Crystal Structure of Aluminium Iodate–Hydrogen Iodate–Water (1/1/6) and Preparation of Anhydrous Aluminium Iodate

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The crystal structure of the title compound has been determined by Patterson and Fourier methods using three-dimensional *X*-ray data and has been refined by a full-matrix least-squares procedure to $R = 0.029$ for 2 546 observed reflections. The crystals are hexagonal, space group $P6_3$ with $a = 16.107(2)$, $c = 12.378(2)$ Å, $Z = 6$. The transformation of the structure to that of anhydrous aluminum iodate (hexagonal, $a = 8.97$, $c = 5.25$ Å) is considered. The structure can be formulated as $[Al(OH_2)_6{}^{3+}][IO_3{}^-]_2[HI_2O_6{}^-]\cdot HIO_3$ and contains a very short non-bonded oxygen–iodine contact of 2.476 Å.

PREPARATION of the mixed anion salt $Al[IO_3]_2[NO_3]\cdot 6H_2O$ using an $Al : [IO_3]^-$ ratio $>1 : 3$ (or better, 1 : 6) results in the crystallisation of the acid salt $Al[IO_3]_3\cdot 2HIO_3\cdot 6H_2O$ after all the nitrate salt has been removed from the solution. The crystal structure of aluminium iodate nitrate has already been reported [1] and the structure of the acid iodate is of interest because of the different behaviour of the two compounds on heating. $Al[IO_3]_2[NO_3]\cdot 6H_2O$ loses six water molecules and 20% of the nitrate (by analysis) at 200 °C. The remainder of the nitrate is removed between 300 and 340 °C and the $[IO_3]^-$ decomposes at 425 °C. Up to the decomposition temperature, the powder diffraction pattern is not noticeably altered; a result of the fact that the positions of the iodate ions, which contain 60% of the scattering material, are unaltered. $Al[IO_3]_3\cdot 2HIO_3\cdot 6H_2O$, on the other hand, loses six water molecules at 135 °C, and a seventh, resulting from the decomposition of $2HIO_3$ to $H_2O + I_2O_5$, at 195 °C. The powder diffraction pattern remains basically unchanged until I_2O_5 is lost from the structure at 340 °C, when anhydrous aluminium iodate is formed. This material is stable up to its decomposition temperature of 530 °C, can be reliably prepared in this manner and gives a powder pattern (at room temperature) that can be indexed on the basis of a hexagonal cell, $a = 8.97$, $c = 5.25$ Å.

EXPERIMENTAL

Crystal Data.—$AlH_{14}I_5O_{21}$, $M = 1\,011.59$, Hexagonal, $a = 16.107(2)$, $c = 12.378(2)$ Å, $U = 2\,781.1$ Å^3, $D_c = 3.62$ g cm^{-3}, $Z = 6$, $D_m > 2.9$ g cm^{-3} (bromoform), $F(000) = 460$. Space group $P6_3$ (C_6^6); systematic absences, $00l$, $l = 2n + 1$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 85.8 cm^{-1}.

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[1] P. D. Cradwick and A. S. de Endredy, *J.C.S. Dalton*, 1975, 1926.

