

The crystal structure of barium perchlorate trihydrate $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ and the crystal coordination of Ba^{++} Ion

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With 6 figures

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Auszug

Eine Röntgen-Strukturanalyse von Bariumperchlorat-Trihydrat ergab $a = 7,278 \pm 0,005 \text{ \AA}$, $c = 9,64 \pm 0,01 \text{ \AA}$ und zwei Moleküle in der Elementarzelle. Die Raumgruppe ist $P6_3$ oder $P6_3/m$. Es werden die Atomparameter für beide Raumgruppen angegeben. Die Perchlorationen sind nahezu vollkommene Tetraeder mit einem mittleren Cl—O-Abstand von $1,44_3 \text{ \AA}$ und einem O—O-Abstand von $2,35_6 \text{ \AA}$. Jedes Ba^{++} -Ion ist von zwölf Sauerstoffionen in einer leicht gestörten ikosaedrischen Anordnung umgeben; die Ba—O-Abstände betragen $2,96 \text{ \AA}$ bis $3,18 \text{ \AA}$. Die Ikosaeder sind durch gemeinsame Dreieckflächen längs der 6_3 -Achse miteinander verbunden. Die Ikosaeder-Koordination, die für ein Ionenradien-Verhältnis von 0,902 sehr plausibel ist, scheint noch nicht für Strukturen von Bariumverbindungen angegeben worden zu sein. Deshalb wurden einige solcher Strukturen neu bestimmt; dabei wurde in $\text{Ba}(\text{NO}_3)_2$ und BaSiF_6 die Ikosaeder-Koordination gefunden.

Abstract

A detailed x-ray study has been made of the crystal structure of barium perchlorate trihydrate which is hexagonal with $a = 7.278 \pm 0.005 \text{ \AA}$ and $c = 9.64 \pm 0.01 \text{ \AA}$ containing two molecules in its unit cell. The space group is $P6_3$ or $P6_3/m$. Statistical $N(z)$ tests favoured the choice of $P6_3$, but when the effect of heavy atoms at special positions were considered, some anomalies seemed to result. Hence the atomic parameters for both the space groups are given. The perchlorate ions in this structure are nearly perfect tetrahedra with a mean Cl—O distance of 1.44_3 \AA and O—O distance of 2.35_6 \AA . Each Ba^{++} ion in this structure is surrounded by twelve oxygens in a slightly distorted icosahedral

arrangement, the Ba to O contacts varying from 2.96 Å to 3.18 Å. These icosahedra share triangular faces with their neighbours along the 6_3 axis. The icosahedral coordination, which appears to be very feasible for a univalent ionic radius ratio of 0.902, does not seem to have been brought out explicitly in any other complex ionic structures of Ba compounds. Hence the reported crystal structures of some of these compounds have been re-examined. The central Ba^{++} ion coordination in $Ba(NO_3)_2$ and $BaSiF_6$ has been shown to be icosahedral.

Introduction

As part of a programme in this laboratory on the systematic x-ray analysis of some perchlorates, a complete investigation on the crystal structure of barium perchlorate trihydrate has been carried out. The earliest studies on similar complexes were those due to WEST who worked out the structures of a series of divalent metal perchlorates (hexahydrates)^{1,2} on the basis of his first determination³ on $LiClO_4 \cdot 3H_2O$. During these, he also examined $Ba(ClO_4)_2 \cdot 3H_2O$ and drew attention to its possible similarity to that of the Li compound purely from a qualitative inspection of the weak layer lines in the c axis oscillation photographs. No other details concerning the structure are available from WEST's investigations apart from some preliminary crystal data. Therefore the accurate atomic parameters in this structure have been evaluated by us by Fourier analyses.

During this programme, studies have also been completed⁴ on the crystal structures of $KClO_4$ and $Cu(ClO_4)_2 \cdot 6H_2O$. Besides knowing the atomic arrangements in these structures, we were also concerned with establishing the geometry of the anion polyhedron enveloping each cation in these complexes. It was also of interest to enquire whether the complex perchlorate ion retained its shape when set in different environments and, if so, to derive its exact dimensions which hitherto were not known to any great accuracy^{5,6}.

¹ C. D. WEST, Crystal structures of hydrated compounds. II. Structure type $Mg(ClO_4)_2 \cdot 6H_2O$. *Z. Kristallogr.* **91** (1935) 480—493.

² A. F. WELLS, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1950) p. 441.

³ C. D. WEST, Crystal structures of some hydrated compounds. I. $LiClO_4 \cdot 3H_2O$, $LiI \cdot 3H_2O$, $Ba(ClO_4)_2 \cdot 3H_2O$. *Z. Kristallogr.* **88** (1934) 198—204.

⁴ N. V. MANI, The crystal structure of potassium perchlorate- $KClO_4$. *Proc. Ind. Acad. Sci A* **46** (1957) 143—151.

