Barium aluminate hydrates. I. A barium analogue of hydrogarnet.

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A new compound of probable formula $Ba_3Al_2(OH)_{12}$ was formed at about 90°C from solutions of high BaO/Al_2O_3 ratio. Its composition could not be verified analytically because of contamination with hydrous alumina. Its unit cell (cubic, $a = 13.16$ Å) and space group $(Ia3d)$ are analogous to those of hydrogarnet $[Ca_3Al_2(OH)_{12}]$. Infrared studies and full structural analysis confirm that it is a barium analogue of hydrogarnet.

Hydrogarnet, $Ca_3Al_2(OH)_{12}$, is a well established compound whose structure was first investigated by Brandenberger (1933), and refined by Weiss & Grandjean (1964). The strontium analogue has also been described (Brandenberger, 1933; Maekawa, 1943; Carlson, 1955) but the barium analogue has not been previously reported. We have prepared this compound and confirmed its crystal structure.

In the course of a study of compounds in the system $BaO-Al_2O_3-H_2O$, a new compound was produced at about 90°C from solutions high in barium. In a typical preparation, aluminum wire plus a large excess of saturated barium hydroxide solution was held just below the boiling point under a reflux condenser. The product consisted of colourless octahedral crystals, which were invariably encrusted with hydrous alumina, making accurate analysis difficult. Nevertheless the approximate analysis, combined with details of the unit cell and space group (Table 1) strongly suggested that the material was the barium analogue of hydrogarnet. Comparison of X-ray powder data supported this.

Intensity data were collected from a single crystal with a Hilger and Watts Automatic Linear Diffractometer, and processed by means of an Elliott 803 B computer, mainly using programs kindly provided by Daly, Stephens & Wheatley (1963). Interpretation of the Patterson function and subsequent electron density maps confirmed that the material had the hydrogarnet structure. The atomic coordinates and isotropic temperature factors were refined by the method of least squares (diagonal-block approximation), and the results (after 8 cycles) are given in Table 2. At this point the conventional R value was 0·077 and parameter shifts were no longer significant. Observed and calculated structure factors are given in Table 3, and interatomic distances in Table 4. Al is surrounded by six hydroxyl groups in a slightly distorted octahedron. Ba is surrounded by eight hydroxyl groups whose configuration is between a cube and a square antiprism; two opposite faces are rectangular within the limits of error, while the angles at the corners of the others range from 74 to 103°.

Table 1. *Space groups and cell dimensions of hydrogarnet and its Sr and Ba analogues*

Compound	Space group	a (Å)
$Ca_3Al_2(OH)_{12}$	$Ia3d$	12·573*
$Sr_3Al_2(OH)_{12}$	$Ia3d$	13·04†
$Ba_3Al_2(OH)_{12}$	$Ia3d$	13·16

* Weiss & Grandjean (1964).
† Carlson (1955).

Table 2. *Atomic coordinates*

Figures in brackets represent the estimated standard deviations corresponding to the least significant digit.

	x	y	z	B
Ba	$\frac{1}{8}$	0	$\frac{1}{4}$	2·2 (1) Å^2
Al	0	0	0	0·9 (5)
O	0·279 (2)	0·112 (2)	0·198 (2)	0·8 (5)

Table 3. *Observed and calculated structure factors* ($\times$ 10)

The scattering factors employed were those for Ba^{2+}, Al^{3+} and O^{2-} (hydrogen was ignored). The value for O^{2-} was obtained by extrapolation from the values for O and O^- given in *International Tables for X-ray Crystallography* (1962); those for Ba^{2+} and Al^{3+} were taken directly from the same source.

h	k	l	F_o	F_o	h	k	l	F_o	F_o
4	0	0	574	532	7	6	1	162	160
8	0	0	901	900	9	6	1	218	230
12	0	0	95	104	4	2	2	309	326
4	2	0	−674	−679	8	2	2	−62	−51
6	2	0	−98	−107	3	3	2	179	186
10	2	0	−157	−202	5	3	2	371	371
12	2	0	−281	−309	7	3	2	149	182
4	4	0	−309	−315	9	3	2	225	234
6	4	0	611	648	11	3	2	160	158
8	4	0	406	389	6	4	2	410	414
10	4	0	384	424	8	4	2	−356	−401
6	6	0	−134	−142	10	4	2	289	298
10	6	0	−121	−126	5	5	2	−394	−379
12	6	0	−278	−272	7	5	2	−156	−178
8	8	0	540	564	9	5	2	−200	−196
2	1	1	−378	−390	11	5	2	−149	−150
6	1	1	504	467	12	6	2	214	184
10	1	1	−139	−160	7	7	2	234	236

