Crystal Structure of Aluminium Iodate Nitrate Hexahydrate

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The crystal structure of the title compound has been determined by Patterson and Fourier methods from three-dimensional *X*-ray data, and refined by a full-matrix least-squares procedure to *R* 0.03 for 333 observed independent reflections. Crystals are hexagonal, space group *P*321, with $a = 6.764(8)$, $c = 8.088(10)$ Å, $Z = 1$. The compound exists as the mixed-anion salt $Al(IO_3)_2NO_3,6H_2O$ rather than the double salt $Al(NO_3)_3,2Al(IO_3)_3,18H_2O$. The structure shows an iodate–nitrate association and the hydrated cation $[Al(H_2O)_6]^{3+}$ is hydrogen bonded to iodate but not to nitrate.

ALUMINIUM iodate nitrate hexahydrate crystals[1] have been morphologically identified as trigonal, with a *c*/*a* axial ratio of 1.206.[2] A complete analysis gave the empirical formula $Al(IO_3)_2NO_3,6H_2O$ but this did not preclude the existence of the compound as a double salt $Al(NO_3)_3,2Al(IO_3)_3,18H_2O$. The crystal structure has therefore been investigated as the true nature of the compound could provide information of value in interpreting the behaviour of Al^{3+} in solutions containing more than one anion, *e.g.* during the formation of aluminosilicates under natural conditions in soils and sediments.

Aluminium iodate nitrate forms over a fairly wide range of Al : IO_3 ratios and can be recrystallized from water without disproportionation. It is stable in air and over solid potassium hydroxide. Repeated evapor-

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[1] A. S. de Endredy, *Z. anorg. Chem.*, 1934, **217**, 53.

[2] K. von Sztrókay, *Z. Krist.*, 1935, **90**, 381.

ation of solutions of aluminium nitrate in iodic acid solutions with Al : IO_3 ratios of $\geqslant 1 : 3$ leads to formation of a mixture of aluminium iodate nitrate and the acid salt, $Al(IO_3)_3,2HIO_3,6H_2O$, which has also been isolated and identified.

The preferential formation of the mixed-anion salt instead of the normal salt $Al(IO_3)_3,6H_2O$ from solutions containing both IO_3^- and NO_3^- ions is the result of ion association in concentrated solutions of strong electrolytes. An $[Al(H_2O)(IO_3)_2]^+$ association is probable in concentrated solutions [3] and the results of the present structural determination suggest that iodate–nitrate interactions are also likely.

EXPERIMENTAL

Preparation.—Aqueous solutions of $Al(NO_3)_3,9H_2O$ and HIO_3 were mixed to give Al : IO_3 1 : 2 or 1 : 3, and evaporated to dryness on a steam-bath. The dry mass was dissolved in warm water, filtered, and the solution evaporated once more. The residue was again dissolved and the solution concentrated isothermally at room temperature over anhydrous calcium chloride in a vacuum desiccator. Slow evaporation produced hexagonal platy crystals of $Al(IO_3)_2NO_3,6H_2O$ which were washed with the minimum of ice-cold water [Found: Al, 4.88; IO_3^-, 63.93; NO_3^-, 11.33; Calc. for $Al(IO_3)_2(NO_3),6H_2O$: Al, 4.93; IO_3^-, 63.93; NO_3^-, 11.33%]. The solubility is 60 g/100 g water at 19 °C.

When all aluminium iodate nitrate was removed from solutions containing Al : $IO_3 \geqslant 1 : 3$, the acid salt $Al(IO_3)_3,2HIO_3,6H_2O$ crystallized as hexagonal bipyramids [Found: Al^{3+}, 2.67; IO_3^-, 86.42. Calc. for $Al(IO_3)_3,2HIO_3,6H_2O$: Al^{3+}, 2.67; IO_3^-, 86.41%]. *X*-Ray powder photographs were indexed on the basis of a hexagonal unit cell with $a = 16.11$, and $c = 12.38$ Å.

Crystal Data.—$AlH_{12}I_2NO_{15}$, $M = 546.95$, Hexagonal, $a = 6.764(8)$, $c = 8.088(10)$ Å, $U = 320.5$ Å^3, $D_c = 2.83$, $Z = 1$, $D_m = 2.78$ g cm^{-3}, $F(000) = 258$. Space group $P321$ (D_3^2); no systematic absences. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 50.3 cm^{-1}.