⁵ L. PAULING, *The nature of the chemical bond*. (Cornell University Press, Ithaca, 1948), p. 240.

⁶ A. F. WELLS², p. 268.

Experimental

The colourless deliquescent crystals of barium perchlorate are hexagonal prisms flattened on (10.0); other faces observed were (10·1) and sometimes⁷ (10·2). The dimensions of the hexagonal unit cell are $a = 7.278 \pm 0.005$ Å and $c = 9.64 \pm 0.01$ Å so that $c:a = 1.32$. The only absences in the (00· l) spectra when l is odd lead to $D_6^6-P6_322$, $C_6^6-P6_3$ and $C_{6h}^2-P6_3/m$ as the space group possibilities. Assumption of two molecules in the cell yields a calculated specific gravity of 2.91, in fair agreement with the value 2.84 reported by WEST.

A single crystal having a cross-section 0.04×0.05 cm perpendicular to the c axis was enclosed in a LINDEMANN glass capillary and used to collect the intensity data. Intensities of $hk\cdot l$ reflections for $l = 0, 2, 3$ and 4 were recorded on multiple-film Weissenberg photographs using $CuK\alpha$ radiation, the equi-inclination technique being employed to obtain the higher-level data. It was generally found that reflections due to layer lines having l odd were of very feeble intensity. The intensity estimates were done by visual comparison with calibrated intensity strips. The geometrical corrections such as Lorentz and polarisation factors and the physical corrections for absorption for $\mu r = 9$ were employed in the reduction of the entire data. Difficulties due to extreme hygroscopic nature of the crystals, their slight asymmetric shape and heavy absorption ($\mu = 400$ cm⁻¹) rendered the latter corrections uncertain by about 10%.

Space-group determination

For one of the space groups, $P6_322$, pairs of reflexions $hk\cdot 0$ and $kh\cdot 0$ with the same θ values should have identical intensities. On this basis, this space group could be discarded. Further attempts at distinguishing between the remaining two possibilities $P6_3$ and $P6_3/m$ were made through the application of the statistical $N(z)$ tests⁸. It is well-known that in either of these space groups, the six-fold symmetry along the hexagonal axis, c , causes the $hk\cdot 0$ intensities to have a centric distribution. In the case of the general $hk\cdot l$ reflections, however, the intensity distribution is centric only in the space group $P6_3/m$, but it is not in $P6_3$. The $N(z)$ plots shown in

⁷ P. v. GROTH, *Chemische Krystallographie* 2 (1917) 185.

⁸ E. R. HOWELLS, D. C. PHILLIPS and D. ROGERS, The probability distribution of x-ray intensities. II. Experimental investigation and the x-ray detection of centres of symmetry. *Acta Crystallogr.* 3 (1950) 210–214.

Fig. 1 compares the theoretical distributions with the experimental ones. The latter, obtained from statistical treatment of $hk\cdot 0$ and $hk\cdot l$ intensities, are found to be closer to the theoretical distributions for the centric and acentric cases respectively. The presence of this difference in the two experimental plots in itself appears to be an indication of the absence of centre of symmetry in the unit cell. However, attention must be drawn to a possible anomaly involved here.

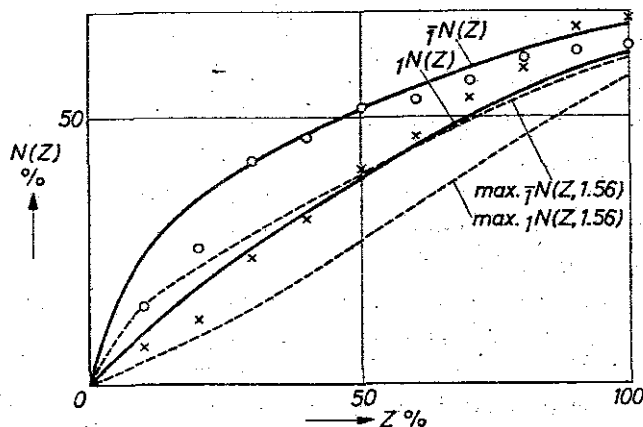


Fig. 1. Comparison of the experimental $N(z)$ distributions in $hk\cdot 0$ (open circles) and $hk\cdot l$ (crosses) reflections with the theoretical centro- and non-centro-symmetric distributions respectively. The SIM's curves, $\max. \bar{I}^N(z, 1.56)$ and $\max. 1^N(z, 1.56)$, are indicated by broken lines

The consideration of symmetries in either of the space groups indicate that one Ba and two Cl atoms are to be in special positions on three-fold axes (multiplicity 2). The location of heavy atoms at the special sites is known to affect the intensity distribution curves appreciably. Recently, SIM⁹ has evaluated the nature of this influence in the case of a triclinic crystal and obtained modified $N(z)$ values in terms of a parameter r defined by $r = f_H / (\Sigma_L)^{1/2}$, where f_H and $(\Sigma_L)^{1/2} = \left(\sum_{j=1}^m f_j^2 \right)^{1/2}$ denote contributions from the heavy atoms and m light atoms respectively. The value of this parameter was found to be 1.56 for $\text{Ba}(\text{ClO}_4)_2 \cdot 3 \text{H}_2\text{O}$ at $\sin \theta = 0$ (if we consider the chlorines also

