SHORT COMMUNICATIONS

Barium aluminate hydrates. VI.* The crystal structure of 'BaO . Al₂O₃ . H₂O.'

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The compound of approximate composition $BaO.Al_2O_3.H_2O$ has a structure analogous to that of sodalite, based on a framework of empirical formula AlO_2. The barium atoms are distributed over a number of sites in the cavities, which also contain the remainder of the aluminum atoms. The latter are octahedrally coordinated, probably by a mixture of OH^- and H_2O.

The exact composition of the cubic compound of approximate empirical formula $BaO.Al_2O_3.H_2O = 1:1:1$ has never been established. Carlson, Chaconas & Wells (1950) suggested mole ratios of 8:7:7 or 9:8:8; Ahmed & Dent Glasser (1971) concluded from single-crystal data and density measurements that the cubic unit cell ($a=9.638$ Å) probably contained $8(BaO.Al_2O_3.H_2O)$. Structure analysis has revealed that this latter conclusion was probably wrong, and tends to support the 8:7:7 formula. Refinement has proved difficult, for reasons given below, but the basic structure will be briefly described.

The available crystals were extremely small, and the intensity data correspondingly poor. Intensities were measured for one half of reciprocal space using a Hilger and Watts Y190 linear diffractometer with Mo $K\alpha$ radiation. Equivalent reflexions agreed poorly, and many of the intensities were extremely weak, especially those with $h+k+l=2n+1$. After reducing intensities to structure amplitudes in the usual way and averaging equivalent reflexions, a total of 120 non-zero independent reflexions remained.

Initially, data were processed on an Elliott 803 computer, mainly using programs kindly supplied by Daly, Stephens & Wheatley (1963). Later an ICL 4/50 computer was used, with programs kindly supplied by Dr F. R. Ahmed and collaborators, of the National Research Council of Canada, and adapted for use on this machine by Mr J. S. Knowles of the Department of Computing, University of Aberdeen.

No systematic absences were observed; the Laue symmetry is consistent with P432, P$\bar{4}$3m or Pm3m. The crystal morphology suggests that Pm3m is the correct space group, but other possibilities were not excluded at this stage.

The Patterson function could most satisfactorily be interpreted by assuming that the eight Ba atoms are statistically distributed over two sets of eightfold sites on the threefold axes in Pm3m; *i.e.* on x,x,x, *etc.* with $x \approx 0.2$ and

0·3 respectively. An alternative, but less satisfactory, interpretation places the Ba atoms on two sets of fourfold sites on the threefold axes in P$\bar{4}$3m; *i.e.* on x,x,x with $x \approx 0.2$ and 0·7.

Initially, the latter solution was preferred, since it did not involve statistically distributed atoms. Adjustment of the x coordinates reduced R to about 0·3; an electron density map showed probable positions for 12 Al and 24 O atoms. When these were included, R dropped to about 0·2.

By this stage the basic features of the structure were apparent. Each Al atom is surrounded tetrahedrally by four O atoms, and these tetrahedra share corners to give a sodalite-like framework. The Ba^{2+} ions lie within the cavities in approximately the positions occupied by the Na^+ ions in sodalite. A difference synthesis showed the probable presence of octahedral $Al(OH)_6^{3-}$ groups at the centres of the cavities, analogous to the Cl^- ions in sodalite.

Both the difference map and the electron density map showed additional large peaks on the threefold axes at $x \approx 0.3$ and 0·8. These are less than 2 Å from the original Ba atoms, and the most probable interpretation is that they represent alternative sites for Ba. If the Ba atoms are distributed over these and the original sites, the resulting arrangement is similar to that described above as the more satisfactory Patterson solution. It was in fact found impossible to progress without making this assumption.

Table 1. *Final atomic parameters*

In this Table, and in Table 2, figures in brackets represent the e.s.d. corresponding to the least significant digit. No errors are given for the occupation factors, because these couple so strongly with the scale and temperature factors that it was felt that the values from the least-squares output were unreliable.

	x/a	y/b	z/c	Occupation factor
Ba(1)	0·214 (1)	0·214 (1)	0·214 (1)	0·61
Ba(2)	0·289 (1)	0·289 (1)	0·289 (1)	0·28
Al(1)	0·248 (1)	0·5	0·0	
O(1)	0·0	0·347 (2)	0·347 (2)	
O(2)	0·5	0·161 (2)	0·161 (2)	
Al(2)	0·0	0·0	0·0	
O(3)	0·218 (4)	0·0	0·0	
Al(3)	0·5	0·5	0·5	
O(4)	0·317 (4)	0·5	0·5	

Accordingly, the Ba atoms were distributed over four fourfold sites in $P\bar{4}3m$, and the refinement, including occupation factors, was continued; R dropped to about 0·10 for all reflexions.

