

atoms divided by the volume of the unit cell is 0.64. This structure is less densely packed than a b.c.c. structure for which this ratio is 0.68, but is more densely packed than crystalline Hg (at 227°K) for which this ratio is 0.61.

The low density of packing, the low coordination numbers, and the existence of short interatomic distances at 2.750 and 2.780 Å suggest that the bonding is not entirely metallic in nature but has some covalent character.

Conclusions

Rolfe & Hume-Rothery (1967) have presented powder data for a compound they identify as Au₂Hg. Powder patterns prepared from our samples and the single-crystal data are all in excellent agreement with their data. This proves the identity between the compound they call Au₂Hg and the compound described here. Since the structure is disordered the exact stoichiometry could not be determined. The structure of the Au₂Hg phase is a new structure type.

The authors wish to thank Professor E. R. Corey for helpful comments and for review of the manuscript. This research received financial support from NIH under grant number DE 02788-01.

References

- BRADLEY, A. J. (1935). *Proc. Phys. Soc. (London)*, **47**, 879.
 BRALEY, R. A. & SCHNEIDER, R. F. (1921). *J. Amer. Chem. Soc.* **43**, 740.
 HANSEN, M. & ANDERKO, K. (1958). *Constitution of Binary Alloys*. New York: McGraw-Hill.
International Tables for X-ray Crystallography (1962). Vol. III, p. 212. Birmingham: Kynoch Press.
 KULIFAY, S. M. (1961). *J. Amer. Chem. Soc.* **83**, 4916.
 LINGANE, J. (1966). *Analytical Chemistry of Selected Metallic Elements*. New York: Reinhold.
 MASSALSKI, T. B. (1957). *Acta Met.* **5**, 541.
 PABST, A. (1929). *Z. Phys. Chem.* **B3**, 443.
 PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
 ROLFE, C. & HUME-ROTHERY, W. (1967). *J. Less-Common Met.* **13**, 1.
 STENBECK, S. (1933). *Z. anorg. Chem.* **214**, 16.
 WINTERHAGER, H. & SCHLOSSER, W. (1960). *Metall*, **14**, 1.

Acta Cryst. (1970). **B26**, 867

Barium Aluminate Hydrates. II. The Crystal Structure of Ba₂[Al₂(OH)₁₀]

BY A. H. MOINUDDIN AHMED AND LESLEY S. DENT GLASSER

Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

(Received 5 July 1969)

The compound 2BaO·Al₂O₃·5H₂O has been shown by X-ray structural analysis to contain complex anions of formula [Al₂(OH)₁₀]⁴⁻, which are built from two Al(OH)₆ octahedra sharing an edge. These are linked by the barium ions and by hydrogen bonding. The compound is thus a complex hydroxide and the formula should be written Ba₂[Al₂(OH)₁₀].

Introduction

The compound of empirical formula 2BaO·Al₂O₃·5H₂O has been known for some time, having first been prepared by Beckmann (1882) who boiled together unspecified quantities of hydrated alumina and baryta water, and concentrated the filtrate by boiling. Morphological data for his product, which was triclinic, are given in Table 1. Many subsequent preparations have been reported and its stability relationships have been investigated (e.g. Malquori, 1926; Carlson & Wells, 1948; Carlson, Chaconas & Wells, 1950).

Table 1. *Crystal data for Ba₂[Al₂(OH)₁₀]*

Unit cell		
$a = 6.70_4$	$b = 5.75_8$	$c = 6.17_9$ Å
$\alpha = 90^\circ 4'$	$\beta = 98^\circ 25'$	$\gamma = 109^\circ 36'$
$P\bar{1}$	$Z = 1$	X-ray density
		3.723 g.cm ⁻³

Table 1 (cont.)

Goniometric data

(1) $a:b:c$ 0.8545:1:0.9888	(2) $a:b:c$ 0.859:1:0.922
$\alpha = 99^\circ 20\frac{1}{2}'$	$\alpha = 98^\circ 25'$
$\beta = 91^\circ 52'$	$\beta = 90^\circ 4'$
$\gamma = 109^\circ 26\frac{1}{2}'$	$\gamma = 109^\circ 36'$

Refractive indices and observed density

	Carlson & Wells (1948)	Present work
α	1.642	1.643 ± 0.003
β	1.655	1.655 ± 0.003
γ	1.676	1.675 ± 0.003
D_{obs}	3.42 g.cm ⁻³	3.66 g.cm ⁻³

(1) Quoted by Beckmann (1882).

(2) Calculated from the X-ray cell transformed into Beckmann's setting.