⁹ G. A. SIM, The probability distributions of x-ray intensities: the effect of one heavy atom in a triclinic cell containing a number of light atoms. Acta Crystallogr. 11 (1958) 123-124.

as light atoms). The new curves computed by SIM for this value, represented by broken lines in Fig. 1, show significant differences from the experimental distributions. Also one observes a sensible disparity in the latter curves due to the $hk \cdot 0$ and $hk \cdot l$ set of intensities, notwithstanding that either of them is similarly influenced by the special location of the barium atom at the origin. Although this might lend sufficient support to our choice, these arguments may be fallacious. For, it must be remembered, SIM's expressions are derived for a triclinic cell with one heavy atom at the origin which renders its full contribution (trigonometric part) to all types of reflections, whereas an atom at the origin in our case gives for the $hk \cdot l$ reflections its full complement only when $l = \text{even}$ and nothing at all when $l = \text{odd}$. The Cl and O atoms situated on the triad axis contribute varying amounts to the three types of reflections $h-k = 3n$ or $3n \pm 1$, but these contributions are fixed for the same value of l for each of these groups. Hence, to allow for these, it is obvious that corresponding alterations should be made using SIM's general approach. Our preliminary computations lead us to believe that the experimental plots are irreconcilable with the space group $P6_3/m$ and so $P6_3$ was employed for the solution of the structure. However, as it is widely known to crystallographers that the intensity distributions can vary depending on the sampling procedures followed, the alternative space group could not be totally ignored. Consequently, this was reconsidered after the structure analysis was complete and the corresponding atomic parameters derived.

Structure analysis

(a) $hk \cdot 0$ projection

The preliminary structure in projection was resolved from a Patterson synthesis on (00.1). A knowledge of the Ba and Cl parameters given by the vector map enabled an unequivocal assignment of the signs of the $hk \cdot 0$ structure factors. An F_o -synthesis computed subsequently did not, however, reveal the perchlorate and water oxygens owing to series-termination errors. Consequently, for more precise location of oxygens at the general positions, the temperature-corrected contributions from one Ba, two Cl and two O atoms (which overlap on chlorines in this projection) were subtracted from the F_o values and employed as coefficients in a Fourier summation. This synthesis (Fig. 2), which had a better resolution of atomic peaks, yielded the oxygen parameters and these were used as basis for a recalculation of structure factors. The observed values were now in good agreement

with the calculated ones. Further refinement was achieved through the iterative process of difference Fourier syntheses. For the $hk\cdot 0$ reflexions, the final value of $R = \Sigma |F_o - F_c| / \Sigma |F_o|$ was found to be 0.108.

(b) Determination of z parameters

Owing to the tendency of the crystals to deliquesce rapidly in air and the extreme smallness of the samples grown, intensity data were not collected for other than c axis as the axis of rotation. Hence, the

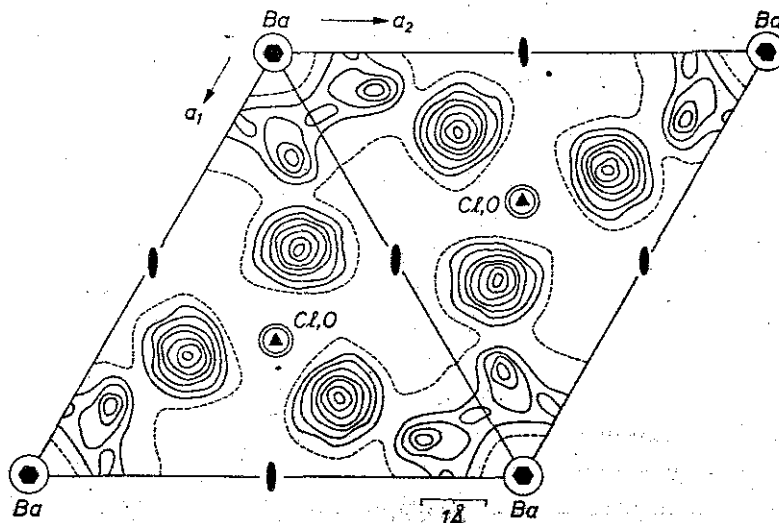


Fig. 2. The c -axis Fourier projection with Ba, Cl and O atoms at special positions removed. Contours are drawn at arbitrary intervals

general $hk\cdot l$ reflexions for $l = 2$ to 4 were employed in the evaluation of the third coordinate in the structure. From these data, the intensities of $h0\cdot l$ reflexions (nearly thirty in number) were isolated and employed to construct a Patterson synthesis. The interactions due to Ba—Ba, Ba—Cl and Cl—Cl vectors were distinguishable in the vector map. The phase angles evaluated from a knowledge of the z heights of Cl atoms were used in an F_o -synthesis on $(01\cdot 0)$. The oxygen atoms, as expected, were not resolved in this map since the errors in the scaling process (effected independently for each layer by WILSON'S¹⁰ procedure) and those due to diffraction (as a result of the paucity of

