0.92*	0.81*
Cl	0.33	0.52	0.73	0.82	0.93
Br	0.31	0.49	0.68	0.76	0.87
I	0.28	0.44	0.62	0.69	0.78

\* Where  $r_A$ , radius of the cation, is greater than  $r_X$ , radius of the anion,  $r_X/r_A$  is given.

TABLE V  
*Values of univalent radius ratio for alkaline earth metals*

	Ca	Sr	Ba
O	0.67	0.75	0.87
S	0.54	0.60	0.70
Se	0.51	0.57	0.66
Te	0.47	0.53	0.61

Crystals with radius ratios enclosed by full lines are expected to crystallise with NaCl structure.

Except those enclosed by broken lines which have the CsCl structure, the rest of the crystals exhibit the rocksalt structure.

As Wells<sup>91</sup> points out, it is not clear why salts like RbBr, RbCl, CsF as also SrO do not adopt the CsCl type of structure with a larger co-ordination number eight, or why KF, RbF and BaO do not prefer still higher co-ordination of the cations. The difference between the lattice energy for NaCl and CsCl types of structures is too small to account for the structural differences. One could enumerate all possible factors such as the variation in the Madelung constant, effective charge, the repulsion exponent, etc., on which the inter-ionic distance and hence the co-ordination number depends to a greater or smaller degree. Co-ordination in complex ionic crystals is not entirely a geometrical problem of radii and sizes but also depends on the polarisation of the ions. Thus Ba<sup>2+</sup> is itself highly polarisable unlike other smaller positive ions and this must be responsible for the large variety in its co-ordination. Although the factors that affect the inter-atomic distances are well known, a quantitative assessment of their effects in any specific crystal is in our present state of knowledge not possible.

In many crystals the positive ion plays a vital role in determining the structure. The unique co-ordination polyhedron round that positive ion is an important factor in the geometry of the crystal architecture. Ba<sup>2+</sup> ion shows a bewildering number of co-ordination polyhedra. Whatever be the reasons for this, one cannot but conclude that the barium ion does not play a primary role in deciding the structure as most other ions do. Indeed its role is comparatively secondary and it enters the vacant spaces in the structure provided by the other atoms of the crystal.

#### SUMMARY

A systematic study has been made of the crystal co-ordination of the barium ion in various compounds whose structures have been solved. Apart from the more common co-ordination polyhedra which are enumerated in text-books, a number of new polyhedra have been identified, particularly in cases where the co-ordination numbers are unusual, such as ten or eleven. According to the radius-ratio rule of Pauling, a co-ordination number of nine or ten is normally expected for the barium ion. The present investigations, however, reveal that it shows a variety of co-ordinations with ligancies from six up to twelve. Some of the factors that might possibly enter in explaining this wide range of co-ordination numbers are discussed. It appears as though the part played by the Ba<sup>2+</sup> ion in deciding the structure is secondary, limiting itself only to occupying vacant spaces provided by other atoms in the crystal.

## ACKNOWLEDGEMENT

The authors thank Professor R. S. Krishnan for his kind interest in this investigation. Thanks are also due to Dr. N. V. Mani for his assistance in the earlier part of this study.

## REFERENCES

1. Pauling, L. .. "The principles determining the structures of complex ionic crystals," *J. Amer. Chem. Soc.*, 1929, **51**, 1010-26.
2. Mani, N. V. and Ramaseshan, S. "The crystal structure of barium perchlorate trihydrate  $Ba(ClO_4)_2 \cdot 3H_2O$  and the crystal co-ordination of  $Ba^{++}$  ion," *Z. Kristallogr.*, 1960, **114**, 200-14.
3. Manohar, H. and Ramaseshan, S. "The crystal structure of  $Ba(OH)_2 \cdot 8H_2O$  and the crystal co-ordination of the barium ion," *Curr. Sci.*, 1963, **32**, 248-49.
4. ————— .. "The crystal structure of barium hydroxide octahydrate,  $Ba(OH)_2 \cdot 8H_2O$ ," *Z. Kristallogr.*, 1964, **119**, 357.
5. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 462.
6. Wyckoff, R. W. G. .. *The Structure of Crystals, Supplement*, Reinhold Publishing Corporation, New York, 1935, p. 16.
7. Faivre, R. .. *Structure Reports* (N.V.A. Oosthoek's Uitgevers Mij, Utrecht) 1945-46, **10**, 173-74.
8. Hilmer, W. .. "Die Struktur der Hochtemperaturform des Bariumgermanates,  $BaGeO_3$  (h)," *Acta Crystallogr.*, 1962, **15**, 1101-05.
9. Dornberger-Schiff, K. .. "The symmetry and structure of  $Sr(GeO_3)$  as a structure mode for  $\alpha$ -Wollastonite  $CaSiO_3$ ," *Kristallografia*, 1961, **6**, 859-68. English translation in *Soviet Physics Crystallography*, 1962, **6**, 694-700.
10. Zachariasen, W. H. .. "The crystal structure of benitoite  $BaTiSi_3O_{10}$ ," *Z. Kristallogr.*, 1930, **74**, 139-46.
11. Vannerberg, N. G. .. "The structure of barium peroxide monohydroperoxidate," *Arkiv Kemi*, 1959, **14**, 149-59.
12. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 630.
13. ————— .. *Ibid.*, 1962, p. 499.
14. Steward, E. G. and Rooksby, H. P. "Pseudo-cubic alkaline-earth tungstates and molybdates of the  $R_3MX_6$  type," *Acta Crystallogr.*, 1951, **4**, 503-07.
15. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 369.
16. ————— .. *Ibid.*, 1962, p. 74.
17. Schnering, H. G. and Hoppe, R. "Zur Kenntnis des  $Ba_2ZnS_3$ ," *Z. anorg. allg. Chem.*, 1951, **312**, 99-109.