Examination of the parameters at this stage showed that all, including the Ba occupation factor, were consistent, within the limits of error, with the space group $Pm3m$. Accordingly, refinement was continued in $Pm3m$, and insofar as this resulted in a slightly improved value of R (0·09) with fewer parameters, it seems likely that this is in fact the true space group.

Table 1 gives the final positional parameters, and occupancy fractions for Ba, and Table 2 some of the more important bond distances. The geometry of the framework and the coordination of the barium ions is satisfactory, and the proposed structure explains the observed chemical behaviour of the material. This, together with the reasonably good agreement between F_o and F_c,* gives confidence in the basic correctness of the structure.

Nevertheless, some unsatisfactory features remain. (1) The formula $Ba_8(AlO_2)_{12}[Al(OH)_6]_2$ has a net charge of -2, or more if the sum of the occupation fractions (which suggests that the average number of barium atoms per cell is slightly less than 8) is to be believed. The deficiency might be made good by the addition of protons, $e.g.$ $Ba_8(AlO_2)_{12}[Al(OH)_5H_2O]_2$, which corresponds to the 8:7:7 mole ratio. (2) When temperature factors are allowed to refine, those of the framework oxygen atoms tend to run negative. (3) The bond lengths about the octahedral Al are not satisfactory.

Attempts to resolve these difficulties by postulating different arrangements for the cavity contents (including other sorts of disorder) all failed to produce satisfactory convergence. Coupling between the occupation factors,

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* A list of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30075 (2pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths and angles*

(a) The framework

Al(1)–O(1)	1·76 (2) Å ($\times 2$)
Al(1)–O(2)	1·76 (2) ($\times 2$)
O(1)–Al(1)–O(2)	114 (1)°
O(1)–Al(1)–O(2)	105 (1) ($\times 4$)
O(2)–Al(1)–O(2)	123 (1)
Al(1)–O(1)–Al(1)	156 (1)
Al(1)–O(2)–Al(1)	147 (1)

(b) The cavity contents

Ba(1)–O(1)	2·74 (1) Å	
Ba(1)–O(2)	2·85 (1)	(All $\times 3$)
Ba(1)–O(3)	2·94 (2)	
Ba(2)–O(1)	2·89 (1)	
Ba(2)–O(2)	2·68 (1)	(All $\times 3$)
Ba(2)–O(4)	2·89 (1)	
Al(2)–O(3)	2·10 (3)	(Both $\times 6$)
Al(3)–O(4)	1·77 (3)	

temperature and scale factors (even though the two first were never allowed to refine simultaneously), together with the uncertainty regarding the exact composition, certainly contributed to this, and about 100 least-squares cycles were run without further progress. In these circumstances, the presence of the heavy barium atoms is an embarrassment. The isostructural strontium compound has now been prepared in these laboratories; should it prove possible to grow reasonably sized crystals of this, it might well be a more fruitful subject for refinement.

References

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Refinement of hydrogen-atom positions in L-cysteic acid.H₂O from neutron diffraction data.

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From partial three-dimensional neutron-diffraction intensity data (280 reflexions) and starting from the X-ray structure of Hendrickson & Karle [*Acta Cryst.* (1971) B**27**, 427–431], the parameters for the hydrogen atoms in L-cysteic acid. H_2O ($C_3H_7NO_5S$ H_2O) have been refined by the method of least-squares. The final R value is 0·040. The details of the hydrogen atom stereochemistry in the molecule and the hydrogen bonding are presented.

Introduction

The neutron diffraction study of L-cysteic acid monohydrate ($NH_3^+CHCH_2SO_3^-COOH.H_2O$) was undertaken as part of our current program of locating precisely the positions of hydrogen atoms in amino acids and their derivatives. The X-ray study of this amino acid has been done by Hendrickson & Karle (1971), in which the approximate positions of hydrogen atoms were determined. The orientation of the H–H vector of the water molecule was determined by El Saffar, Hendrickson & Koski (1969) using proton magnetic resonance technique.

Experimental

The crystal used for data collection was prismatic in shape, weight 38 mg. It was mounted with its c axis along the φ-