¹⁰ A. J. C. WILSON, Determination of absolute from relative x-ray intensity data. Nature [London] 150 (1942) 152.

terms in the synthesis) were so pronounced as to mask the position of the lighter oxygens. Two of the eight O atoms of the perchlorate groups are on three-fold axis and hence the position of the perchlorate group is characterised by an unknown parameter representing a translation of the whole group along the three-fold axis. This parameter, as well as the height of one water molecule in the asymmetric unit, was determined by trial aided by other considerations such as known inter-ionic separations etc. As the ultimate z parameters are essentially derived

Table 1. Observed and calculated structure factors * for barium perchlorate trihydrate

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
100	39.7	29.8	102	25.8	27.5	103	23.4	25.9	104	50.5	45.5
200	16.6	15.3	202	16.8	15.3	203	11.2	10.3	204	31.0	32.1
300	45.5	48.3	302	47.6	44.0	303	8.8	9.6	304	34.5	35.2
400	21.2	24.2	402	21.4	20.7	403	4.6	4.6	404	25.2	23.6
500	9.9	11.1	502	15.4	16.0	503	7.0	5.3	504	19.1	18.1
600	21.7	20.3	602	24.1	20.1	603	2.6	3.1	604	17.0	15.3
700	7.1	7.1	702	8.5	8.4	703	1.1	1.4	704	9.5	10.6
800	5.6	2.3	802	5.7	5.2	113	11.9	11.8	114	31.8	33.4
110	87.6	79.0	112	72.0	66.1	123	5.0	3.3	124	20.6	24.6
120	44.9	44.8	122	36.2	37.3	133	7.7	6.7	134	32.4	35.0
130	15.4	15.3	132	15.6	15.0	143	2.6	1.4	144	39.6	27.4
140	35.2	36.3	142	25.9	25.3	153	2.8	1.5	154	16.6	16.6
150	6.9	6.3	152	11.1	12.6	163	2.7	1.3	164	8.3	10.9
160	7.2	9.4	162	10.5	10.7	173	0.9	0.6	174	11.0	11.0
170	10.9	10.5	172	12.5	10.6	213	5.9	5.7	214	23.4	26.7
210	18.8	20.2	212	33.3	33.4	223	8.7	9.1	224	35.6	32.5
220	37.6	46.1	222	34.4	36.5	233	4.9	3.4	234	25.2	25.2
230	22.2	25.7	232	13.0	14.9	243	5.5	3.4	244	19.1	16.2
240	14.9	15.9	242	12.8	15.0	253	3.5	4.6	254	18.2	16.2
250	15.5	15.9	252	18.4	17.1	263	1.8	1.4	264	11.3	12.7
260	4.0	5.3	262	7.0	5.7	313	3.1	4.6	314	22.4	23.9
310	13.7	14.7	312	21.6	24.6	323	4.3	5.4	324	24.0	23.1
320	10.9	9.9	322	12.9	17.4	333	2.1	1.1	334	24.0	19.0
330	32.8	30.3	332	23.4	26.9	343	2.4	2.1	344	14.8	14.0
340	7.0	5.4	342	9.8	11.2	353	2.2	1.8	354	9.5	11.2
350	6.3	7.8	352	7.9	7.8	413	4.1	5.3	414	21.1	17.3
360	11.8	10.6	362	9.4	8.1	423	9.3	10.6	424	18.8	18.4
410	38.2	41.4	412	37.6	35.4	433	5.6	5.7	434	12.4	14.7
420	6.4	6.1	422	13.2	13.2	443	2.4	1.5	444	14.5	12.7
430	6.5	6.6	432	10.5	10.5	453	1.1	1.6	454	14.5	17.9
440	13.8	13.0	442	13.8	13.7	513	5.1	6.9	524	15.3	15.8
450	5.4	5.6	452	5.8	5.9	523	2.8	0.1	534	9.8	11.7
510	6.2	6.9	512	12.8	11.5	533	1.8	2.6	614	12.8	15.4
520	22.0	24.4	522	20.7	17.2	543	1.6	1.7	624	11.5	12.8
530	7.0	7.7	532	8.8	7.4	613	8.8	2.5	714	14.0	12.0
540	3.2	3.0	542	5.3	5.5	623	0.6	0.5			
610	6.5	7.0	612	9.9	7.1	713	2.5	2.5			
620	7.2	7.5	622	7.0	5.6						
630	9.2	8.4	632	9.0	8.4						
710	13.4	10.3	712	10.9	9.9						