In the present work it was found possible to prepare the compound by many methods. Beckmann's original

method yielded the best crystals; the quantities of hydrated alumina and of baryta were found not to be critical. The refractive indices of the product (Table 1) agreed well with those given by Carlson & Wells (1948).

Single-crystal X-ray studies confirmed that the crystals were triclinic. In Table 1 angles and axial ratios obtained from the X-ray work are compared with those reported by Beckmann (1882). The agreement is good except for one of the axial ratios. It is possible that the transformation of the X-ray cell to Beckmann's

setting has been done incorrectly, and that the agreement of the other values is fortuitous, but this does not seem very likely.

The cell contents are $Ba_2Al_2O_{10}H_{10}$.

Experimental

Intensity data were collected using a Hilger & Watts automatic linear diffractometer with Mo $K\alpha$ radiation. Accurate setting of triclinic crystals on this instrument is not easy; data were obtained from two different

Table 2. Observed and calculated structure factors ($\times 10$)

Reflexions marked with asterisks were omitted from the least-squares refinement.

h	k	l	F _o	F _c
0	0	0	1000	1000
0	0	1	1000	1000
0	0	2	1000	1000
0	0	3	1000	1000
0	0	4	1000	1000
0	0	5	1000	1000
0	0	6	1000	1000
0	0	7	1000	1000
0	0	8	1000	1000
0	0	9	1000	1000
0	0	10	1000	1000
0	0	11	1000	1000
0	0	12	1000	1000
0	0	13	1000	1000
0	0	14	1000	1000
0	0	15	1000	1000
0	0	16	1000	1000
0	0	17	1000	1000
0	0	18	1000	1000
0	0	19	1000	1000
0	0	20	1000	1000
0	0	21	1000	1000
0	0	22	1000	1000
0	0	23	1000	1000
0	0	24	1000	1000
0	0	25	1000	1000
0	0	26	1000	1000
0	0	27	1000	1000
0	0	28	1000	1000
0	0	29	1000	1000
0	0	30	1000	1000
0	0	31	1000	1000
0	0	32	1000	1000
0	0	33	1000	1000
0	0	34	1000	1000
0	0	35	1000	1000
0	0	36	1000	1000
0	0	37	1000	1000
0	0	38	1000	1000
0	0	39	1000	1000
0	0	40	1000	1000
0	0	41	1000	1000
0	0	42	1000	1000
0	0	43	1000	1000
0	0	44	1000	1000
0	0	45	1000	1000
0	0	46	1000	1000
0	0	47	1000	1000
0	0	48	1000	1000
0	0	49	1000	1000
0	0	50	1000	1000
0	0	51	1000	1000
0	0	52	1000	1000
0	0	53	1000	1000
0	0	54	1000	1000
0	0	55	1000	1000
0	0	56	1000	1000
0	0	57	1000	1000
0	0	58	1000	1000
0	0	59	1000	1000
0	0	60	1000	1000
0	0	61	1000	1000
0	0	62	1000	1000
0	0	63	1000	1000
0	0	64	1000	1000
0	0	65	1000	1000
0	0	66	1000	1000
0	0	67	1000	1000
0	0	68	1000	1000
0	0	69	1000	1000
0	0	70	1000	1000
0	0	71	1000	1000
0	0	72	1000	1000
0	0	73	1000	1000
0	0	74	1000	1000
0	0	75	1000	1000
0	0	76	1000	1000
0	0	77	1000	1000
0	0	78	1000	1000
0	0	79	1000	1000
0	0	80	1000	1000
0	0	81	1000	1000
0	0	82	1000	1000
0	0	83	1000	1000
0	0	84	1000	1000
0	0	85	1000	1000
0	0	86	1000	1000
0	0	87	1000	1000
0	0	88	1000	1000
0	0	89	1000	1000
0	0	90	1000	1000
0	0	91	1000	1000
0	0	92	1000	1000
0	0	93	1000	1000
0	0	94	1000	1000
0	0	95	1000	1000
0	0	96	1000	1000
0	0	97	1000	1000
0	0	98	1000	1000
0	0	99	1000	1000
0	0	100	1000	1000

crystals for reasons explained below. The crystals were roughly equant, about 100μ across. No corrections were made for absorption or extinction. Data were processed on an Elliott 803B computer, mainly using programs kindly supplied by Daly, Stephens & Wheatley (1963).