TABLE 1

Atomic parameters with estimated standard deviations in parentheses *

Atom	x	y	z	U_{iso}, U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	0.334 2(0)	0.296 9(0)	0.485 8(1)	0.010 5(2)	0.012 9(2)	0.009 4(2)	0.005 2(2)	0.000 9(2)	0.001 3(2)
I(2)	0.500 5(0)	0.554 0(0)	0.25	0.013 4(3)	0.015 1(3)	0.015 0(3)	0.007 9(2)	−0.002 7(2)	−0.003 3(2)
I(3)	0.111 7(0)	0.276 4(0)	0.246 4(1)	0.014 2(2)	0.011 0(2)	0.012 8(3)	0.007 3(2)	0.001 8(2)	−0.000 1(2)
I(4)	0.399 3(0)	0.165 8(0)	0.215 9(1)	0.009 5(2)	0.011 0(2)	0.015 5(3)	0.003 3(2)	0.000 3(2)	−0.000 8(2)
I(5)	0.318 8(0)	0.339 0(0)	0.010 8(1)	0.020 3(3)	0.015 8(3)	0.020 7(3)	0.007 0(2)	0.000 2(3)	0.000 2(2)
Al(1)	2/3	1/3	−0.032 3(4)	0.010 0(9)					
O(W11)	0.616 8(6)	0.221 1(5)	0.052 3(6)	0.019(2)					
O(W12)	0.716 2(5)	0.445 4(5)	−0.118 3(6)	0.016(1)					
Al(2)	0	0	−0.032 8(4)	0.010 0(8)					
O(W21)	0.111 5(5)	0.065 4(5)	0.052 8(6)	0.015(1)					
O(W22)	0.046 4(5)	0.111 0(5)	−0.115 9(6)	0.013(1)					
Al(3)	1/3	2/3	−0.030 2(4)	0.010 8(9)					
O(W31)	0.292 6(5)	0.555 6(5)	0.054 7(6)	0.018(1)					
O(W32)	0.401 0(5)	0.623 7(5)	−0.114 7(6)	0.015(1)					
O(11)	0.432 5(5)	0.328 3(6)	0.579 0(6)	0.018(1)					
O(12)	0.341 8(6)	0.209 0(6)	0.406 5(7)	0.025(2)					
O(13)	0.235 9(5)	0.220 0(5)	0.578 3(6)	0.019(2)					
O(21)	0.392 5(5)	0.557 2(5)	0.222 3(6)	0.019(1)					
O(22)	0.461 2(6)	0.477 0(6)	0.368 8(7)	0.022(2)					
O(23)	0.566 5(5)	0.667 1(6)	0.321 1(6)	0.019(1)					
O(31)	−0.004 2(6)	0.222 7(6)	0.309 8(7)	0.020(1)					
O(32)	0.114 8(5)	0.168 2(5)	0.220 3(6)	0.015(1)					
O(33)	0.183 8(6)	0.305 0(6)	0.376 6(7)	0.021(2)					
O(41)	0.430 0(6)	0.122 5(6)	0.098 7(7)	0.021(2)					
O(42)	0.495 5(5)	0.288 4(5)	0.215 6(7)	0.022(2)					
O(43)	0.447 1(5)	0.116 7(5)	0.313 1(6)	0.016(1)					
O(51)	0.335 2(6)	0.238 4(6)	0.039 7(8)	0.028(2)					
O(52)	0.442 1(6)	0.441 1(6)	0.036 3(7)	0.029(2)					
O(53)	0.269 6(7)	0.350 0(7)	0.134 1(8)	0.039(2)					

* Values without errors were unrefined; the aluminium atoms have occupation factors of 1/3.

Crystallographic Measurements.—The Laue symmetry was determined as $6/m$ from Weissenberg and precession photographs and preliminary values for the cell dimensions obtained from these were refined by a least-squares procedure to minimise the differences between calculated and observed 2θ values of 57 powder lines obtained by the use of a Philips Debye–Sherrer camera of diameter 114.83 mm. The crystals were hexagonal bipyramids and that used for data collection was asymmetrical about the equatorial plane, having dimensions 0.15 and 0.06 mm along the symmetry axis, and diameter 0.21 mm. From the systematic absences, the space group could be $P6_3$ or $P6_3/m$, but a positive test for piezo-electricity eliminated the centrosymmetric space group. Intensities were initially recorded on Weissenberg multi-pack films for the layers $hk0$—11 using Cu-K_α radiation (μ = 689.8 cm^{-1}). They were measured by the S.R.C. microdensitometer service * and corrected for absorption giving a total of 1 349 observed reflections (see ref. 2 for details of measurement procedure). After solution of the structure using these data, a second data set was collected on a Philips PW1100 four circle diffractometer (at the Northern Polytechnic, London) using Mo-K_α radiation giving a total of 2 546 observed reflections.