Table 3 (cont.)

h	k	l	F_o	F_c	h	k	l	F_o	F_c
3	2	1	340	345	9	7	2	131	166
5	2	1	−461	−431	6	3	3	−184	−210
7	2	1	219	252	10	3	3	134	171
9	2	1	−226	−213	5	4	3	−85	−52
11	2	1	206	215	6	5	3	−196	−213
4	3	1	146	101	10	5	3	150	199
6	3	1	185	219	7	6	3	−199	−207
10	3	1	−220	−180	9	6	3	164	192
5	4	1	20	17	8	4	4	−65	−41
9	4	1	94	84	7	6	4	68	50
6	5	1	306	302	6	6	4	324	335
10	5	1	−210	−247	8	6	4	308	364

Table 4. Bond lengths (e.s.d. 0·03 Å) and angles (e.s.d. 1°)

Al–O		1·97	O–Al–O	(i)	86°	
				(ii)	94	
Ba–O	(i)	2·66	O–Ba–O	(i)	61°	⎫
	(ii)	2·59	(adjacent oxygen atoms)	(ii)	74	⎬ Value for regular cube = 73·32°
				(iii) & (iv)	77	⎭

Table 5. Infrared absorption bands (cm⁻¹) for the hydrogarnet group of compounds

	$Ca_3Al_2(OH)_{12}$	$Sr_3Al_2(OH)_{12}$	$Ba_3Al_2(OH)_{12}$
O–H stretching	3658	3655	3660
Al–O–H bending	800	785	780
Al–O₆ stretching	530	510	490

The chemical analysis indicated a BaO:Al₂O₃ ratio of about 2·5, which is too low. This can probably be attributed to the contamination with hydrous alumina mentioned above; the presence of only 4% by weight would be sufficient to account for the analytical result. However, it is also just possible that there are vacancies in the barium sites, balanced by omission of OH⁻ or substitution of H₂O for OH⁻. We attempted to check this by refinements assuming statistical occupancy of the barium sites, but were unable to reach any definite conclusion: the barium is very much the heaviest atom in the structure and reducing the number of barium atoms in the cell results in little more than a change in the scale factor. Attempts to settle the matter from consideration of the density, refractive index or thermal weight loss curves were also inconclusive. On balance it seems likely that the material does have the ideal formula.

The infrared absorption spectrum of Ba₃Al₂(OH)₁₂ was recorded over the range 4000–400 cm⁻¹ using a Perkin–Elmer 457 Grating Spectrophotometer. The sample, prepared as a Nujol mull, was held between two KBr discs. The principle bands recorded are given in Table 5, together with those quoted for the Sr and Ca analogues by Tarte (1967). They are in excellent agreement.

References

Brandenberger, E. (1933). Schweiz. min. petrogr. Mitt. 13, 569.
Carlson, E. T. (1955). J. Res. nat. Bur. Stand. 54, 329.
Daly, J. J., Stephens, F. S. & Wheatley, P. J. (1963). Monsanto Research S.A. Final Report No. 52.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Maekawa, G. (1943). J. Soc. chem. Ind. Japan, 45, 751.
Tarte, P. (1967). Private communication.
Weiss, R. & Grandjean, D. (1964). Acta Cryst. 17, 1329.

The effects of extinction corrections on the variable position and thermal parameters of Ca₂PO₄Cl and Ca₂CrO₄Cl.

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The crystal structures of Ca₂PO₄Cl and Ca₂CrO₄Cl which have been described in a recent publication, have been refined further by applying isotropic extinction corrections. The estimated standard errors of thermal and position parameters decreased significantly. The conventional R factor decreased from about 8% (for all observed reflections) to 2·5%.

We recently reported the determination of the crystal structures of the isomorphous Ca₂PO₄Cl and Ca₂CrO₄Cl (Greenblatt, Banks & Post, 1967). These were refined by conventional full-matrix least-squares methods. Initial efforts led to values of the conventional R index ($\Sigma |\Delta F| / \Sigma |F|$) of 7·1% for Ca₂CrO₄Cl and 9·6% for Ca₂PO₄Cl.