Application of the statistical test of Howells, Phillips & Rogers (1950) indicated the presence of a centre of symmetry. The approximate positions of the barium and aluminum atoms were derived from the Patterson function. An electron density map computed using the phases thus obtained enabled all the oxygen atoms to be located. From this point refinement was by least-square methods (block-diagonal approximation). The procedure used followed that suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) and incorporated the same weighting scheme and method of calculation of the estimated standard deviations. Initially positional parameters only were refined; at later stages isotropic temperature factors were refined, and finally, after the difficulties described below had been overcome, 3 cycles were computed using anisotropic temperature factors. Scattering factors for Ba^{2+} and Al^{3+} were taken from *International Tables for X-ray Crystallography* (1962). A curve for O^{2-} was constructed by extrapolation from values for O^- and O taken from the same source. (It was hoped that this would to some extent compensate for neglecting the contribution of the hydrogen atoms.)

Using the data from the first crystal (about 700 independent reflexions), the structure would not refine below $R=0.21$. It was at first thought that this might indicate that the assumed centre of symmetry was in fact lacking. Accordingly refinement was continued in

$P1$, but the improvement in the agreement was negligible ($R=0.20$). It was then suspected that the data might be at fault. Accordingly a second crystal was mounted and a completely new set of data was collected (760 independent reflexions). Once again refinement stopped before satisfactory agreement had been obtained. Examination of the two sets of data revealed that those reflexions for which agreement between F_o and F_c was poorest also showed poor agreement between the values for the first and second crystals. This appeared to justify our suspicions of the data. We believe that most of the trouble arises from the difficulty, mentioned above, of setting triclinic crystals accurately, although absorption might also play some part.

Accordingly 14 reflexions were omitted from the data for the second crystal, and refinement was continued with isotropic temperature factors, finally ceasing at $R=0.14$. Introduction of anisotropic temperature factors reduced the R value to 0.11 after three cycles without significantly changing the positional parameters; agreement analyses in terms of F_o and of $\sin \theta$ showed no systematic trends. The structure was thus considered to be refined as far as the data would permit. Table 2 gives the values of F_o and F_c obtained (reflexions omitted from the final cycles are marked with an asterisk), Table 3 the corresponding final parameters and Table 4 some details of the coordination polyhedra. Because of the somewhat unsatisfactory data, most of the fine details of differences in bond lengths, *etc.* are not significant, although the structure is undoubtedly basically correct. A difference map computed after refinement was complete showed no unusual features; not surprisingly, it was not possible to locate the hydrogen atoms from it.

Table 3. *Final parameters for* $Ba_2[Al_2(OH)_{10}]$

Figures in brackets represent the estimated standard deviation corresponding to the least significant digit(s).

Positional parameters						
	x/a	y/b	z/c			
Ba	0.0370 (4)	0.2761 (3)	0.2943 (3)			
Al	0.318 (1)	0.346 (2)	0.826 (2)			
O(1)	0.278 (3)	0.084 (4)	0.029 (3)			
O(2)	0.306 (3)	0.141 (4)	0.591 (3)			
O(3)	0.339 (4)	0.618 (4)	0.653 (3)			
O(4)	0.018 (4)	0.294 (4)	0.768 (4)			
O(5)	0.630 (3)	0.431 (4)	0.911 (3)			
Temperature factors (\AA^2)*						
	u_{11}	u_{22}	u_{33}	$2u_{12}$	$2u_{23}$	$2u_{13}$
Ba	0.024 (1)	0.018 (1)	0.044 (1)	0.012 (1)	0.004 (1)	0.019 (1)
Al	0.024 (4)	0.016 (4)	0.034 (4)	0.009 (6)	0.005 (6)	0.007 (7)
O(1)	0.012 (10)	0.023 (11)	0.027 (11)	-0.004 (16)	0.020 (15)	-0.014 (16)
O(2)	0.019 (10)	0.022 (11)	0.024 (10)	0.023 (16)	-0.006 (14)	-0.016 (15)
O(3)	0.021 (11)	0.036 (13)	0.024 (11)	0.003 (18)	-0.001 (15)	0.016 (17)
O(4)	0.048 (15)	0.022 (13)	0.063 (15)	0.029 (21)	0.002 (20)	0.103 (26)
O(5)	0.010 (9)	0.026 (11)	0.030 (11)	0.019 (16)	0.006 (15)	-0.014 (15)

* As defined by the expression

$$f = f_0 \exp [-2\pi^2(h^2a^*u_{11} + k^2b^*u_{22} + l^2c^*u_{33} + 2hka^*b^*u_{12} + 2hla^*c^*u_{13} + 2klb^*c^*u_{23})]$$

(a^* , b^* , c^* are in \AA^{-1}).