* These structure factors, which are computed on the basis of an asymmetric unit using the space group $P6_3$, have been corrected with temperature factor parameters $B = 3.8 \text{ \AA}^2$, 3.4 \AA^2 , 3.21 \AA^2 and 2.28 \AA^2 for groups of $hk \cdot l$ reflections when $l = 0, 2, 3$ and 4 respectively. The corresponding structure factors calculated for the space group $P6_3/m$ are practically the same except in the layer $l = 3$. The variation in B suggests a small error in the absorption correction.

from these methods, much accuracy cannot be claimed for them. The comparison of the final structure factors, shown in Table 1, reveal that the agreement between the values is very good except for $hk \cdot 3$ reflections. For the latter, since there are no barium contributions and sometimes no Cl contributions (when $h-k = 3n$), the quality of the final agreement ($R = 0.22$) reflects the measure of accuracy attained in the assignment of the oxygen parameters.

Atomic parameters

(a) Non-centrosymmetric space group — $P6_3$

The proposed structure is hexagonal based on the non-centrosymmetric space group and in this arrangement, atoms are in positions indicated in Table 2. The values are listed in terms of the fractional coordinates. It might be pointed out that, in this space group, the three oxygens O_1' of one perchlorate group (related by three-fold symmetry) need not necessarily have the same xy parameters as the corresponding atoms O_2' of another group. Likewise, the water oxygens need not be at heights $\pm 1/4 c$. Nevertheless, it was found that the best intensity agreement from a series of trial movements resulted only when the oxygens are at these positions.

Table 2. Atomic coordinates in barium perchlorate trihydrate expressed in fractions of cell edges

Space group: $P6_3$					Space group: $P6_3/m$				
Atom	Position	Coordinates			Atom	Position	Coordinates		
		x	y	z			x	y	z
Ba	$2a$	0	0	0	Ba	$2b$	0	0	0
Cl ₁	$2b$	$\frac{1}{3}$	$\frac{2}{3}$	0.004	Cl	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	0.043
Cl ₂	$2b$	$\frac{1}{3}$	$\frac{2}{3}$	0.419					
O ₁	$2b$	$\frac{1}{3}$	$\frac{2}{3}$	-0.146	O	$4f$	$\frac{1}{3}$	$\frac{2}{3}$	-0.107
O ₂	$2b$	$\frac{1}{3}$	$\frac{2}{3}$	0.569					
O ₁ '	$6c$	0.183	0.458	0.054	O'	$12i$	0.183	0.458	0.093
O ₂ '	$6c$	0.183	0.458	0.369					
O _w	$6c$	0.283	0.200	0.250	O _w	$6h$	0.283	0.200	$\frac{1}{4}$

(b) Centrosymmetric space group — $P6_3/m$

The above structure can easily be rearranged to satisfy the additional symmetry of this space group by a translation of the ClO_4 groups along c by 0.039 in fractional units so that adjacent groups are related by reflection symmetry. The barium ion and the water oxygens, however, occupy the same sites as before. The corresponding atomic parameters derived for this new arrangement are listed in the same table (Table 2). Recalculation of structure factors using this set of parameters revealed that the R factors for the $hk \cdot l$ reflections, which had values 0.084, 0.22 and 0.095 for $l = 2, 3$ and 4 respectively for the previous structure, now showed the corresponding values 0.086, 0.254 and 0.098. Calculations for $l = 0$ remain unaltered. The slightly worse intensity agreement in the new computations for $hk \cdot 3$ reflections may

not be significant as their intensities are very weak as indicated already. Thus it is seen that the R factors are essentially insensitive despite the appreciable modification in the structure. Consequently, it appears that much more reliable intensity data are required before the space group can be unambiguously established. Although the structural environments are similar in both cases, the various dimensions mentioned in the description of the structure are those computed for the arrangement in the space group $P6_2$.

Structure

The structure consists of Ba—H₂O groups distributed around the 6₂ axis at the cell corners, and columns of tetrahedral perchlorate groups in close packing along the threefold axes (at $\frac{1}{3}\frac{2}{3}$ and $\frac{2}{3}\frac{1}{3}$).

Table 3. Dimensions of the perchlorate groups

Cl ₁ —O ₁	1.45 Å	O ₁ —O ₂	2.75 Å
Cl ₁ —O ₁ '(3)	1.44	O ₁ '—O ₂ '(3)	3.04
Cl ₂ —O ₂	1.45		
Cl ₂ —O ₂ '(3)	1.44		
O ₁ —O ₁ '(3)	2.36	O ₁ —Cl ₁ —O ₁ '(3)	109° 32'
O ₁ '—O ₁ '(3)	2.35	O ₁ '—Cl ₁ —O ₁ '(3)	109° 26'
O ₂ —O ₂ '(3)	2.36	O ₂ —Cl ₂ —O ₂ '(3)	109° 32'
O ₂ '—O ₂ '(3)	2.35	O ₂ '—Cl ₂ —O ₂ '(3)	109° 26'