Structure Determination.—The structure was solved from the film data by the heavy-atom Patterson and Fourier methods and refined (using the rigid-body full-matrix least-squares program, RBLS) to an R factor of 0.06. One oxygen atom [O(53)] could not be satisfactorily located using these data; however, using the diffractometer data its position was unequivocally determined and the refinement proceeded to an R factor of 0.029. All processing using the diffractometer data was carried out using the SHELX program system at the Atlas computer laboratory. The final atomic parameters are given in Table 1 and the interatomic distances in Table 2.

DISCUSSION

The structure (Figure 1) consists of discrete iodate and hydrated aluminium ions linked together through hydrogen bonds. The water co-ordination polyhedra approximate to octahedral symmetry as shown by the dihedral angles associated with the edges b_1, b_2, b_3, b_4 in Figure 2. These values for a regular octahedron are all 70.5°, whilst those observed range from 69.37 to 72.63° with a mean value of 70.5°. Although the lengths of the edges b_3 and b_4 are not required to be equal by symmetry,

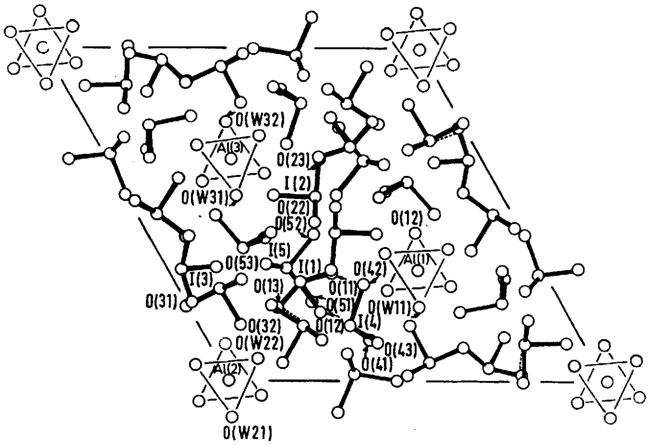

FIGURE 1 Projection of the unit cell on the (001) plane. The broken lines show the I(3) · · · O(13) contact of 2.4 Å

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* Atlas Computer Laboratory, Chilton, Didcot, Oxfordshire OX11 0QY.

[2] P. A. Machin and M. Elder, S.R.C. Microdensitometer service, Notes for Weissenberg film processing, 1974.

all values are within 1σ (0.01 Å) of the mean, 2.707 Å, taken over the three polyhedra. The same is true of the edges b_1 and b_2 which have a mean of 2.616 Å and the inequality of these two sets of edges precludes octahedral symmetry; a regular figure would have edges of 2.66 Å (based on Al–O distance of 1.88 Å), which is in fact the mean of the observed values. The co-ordination polyhedron of the mixed anion salt $Al[IO_3]_2[NO_3]\cdot 6H_2O$, while of formally higher symmetry (32), is less regular due to distortions caused by the nitrate ion.[1] The lack of the two-fold symmetry restriction for polyhedra in the acid salt results in the aluminium ions not being located at the exact centre (along the *c* axis) and in an unconstrained orientation about the three-fold axes.

TABLE 2

Interatomic distances and angles

(*a*) Distances (Å)

I(1)–O(11)	1.814(8)	I(5)–O(51)	1.803(9)
I(1)–O(12)	1.775(9)	I(5)–O(52)	1.866(9)
I(1)–O(13)	1.841(8)	I(5)–O(53)	1.769(9)
I(2)–O(21)	1.798(7)	Al(1)–O(W11)	1.886(8)
I(2)–O(22)	1.821(9)	Al(1)–O(W12)	1.894(8)
I(2)–O(23)	1.813(8)		
		Al(2)–O(W21)	1.888(8)
I(3)–O(31)	1.799(8)	Al(2)–O(W22)	1.864(8)
I(3)–O(32)	1.796(7)		
I(3)–O(33)	1.903(8)	Al(3)–O(W31)	1.888(8)
		Al(3)–O(W32)	1.875(8)
I(4)–O(41)	1.784(9)		
I(4)–O(42)	1.800(8)		
I(4)–O(43)	1.810(8)		