Description of the structure

Fig. 1 shows the structure viewed along *b*. Each aluminum atom is surrounded by six oxygen atoms in a

Table 4. *Coordination polyhedra in Ba [Al₂(OH)₁₀]*

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

(a) Al(OH)₆ octahedra

Bond distances		Mean	
Al-O(1)	1.94 (2) Å	}	1.89 (4) Å (non-bridging)
O(2)	1.84 (2)		
O(3)	1.88 (3)		
O(4)	1.91 (3)		
O(5)	1.97 (2)		
O(5')	1.99 (2)		
Bond angles		}	
O(1)-Al-O(2)	94 (1)°	O(2)-Al-O(3)	93 (1)°
O(4)	92 (1)	O(4)	93 (1)
O(5)	89 (1)	O(5)	93 (1)
O(5')	85 (1)	O(3)-Al-O(4)	84 (1)
O(4)-Al-O(5')	94 (1)	O(5)	95 (1)
		O(5')	89 (1)

Mean of all above: 91 (4)

O(5)-Al-O(5') 79 (1)

(b) Ba-O polyhedron

Table 4 (cont.)

Bond distances		Mean	
Ba-O(1)	2.91 (2) Å	}	2.84 (12) Å
O(1')	2.90 (2)		
O(2)	2.68 (2)		
O(2')	2.89 (2)		
O(3)	2.98 (2)		
O(3')	2.85 (2)		
O(4)	2.95 (3)		
O(4')	2.65 (3)		
O(5')	2.78 (2)		
[O(4'')]	3.19 (3)]		
[O(4''')]	3.24 (3)]		

slightly distorted octahedron. These octahedra occur in centrosymmetrically related pairs, sharing an edge. The 'water' is thus presumably all present as hydroxyl groups and the anion can be written [Al₂(OH)₁₀]⁴⁻. For purposes of discussion the oxygen atoms (or hydroxyl ions) which form the shared edge, O(5) and O(5'), will be referred to as 'bridging' and the remainder, O(1), O(2), O(3) and O(4), as 'non-bridging'.

These [Al₂(OH)₁₀]⁴⁻ groups are linked through the barium atoms, which have large, irregular coordination polyhedra. There are nine Ba-O contacts below 3.0 Å, and two more of about 3.2 Å. Omitting the longer contacts (as in Fig. 1) each barium atom makes