Individual ClO₄ ions are disposed in such a way that the bonds Cl₁—O₁ and Cl₂—O₂ of the two different groups coincide with the symmetry axis, and these point to opposite directions. The distances in the two perchlorate groups and the O—Cl—O angles are represented in Table 3, where O₁' and O₂' denote oxygens at general positions (three each equivalent by threefold symmetry) belonging to two non-equivalent perchlorate groups. The mean Cl—O and O—O dimensions are 1.44₃ Å and 2.35₆ Å respectively and comparable to those found in other perchlorates^{11,4} (viz. 1.48 Å and 2.37 Å in NH₄ClO₄ and 1.46 Å and 2.39 Å in KClO₄). Each Ba⁺⁺ ion in this structure is surrounded by six water molecules arranged in groups of three on either side, the successive groups being related by the 6₂ axis along c . These six barium-to-water oxygen contacts are all identical and equal to 3.03 Å. Besides these water molecules, six more nearest neighbours of oxygens, each belonging to different perchlorate groups, are also coordinated to the

¹¹ K. VENKATESAN, The crystal structure of ammonium perchlorate—NH₄ClO₄, Proc. Ind. Acad. Sci. A 46 (1957) 134—142.

central atom in the structure. Three of these oxygens (O_1'), equivalent by trigonal symmetry, are found at a distance of 2.96 Å from Ba^{++} ion, and a similar group of three atoms (O_2') at 3.18 Å, so that these six are arranged in a puckered hexagonal ring with barium at the centre. The distribution of the twelve oxygens, illustrated in projection on (00.1) in Fig. 3, shows that they are at the corners of a slightly distorted icosahedron with its threefold axis along the 6_3 axis of the space group.

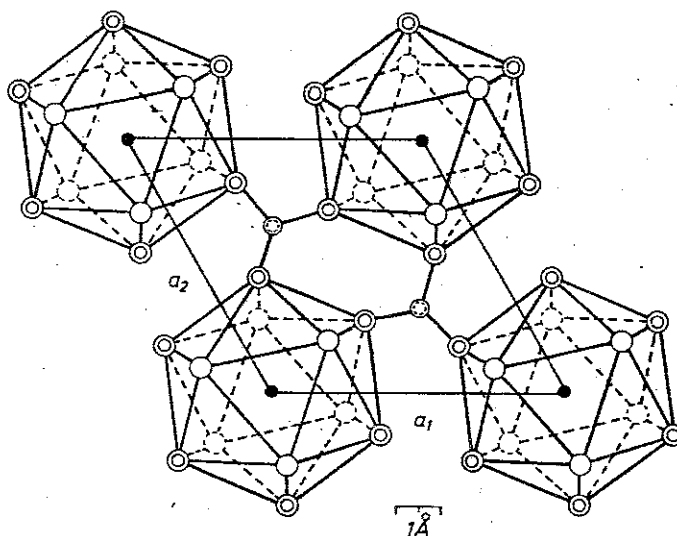


Fig. 3. The projection of the hexagonal structure on the (00.1) plane indicating atomic positions. The small black circles represent Ba^{++} ions at the centres of the oxygen (large open circles) icosahedra at the cell corners. The chlorines are denoted by broken circles

These polyhedra at the hexagonal cell corners share a common triangular face along c so that at these corners there is an infinite array of icosahedral groups.

If now, the structure is viewed as belonging to the centrosymmetric space group, it is seen that the above icosahedral coordination is essentially retained, with the modification that the six perchlorate oxygen neighbours which coordinate with the barium ion are all equidistant from it ($Ba-O = 3.05$ Å) so that the puckering in the six-membered ring of these oxygens becomes symmetrical about the central barium.

Each water molecule in this structure is equidistant from two barium ions ($Ba-O_w = 3.03$ Å) and nearly so from two closest oxygen

neighbours O and O' of the perchlorate groups at two different triad axes, the actual distances being 2.60 Å and 2.66 Å respectively. All these four atoms are found at the corners of a highly deformed tetrahedron with the water oxygen at the centre. The relatively short approach of the two perchlorate oxygens towards each water molecule shows evidence of hydrogen-bond formation along the two tetrahedral directions.

Crystal coordination of Ba⁺⁺ ion

The anion polyhedra in the structure of barium perchlorate are seen to be built-up of continuous oxygen frameworks in distorted icosahedral formation. It might be pointed out that the icosahedral configuration does not seem to have been mentioned in conjunction with any other complex ionic crystals, though it is known to be prevalent in some complex alloy structures, particularly of transition metals¹², and also in the structure of boron (tetragonal¹³) and some of its compounds^{14,15}.