O(52) (IV; $X + 1, Y + 1, Z - 1$)–O(22)	2.531
O(51) (V; $Z - 1$)–O(33)	2.637
O(W11) (I)–O(41)	2.669
O(W11) (III; $X + 1, Y + 1$)–O(42)	2.610
O(W12) (IV; $X + 1, Y + 1$)–O(21)	2.624
O(W12) (V; $Y + 1$)–O(23)	2.705
O(W21) (I)–O(32)	2.637
O(W21) (VI)–O(13)	2.675
O(W22) (V)–O(32)	2.607
O(W22) (VI)–O(31)	2.663
O(W31) (I)–O(21)	2.617
O(W31) (V)–O(11)	2.685
O(W32) (IV; $X + 1, Y + 1$)–O(42)	2.614
O(W32) (V)–O(43)	2.635
O(W31) (I)–O(W32)	2.594
O(W31) (III; $Y + 1$)–O(W31)	2.715
O(W32) (III; $Y + 1$)–O(W31)	2.634
O(W32) (III; $Y + 1$)–O(W32)	2.695
O(W21) (I)–O(W22)	2.601
O(W21) (III)–O(W21)	2.707
O(W22) (III)–O(W21)	2.610
O(W22) (III)–O(W22)	2.693
O(W11) (III; $X + 1, Y + 1$)–O(W12)	2.627
O(W11) (III; $X + 1, Y + 1$)–O(W11)	2.717
O(W12) (III; $X + 1, Y + 1$)–O(W12)	2.713
O(W12) (III; $X + 1, Y + 1$)–O(W11)	2.632

(*b*) Angles (°)

O(11)–I(1)–O(12)	100.1(4)	O(21)–I(2)–O(22)	99.3(4)
O(11)–I(1)–O(13)	97.4(4)	O(21)–I(2)–O(23)	99.9(3)
O(12)–I(1)–O(13)	100.8(4)	O(22)–I(2)–O(23)	97.0(4)
O(31)–I(3)–O(32)	97.9(3)	O(41)–I(4)–O(42)	99.9(4)
O(31)–I(3)–O(33)	96.2(4)	O(41)–I(4)–O(43)	96.2(4)
O(32)–I(3)–O(33)	94.5(3)	O(42)–I(4)–O(43)	99.2(4)
O(51)–I(5)–O(52)	100.9(4)		
O(51)–I(5)–O(53)	101.1(4)		
O(52)–I(5)–O(53)	95.6(4)		

Roman numerals refer to the following symmetry:

I x, y, z
II $\bar{y}, x - y, z$
III $y - x, \bar{x}, z$
IV $x, y, \frac{1}{2} + z$
V $y, y - x, \frac{1}{2} + z$
VI $x - y, x, \frac{1}{2} + z$

Although the hydrogen atoms of the acid molecules could not be located directly, their positions were inferred from the hydrogen bonds occurring between iodate oxygen atoms. These are O(22) ··· O(52) (2.531 Å) and O(33) ··· O(51) (2.637 Å) and as the I(5)–O(52) and I(3)–O(33) bond lengths of 1.866 and 1.903 Å, respectively, are significantly longer than the remainder, O(52) and O(33) are probably OH groups, making the iodates associated with I(3) and I(5) the HIO_3 molecules. The negative charges of the iodate ions represented by I(1), I(2), and I(4) are neutralised by the formation of hydrogen bonds with water molecules of the hydrated aluminium ions, and I(2) and I(4) both accept three such bonds. I(1) however, forms only two [through O(11) and O(13)] and it therefore compensates by forming a strong association through a short O(13) ··· I(3) contact (2.476 Å) with the neutral iodic acid molecule represented by I(3), which is itself hydrogen-bonded to water molecules. Since all water molecules are involved in the maximum number of hydrogen bonds (2 each) the lack of involvement of O(12) in such an interaction is due to the absence of a donor. The only other oxygen atom that is not involved in hydrogen bonding is O(53) which is on a neutral iodic acid molecule. All iodine atoms are involved in the expected non-bonded interactions (2.605—3.078 Å) with oxygen atoms of other iodate ions (see ref. 1 and refs. therein for other examples).