18. Lander, J. J. .. "The crystal structures of  $\text{NiO} \cdot 3\text{BaO}$ ,  $\text{NiO} \cdot \text{BaO}$ ,  $\text{BaNiO}$  and intermediate phases with composition near  $\text{Ba}_2\text{Ni}_3\text{O}_8$ ; with a note on  $\text{NiO}$ ." *Acta Crystallogr.*, 1951, 4, 148-56.
19. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford 1962, p. 337.
20. Dryden, J. S. and Wadsley, A. D. "The structure and dielectric properties of compounds with the formula  $\text{Ba}_x(\text{Ti}_{8-x}\text{Mg}_x)\text{O}_{16}$ ," *Trans. Faraday Soc.*, 1958, 54, 1574-80.
21. Hoard, J. L. and Silverton, G. L. "The configuration of  $\text{Zr}(\text{Cr}_2\text{O}_4)_4^{-4}$  and the stereochemistry of discrete eight-co-ordination," *J. Amer. Chem. Soc.*, 1961, 83, 4293-295.
22. Pauling, L. .. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1960, p. 544.
23. Höhne, E. and Dornberger-Schiff, K. "Die Kristallstruktur des Wasserhaltigen Barium-Silikats  $\text{BaO} \cdot \text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ," *Acta Crystallogr.*, 1961, 14, 1298.
24. Pabst, A. .. "Crystal structure of gillespite,  $\text{BaFeSi}_4\text{O}_{16}$ ," *Structure Reports*, 1942-44, 9, 249-50.
25. Wyckoff, R. W. G. .. *Crystal Structures*, Vol. II, Interscience Publishers, New York, Chap. 8, Text page 6, Table page 13.
26. Schnering, H. G., Hoppe, R. and Zemann, J. "Die Kristallstruktur des  $\text{BaZnO}_2$ ," *Z. anorg. allg. Chem.*, 1960, 305, 241-54.
27. Phillips, F. C. .. *Introduction to Crystallography*, Longmans, Green and Co., 1956, p. 115.
28. Spitsbergen, U. .. "The crystal structures of  $\text{BaZnO}_2$ ,  $\text{BaCoO}_2$  and  $\text{BaMnO}_2$ ," *Acta Crystallogr.*, 1960, 13, 197-98.
29. Samson, S. and Sillen, L. G. "Die Kristallstruktur des Bariumuranates," *Structure Reports*, 1947-48, 11, 441-43.
30. Hardy, A., Piekarski, C. and Hagen-Muller, M. P. "Structure cristalline du permanganate de baryum," *Comptes rendus*, 1959, 249, 2579-581.
31. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 338.
32. Wagner, G. and Binder, H. "Untersuchung der binären Systeme  $\text{BaO}-\text{SnO}_2$  und  $\text{BaO}-\text{PbO}_2$ . Part II. Kristallstruktur-bestimmungen," *Z. anorg. allg. Chem.*, 1959, 298, 12-21.
33. Jensen, A. T. .. "On the structure of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ," *Structure Reports*, 1940-41, 8, 133-34.
34. Wyckoff, R. W. G. .. *The Structure of Crystals, Supplement*, Reinhold Publishing Corporation, New York, 1935, p. 83.
35. Vainstein, B. K. and Pinsker, Z. G. "Electronographic determination of the structure of barium chloride monohydrate," *Structure Reports*, 1949, 12, 160-61.
36. \_\_\_\_\_ .. "Electronographic study of barium bromide monohydrate," *Zhur. Fiz. Khim.*, 1950, 24, 432-36.
37. Foss, O. and Zachariasen, H. "The crystal structure of barium pentathionate dihydrate," *Structure Reports*, 1954, 18, 499-502.