The regular icosahedron, which is one of the five regular solids, has twenty equilateral triangular faces and there are six five-fold axes and ten three-fold axes. This coordination polyhedron can be viewed as built up from geometrical packing of identical rigid spheres. It is seen that a group of these spheres in pentagonal pyramidal arrangement, when set in contact with a similar group but rotated through 36°, will produce a perfect icosahedral sphere-packing. The pocket formed at the centre of this composite solid can be filled by a sphere of slightly smaller radius, the theoretical ratio of the two radii being 0.902. This spatial arrangement seems to have been overlooked by PAULING¹⁶ in his evaluation of the limiting radius ratios for other symmetrical coordination polyhedra.

An attempt has been made to look for this type of coordination exhibited by divalent barium ion. For this, we re-examined the re-

¹² F. C. FRANK and J. C. KASPER, Complex alloy structures regarded as sphere packings. I. Definitions and basic principles. *Acta Crystallogr.* **11** (1958) 184-190.

¹³ J. L. HOARD, R. E. HUGHES and D. E. SANDS, The structure of tetragonal boron. *J. Amer. Chem. Soc.* **80** (1958) 4507-4515.

¹⁴ H. K. CLARK and J. L. HOARD, The crystal structure of boron carbide. *J. Amer. Chem. Soc.* **65** (1943) 2115-2119.

¹⁵ W. N. LIPSCOMB, Structures of boron hydrides. *J. Chem. Physics* **22** (1954) 985-988.

¹⁶ L. PAULING⁵, p. 382.

ported crystal structures of some barium compounds. The ratio of the ionic radius of Ba^{++} with reference to O^{--} is evaluated as 0.87 and it is recognized that for this value the anion polyhedron is most stable when the cation coordination number ranges from nine to the extreme value of twelve. The symmetrical configuration for the nine neighbours arises by adding atoms beyond the centres of each of the vertical faces of a right triangular prism. This coordination group has been found in

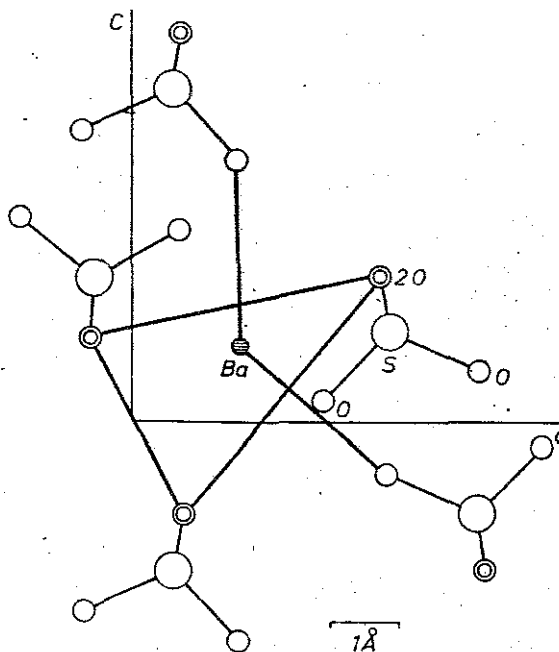


Fig. 4. The orthorhombic structure of $BaSO_4$ projected on the (010) plane. The coordination group around the Ba^{++} ion, which is a triangular prism with two of its faces centred, is outlined

a number of crystals¹⁷. In barite, which is known to be isostructural with $KClO_4$ ⁴, the barium ion appears to possess an eight-fold coordination. In the structure of $KClO_4$, each K^+ ion is surrounded by a cage of eight oxygens found at the vertices of a distorted triangular prism, as mentioned above, but with only two of its vertical faces centred. This configuration can also be viewed as a highly distorted Archimedean antiprism. The projection of this structure in (010) plane indicating atomic positions is given in Fig. 4 to show the central atom coordination in typical barite-like structures.

¹⁷ A. F. WELLS², p. 91.

An interesting example of icosahedral coordination for Ba^{++} ion is provided by the cubic structure of anhydrous barium nitrate¹⁸. In this, four molecules are arranged in a cell of dimension $a = 8.11 \text{ \AA}$ according to the space group $T_h^6 - Pa\bar{3}$. The cation coordination is not explicitly mentioned in the original work but is seen to manifest itself with clarity in the projection of the structure on the (111) face of the cube given in Fig. 5. In this figure, one of the coordination groups around the origin is heavily outlined. The dimensions of the two edges