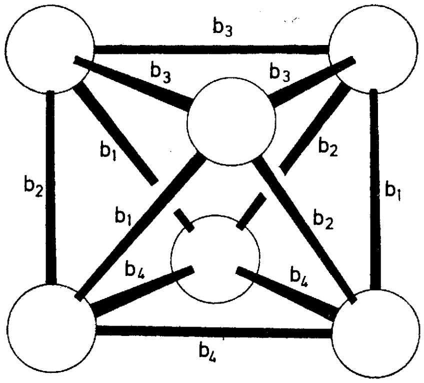
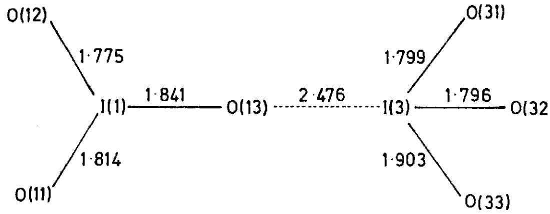


FIGURE 2 Water co-ordination polyhedron showing the edges that are equivalent by symmetry

The association between I(1) and I(3) is of further interest as it suggests the method by which the iodic acid molecules dehydrate to form I_2O_5. The geometry involved is shown below.



This group forms an $[HI_2O_6]^-$ or $[I_2O_5(OH)]^-$ ion, and it appears likely that on dehydration the I–OH bond is broken along with the O–H bond on O(52), converting the above ion to I_2O_5 and the I(5) iodic acid molecule to an iodate ion.

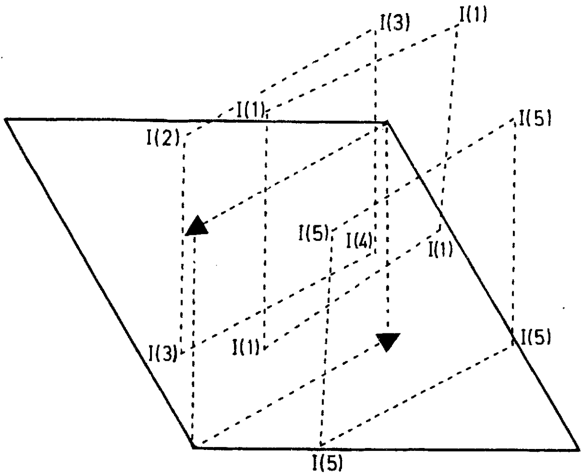


FIGURE 3 Relationship of the sub-cell to the real cell and the positions of the iodine atoms. The I(5) sub-cell is based on the atom related to I(5) of Figure 1 by $y, y - x, \frac{1}{2} + z$

A feature of the data set is the existence of a sub-cell with $a = 9.29$ Å, such that reflections for which $h - k = 3n$ are generally much stronger than the rest, indicating that the true-cell to sub-cell relationship is that of a hexagonal 'triple cell' to its primitive cell. The sub-cell is obtained by using the Al–Al vectors as cell edges, shown in Figure 3 as broken lines joining the origin to the three-fold axes. Also plotted on Figure 3 are the positions of the iodine atoms; the fact that these also lie approximately on a lattice defined by the sub-cell explains the intensities of the stronger reflections. The anhydrous aluminium iodate formed on heating the acid salt has an a axis (8.97 Å) very similar to the sub-cell and suggests that the iodine atoms that remain in the structure do not move appreciably from their positions. A plausible structure for this material is envisaged as an octahedron formed by iodate oxygen atoms about the aluminium ions, each iodate contributing two oxygens, one to the upper triangular face, and one to the lower. To form this structure, the loss of water and I_2O_5 [formed from I(1) and I(3)] must allow the structure to contract in the c direction, with iodate I(5) moving to the position vacated by I(3), and the aluminium ions migrating along the c axis to $z = \pm 0.25$.

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