38. Foss, G. and Tjomsland, O. "The crystal structure of barium seleno-pentathionate dihydrate" *Ibid.*, 1954, **18**, 496-97.
39. ———, Furberg, S. and Zachariassen, H. "The crystal structure of barium tetrathionate dihydrate," *Ibid.*, 1954, **18**, 494-96.
40. Jensen, A. T. .. "The structure of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ," *Ibid.*, 1945-46, **10**, 95-96.
41. Blattner, H., Gränicher, H., Kanzig, W. and Merz, W. "Die Kristallstruktur des hexagonalen und rhombischen Barium-Platinat-Titanats," *Ibid.*, 1947-48, **11**, 452-54.
42. Smith, J. V. .. "The crystal structure of paracelcian,  $\text{BaAl}_2\text{Si}_2\text{O}_8$ ," *Acta Crystallogr.*, 1953, **6**, 613-20.
43. Newnham, R. E. and Megaw, H. D. "The crystal structure of celcian (Barium Felspar)," *Ibid.*, 1960, **13**, 303-12.
44. Colby, M. Y. and Lacoste, L. J. B. .. "The crystal structure of witherite," *Z. Kristallogr.*, 1935, **90**, 1-7.
45. Wyckoff, R. W. G. .. *The Structure of Crystals*, Reinhold Publishing Corporation, New York, 1931, pp. 272-75.
46. Douglass, R. M. .. "The crystal structure of Sanbornite,  $\text{BaSi}_2\text{O}_5$ ," *Amer. Mineral.* 1958, **43**, 517-36.
47. Lander, J. J. .. "Polymorphism and anion rotational disorder in alkaline-earth carbonates," *J. Chem. Phys.*, 1949, **17**, 892-901.
48. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 73.
49. Burley, G. .. "Crystal structure of barium hydrogen orthophosphate," *J. Res. Nat. Bur. Stand.*, 1958, **60**, 23-27.
50. Sadanaga, R., Marumo, F. and Takeuchi, Y. "The crystal structure of Harmotome,  $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ ," *Acta Crystallogr.*, 1961, **14**, 1153-63.
51. Zachariassen, W. H. .. "The crystal structure of the normal orthophosphates of barium and strontium," *Ibid.*, 1948, **1**, 263-65.
52. Scholder, R. and Klemm, W. *Structure Reports*, 1954, **18**, 526-27.
53. Abrahams, S. C. and Kalnajs, J. "The crystal structure of barium peroxide," *Acta Crystallogr.*, 1954, **7**, 838-42.
54. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 761.
55. Templeton, D. H. and Dauben, C. H. "Polarized octahedra in barium tetratitanate," *J. Chem. Phys.*, 1960, **32**, 1515-18.
56. Nardelli, M. and Fava, G. "The crystal structure of barium thiosulphate monohydrate," *Acta Crystallogr.*, 1962, **15**, 477-84.
57. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, pp. 341-42.
58. Kartha, G. .. "Structure of halogenates of the type  $\text{A}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$ . I. Barium chlorate monohydrate,  $\text{Ba}(\text{ClO}_2)_2 \cdot \text{H}_2\text{O}$ ," *Proc. Ind. Acad. Sci.*, 1952, **36 A**, 501-29.