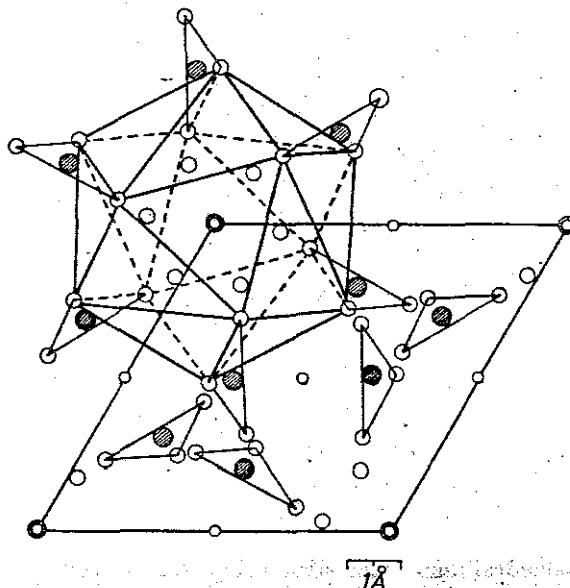


Fig. 5. The projection of the cubic structure of $\text{Ba}(\text{NO}_3)_2$ on its (111) face showing an icosahedral coordination group of oxygens (large open circles) around Ba^{++} ions (small open circles). The nitrogens of the NO_3 groups are hatched

(at 120° to each other) are each equal to $\sqrt{2/3} a$ and that of the (111) axis perpendicular to the projection is $\sqrt{3} a$. In this unit, the atomic parameters given in Angstrom units are as follows:

- 1 Ba_I in 000; 3 Ba_{II} in 3.31, 3.31, 4.68; 2 N_I in 0, 0, 4.92;
 6 N_{II} in 3.31, 1.99, 1.64; 6 O_I in 0.11, 1.29, 4.92;
 6 O_{II} (1) in 4.49, 2.81, 2.29; 6 O_{II} (2) in 2.03, 1.52, 2.14;
 6 O_{II} (3) in 3.42, 1.63, 0.48.

¹⁸ F. M. JAEGER and F. A. VAN MELLE, On the symmetry and the structure of the cubic nitrates of calcium, strontium, barium and lead. Proc. Acad. Sci. Amsterdam **31** (1928) 651-655.

In this structure, six of the Ba—O distances in one coordination group are all equal to 2.82 Å and another six, likewise, are identical, being each equal to 3.00 Å, thus making twelve in all. The O—O distances are 2.14 Å (of one NO₃ group), 3.31 Å and 4.08 Å (six each). As one of these oxygen-to-oxygen contacts (O—O = 2.14 Å) is provided by the same NO₃ group, the resulting icosahedral group is deformed despite the fact that the central barium ion is nearly equidistant from all the oxygens. Each coordination polyhedron shares six common corners with similar members of the unit cell.

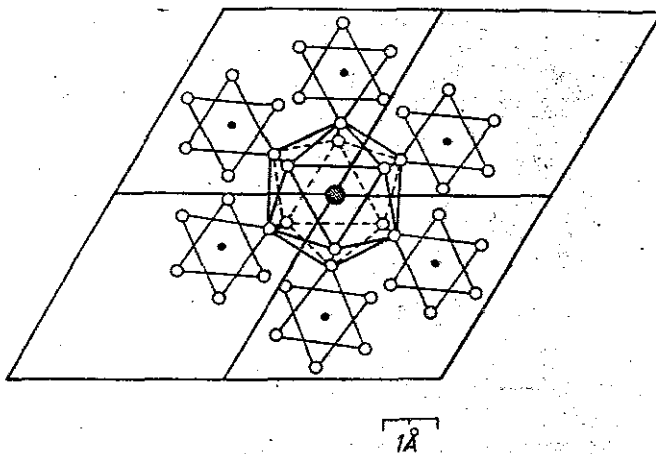


Fig. 6. The rhombohedral unit of the structure of BaSiF₆ projected on the (111) plane. The icosahedral arrangement of F atoms (open circles) around Ba⁺⁺ ion (shaded circle) is outlined. The silicons are denoted by small black circles

A similar coordination was also encountered in the structures of the isomorphous complex fluorides¹⁹—BaSiF₆ and BaGeF₆. These rhombohedral structures have been considered as a distorted CsCl-type arrangement of Ba⁺⁺ and SiF₆⁻ (GeF₆⁻) ions. The coordination of fluorine about barium is twelve. This icosahedral arrangement of all the twelve fluorine atoms is indicated by thick lines in Fig. 6.

Investigations at present are directed towards finding the shape and geometry of the anion polyhedron in other barium complexes. At this stage, it seems highly probable that the most feasible configuration

¹⁹ J. L. HOARD and W. B. VINCENT, Structures of complex fluorides: Barium fluosilicate and Barium fluogermanate. J. Amer. Chem. Soc. 62 (1940) 3126—3129.

around the divalent barium ion is icosahedral as this spatial arrangement permits a highly symmetrical distribution of anion packing and is as satisfactory as the other well-known cubo-octahedron for twelve-fold coordination. Further, it possesses a freedom of distortion to comply with the simultaneous coordination requirements of atoms other than the central one¹². Finally, it agrees with the predicted coordination number from radius-ratio criterion. In view of these, one feels reasonably certain that, in the crystalline state, when the cation size is only slightly smaller than that of the anion, the discrete coordination of the latter in icosahedral groupings around the former appears to be genuine.

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