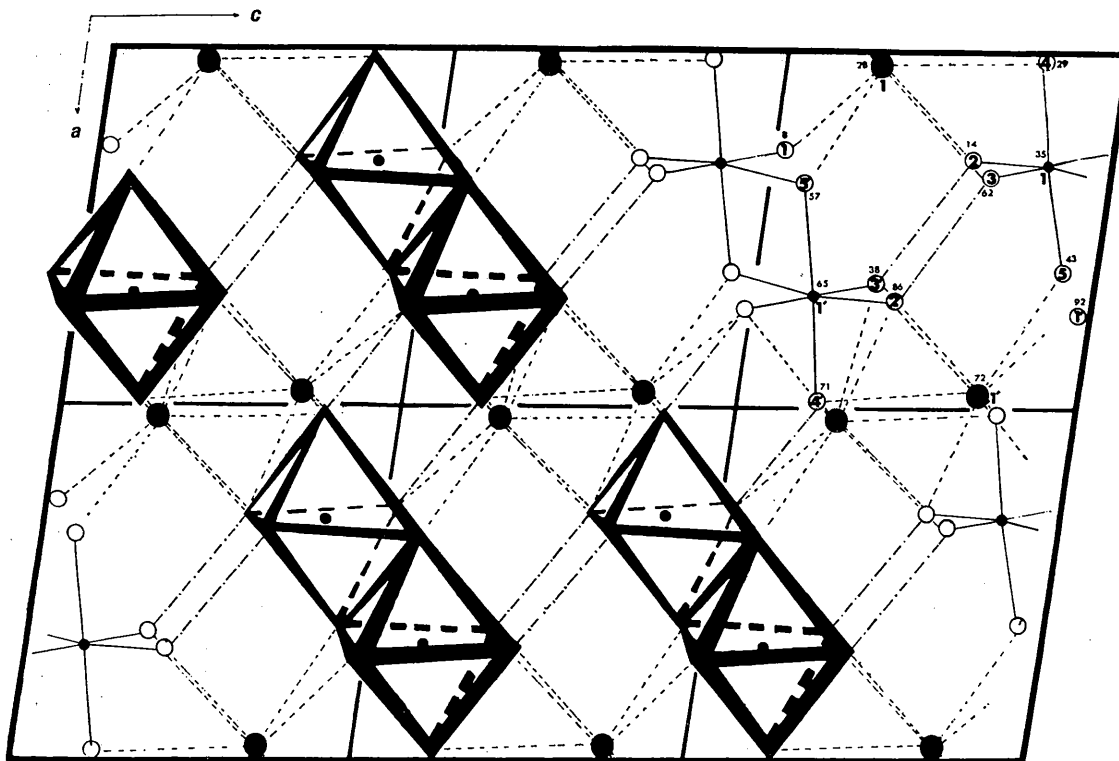


Fig. 1. The structure of Ba₂[Al₂(OH)₁₀] viewed along *b*. Large solid circles represent Ba, small solid circles Al, open circles, O atoms. Large figures give the numbering of the oxygen atoms; small figures give *y/b* in hundredths. Six unit-cells are shown. Dotted lines show Ba-O contacts; dot-dash lines are possible hydrogen bonds.

contact with eight non-bridging hydroxyl groups and one bridging group. Likewise each bridging hydroxyl group contacts one barium atom, while each non-bridging group contacts two. Pauling's electrostatic valency rule can be satisfied if each Al-OH bond is counted as $\frac{1}{2}$; the bridging hydroxyl groups would then have their valences satisfied, while the bonds from barium to the non-bridging hydroxyl groups would count $\frac{1}{4}$. The only drawback to this analysis is that the distance Ba-O(5') is one of the shorter barium-oxygen contacts, and it seems unlikely that these atoms are not interacting. Obviously the true situation is more complicated.

There appears to be some degree of hydrogen bonding between adjacent $[\text{Al}_2(\text{OH})_{10}]^{4-}$ groups, indicated by a number of O-O distances ranging upwards from about 2.84 Å. It is difficult to know how many of these should count as hydrogen bonds. No complete and sensible hydrogen bonding scheme could be worked out; this is probably because of the inaccuracies in the structure analysis discussed above. A better structure determination might well reveal more clear-cut distinctions in interatomic distances; and then again . . .

One detail of the structure which may be significant is the way in which the octahedra are distorted. The mean value of the bond lengths from Al to the bridging OH groups [O(5), O(5')] is longer than the mean value of the bond-lengths from Al to the non-bridging ones [O(1), O(2), O(3), O(4)]. Correspondingly the angle subtended at Al by O(5) and O(5') is smaller than the mean value of all the other O-Al-O angles. This is exactly the type of distortion which would be expected in this grouping, and can be attributed to repulsion between the two Al atoms. This type of distortion has frequently been observed in octahedra sharing edges or faces, for example in diaspore, AlOOH (Ewing, 1935; Busing & Levy, 1958), bayerite, $\text{Al}(\text{OH})_3$ (Roth-

bauer, Zigan & O'Daniel, 1967), and corundum, Al_2O_3 (Newnham & de Haan, 1962). What is more difficult to explain is why a configuration involving a shared edge should be adopted at all, when the requirements of stoichiometry could equally well be satisfied by an arrangement of (say) infinite chains of octahedra having only corners in common. We have no explanation to offer for this.

Note added in proof: - Louis & Moras (1969) have also reported a structure determination on this compound. They do not give atomic parameters, but their description of the structure agrees with that reported here.

References

- BECKMANN, E. (1882). *J. prakt. Chem.* **26**, 385.
 BUSING, W. R. & LEVY, H. A. (1958). *Acta Cryst.* **11**, 798.
 CARLSON, E. T., CHACONAS, T. J. & WELLS, L. S. (1950). *J. Res. Nat. Bur. Stand.* **45**, 381.
 CARLSON, E. T. & WELLS, L. S. (1948). *J. Res. Nat. Bur. Stand.* **41**, 103.
 CRUICKSHANK, D. W., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.
 DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Monsanto Research S. A. Final Report No. 52.
 EWING, F. J. (1935). *J. Chem. Phys.* **3**, 203.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 LOUIS, R. & MORAS, D. (1969). *Bull. Soc. Chim. Fr.*, p. 3471.
 MALQUORI, G. (1926). *Gazz. chim. ital.* **56**, 61.
 NEWNHAM, R. E. & DE HAAN, Y. M. (1962). *Z. Kristallogr.* **117**, 235.
 ROTHBAUER, R., ZIGAN, F. & O'DANIEL, H. (1967). *Z. Kristallogr.* **125**, 1.