59. Kartha, G. .. "Structure of halogenates of the type  $A(BO_2)_2 \cdot H_2O$ . Barium bromate monohydrate  $Ba(BrO_2)_2 \cdot H_2O$ ," *Ibid.*, 1953, 38 A, 1-12.
60. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, pp. 494-96.
61. \_\_\_\_\_ .. *Ibid.*, 1962, p. 496.
62. \_\_\_\_\_ .. *Structural Inorganic Chemistry*, Second Edition, Clarendon Press, Oxford, 1950, p. 377.
63. Rudorff, W. and Pfitzer, F. *Structure Reports*, 1954, 18, 466.
64. Derbyshire, S. W., Fraker, A. C. and Stadelmaier, H. H. "A barium-iron oxide with the perovskite structure," *Acta Crystallogr.*, 1961, 14, 1293-94.
65. Roy, R. .. "Multiple ion substitution in the perovskite lattice," *Structure Reports*, 1954, 18, 439-40.
66. Harrison, F. W. .. "The crystal structure of barium dititanate  $BaO \cdot 2TiO_2$ ," *Acta Crystallogr.*, 1956, 9, 495-500.
67. Wadsley, A. D. .. "The crystal structure of psilomelane  $(Ba, H_2O)_2Mn_5O_{10}$ ," *Ibid.*, 1953, 6, 433-38.
68. Byström, A. and Byström, A. M. "The crystal structure of Hollandite, the related manganese dioxide minerals and  $\alpha$ - $MnO_2$ ," *Ibid.*, 1950, 3, 146-54.
69. Hardy, A. .. "Structures Crystallines de Deux Variétés Allotropiques de Manganite de Baryum. Nouvelle Structure  $ABO_3$ ," *Ibid.*, 1962, 15, 179-81.
70. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 494.
71. Galasso, F. and Katz, L. .. "Preparation and structure of  $Ba_5Ta_4O_{15}$  and related compounds," *Acta Crystallogr.*, 1961, 14, 647-50.
72. Went, J. J., Rathenau, G. W., Gorter, E. W. and van Oosterhout, G. W. "Ferroxdure, a class of new permanent magnet materials," *Philips Tech. Rev.*, 1951-52, 13, 194-208.
73. Braun, P. B. .. "The crystal structures of a new group of ferromagnetic compounds," *Philips Res. Rep.*, 1957, 12, 491-548.
74. Shirane, G., Hoshino, S. and Suzuki, K. .. "Crystal structures of lead titanate and lead-barium titanate," *J. Phy. Soc. Japan*, 1950, 5, 453-55.
75. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 96.
76. Jaeger, F. M. and van Melle, F. A. "On the symmetry and structure of the cubic nitrates of calcium, strontium, barium and lead," *Proc. Acad. Sci., Amsterdam*, 1928, 31, 651-55.
77. Hoard, J. L. and Vincent, W. B. "Structures of complex fluorides: Barium fluosilicate and barium fluogermanate," *J. Amer. Chem. Soc.*, 1940, 62, 3126-29.

78. Vannerberg, N. G. .. "The system  $\text{BaO}_2\text{-H}_2\text{O-H}_2\text{O}_2$ . III. The crystal structures of  $\alpha$ -,  $\beta$ - and  $\gamma$ - barium peroxide dihydroperoxidate and barium peroxide monohydroperoxidate dihydrate," *Arkiv Kemi*, 1959, 14, 125-45.
79. Nitta, I. and Watanabe, T. "Crystal structure of barium dicalcium propionate," *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1935, 26, 164-77.
80. Yoshiki, B. and Matsumoto, K. "High temperature modification of barium feldspar," *Structure Reports*, 1951, 15, 304-05.
81. James, R. W. and Wood, W. A. "The crystal structure of barytes, celestine and anglesite," *Proc. Roy. Soc. (Lond.)*, 1925, 109 A, 598-620.
82. Manohar, H. .. "Refinement of the atomic co-ordinates of  $\text{BaSO}_4$ ," (Unpublished).
83. Wyckoff, R. W. G. .. *Crystal Structures*, Vol. II, Interscience Publishers, New York, Chap. 8, Table p. 21.
84. Rollier, M. A. .. "Dimensioni della cella elementare del fluoberillato di bario," *Gazz. Chim. Ital.*, 1954, 84, 663-66.
85. Scholder, R., Bunsen, H. v., Kindervater, F. and Weiss, W. "Zur Kenntnis der Ferrate (VI)," *Z. anorg. allg. Chem.*, 1955, 282, 268-79.
86. Chackraburty, D. M. .. "The structure of  $\text{BaBOF}_3$ ," *Acta Crystallogr.*, 1957, 10, 199-200.
87. Mitra, G. .. "Hydroxyfluoberyllates. Part II. Hydroxyfluoberyllates of Ca, Ba, Sr, Pb, Ce, La and Hg," *J. Indian Chem. Soc.*, 1955, 32, 246-48.
88. Pauling, L. .. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1960, p. 546.
89. Goldschmidt, V. M. .. "Geochemische Verteilungsgesetze der Elemente," *Skrifter Norske Videnskaps-Akad, Oslo. I. Mat. Naturv. Kl.*, 1926.
90. Wells, A. F. .. *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1962, p. 76.
91. ————— .. *Ibid.*, 1962, pp. 76-77.