Crystallographic Measurements.—The Laue symmetry was determined as $\bar{3}m$ from rotation and Weissenberg photographs and preliminary values for the cell dimensions obtained from these were adjusted by a least-squares procedure to minimize the differences between calculated and observed 2θ values of 54 powder lines obtained by use of a Philips Debye–Scherrer powder camera, diameter 114.83 mm. Crystals were uniaxial when viewed normal to the plates and regular triangular etch figures on the plate surfaces indicated the presence of a three-fold axis in the point group. The *c* axis was taken as normal to the plates, thus defining a hexagonal rather than a rhombohedral unit cell. A suitable crystal for data collection was cut into a roughly cylindrical shape, 0.09 × 0.3 mm, with the axis parallel to *c*. This crystal was mounted about the *c* axis for the collection of three-dimensional intensity data on a Hilger and Watts Y 190 automatic diffractometer by use of Mo-K_α radiation. Each reflection was oscillated through 2.25° in ω and the total time taken in counting background at each end of the scan was equal to that taken for the scan. Balanced α(Y) and β(Zr) filters were employed, two scans being made with each filter so that each reflection was scanned a total of four times. Reflections were considered unobserved when $I < 3\sigma(I)$, where I is the integrated intensity obtained from the difference between the nett counts, $P - \Sigma B$, obtained using the β and the α filters, *i.e.* $I = (P_\beta - P_\alpha) - (\Sigma B_\beta - \Sigma B_\alpha)$ and $\sigma(I) = (P_\beta + P_\alpha + \Sigma B_\beta + \Sigma B_\alpha)^{\frac{1}{2}}$. Half of reciprocal space was scanned for the layers *hk*0—9. Final intensities were obtained by averaging up to six equivalent reflections according to the Laue symmetry (the Bijvoet pairs thus being included in the average) and were corrected for Lorentz and polarization effects, but not for absorption. A total of 333 unique reflections were observed.

Structure Determination.—The lack of systematic absences in *hkl* reflections establishes the lattice type as primitive hexagonal rather than rhombohedral. The presence of 00*l* reflections for $l \neq 3n$ (observed on powder photographs and the linear diffractometer) and the symmetry restrictions imposed by the unit cell contents restrict the possible space groups to $P321$ or $P312$. Three-dimensional Patterson syntheses were computed in both $P\bar{3}m1$ and $P\bar{3}1m$ but only the former could be solved for the iodine atom positions, thus establishing the space group as $P321$. Structure factors calculated using the iodine atoms gave *R* 0.22, and a three-dimensional electron-density map based on these phases showed the positions of all remaining atoms. Since this Fourier synthesis suffered from pseudo-symmetry in the form of a centre of symmetry at the origin, six equal-density peaks corresponding to the nitrate oxygen atoms (O_N) were observed on section $z = 0$. This observation was initially interpreted as disorder of the nitrate ion and half-weight oxygen atoms were located at all six positions. The co-ordinates and isotropic temperature factors of all atoms were then refined by full-matrix least-squares, thereby decreasing *R* from 0.092 to 0.046. Reflections (110) and (011) were found to be affected by secondary extinction and were removed from the data set. Agreement analysis of the individual layers showed that interlayer scaling was necessary to increase the contribution of the higher layers. With these adjustments to the data set and one further cycle of least-squares refinement, *R* was reduced to 0.0326. Inspection of the correlation matrix showed high correlation coefficients between the refining parameters of the nitrate oxygen atoms regarded as disordered. A difference Fourier was therefore calculated without these atom contributions, and confirmed that three of the atoms were spurious. Before discarding the disordered model a refinement in space group $P\bar{3}m1$ was carried out which converged at *R* 0.035. On the basis of Hamilton's *R* factor test, this is significantly worse even at the α 0.005 significance level. The two possible orientations for an ordered nitrate ion are in effect mirror images about the long diagonal but as the deviations of the structure from the symmetry of $P\bar{3}m1$ are small, refinement of the mirror image of the structure shown in Figure 1 would result in an identical structure but rotated about *c* by 180°. The near identity of the enantiomorphs accounts for the absence of significant differences between Bijvoet pairs in the observed data.

The i.r. spectrum indicated that at least one hydrogen bond was present in the structure (ν_{str} 2 963 cm^{-1}). As the water oxygen atom (O_w) was found to be *ca.* 2.6 Å from two iodate oxygen atoms, hydrogen atoms were placed at calculated positions along the appropriate O · · · O vectors. Electron-density sections, calculated through O_w, showed small peaks at these positions but the peak heights were

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[3] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1959, p. 415; J. G. Dawber, *J. Chem. Soc.* (*A*), 1968, 1532.

little above background. Refinement of the water molecule was initially attempted as a rigid body but, as the orientation proved indeterminate, hydrogen atoms were excluded from further consideration.

Least-squares refinement of the structure was continued allowing anisotropic temperature factors for all atoms, but since the principal axes of the representation ellipsoid for the iodine β_{ij} tensor differed by only 0.004 Å, anisotropy is clearly unjustified for the iodine atom and an isotropic temperature factor was retained. The pseudosymmetry imposed on the structure by the iodine atoms is reflected in the positions adopted by the iodate (O_I) and water (O_w) oxygen atoms, these being very close to the mirror planes in the space group $P\bar{3}m1$. This led to instability in the refinement of the β_{ij} tensors for these two atoms, there being high correlation (0.9) between β_{11} and β_{12}. As these parameters would therefore be unreliable, final refinement cycles were carried out with isotropic temperature factors for O_I and O_w. Unit weights were used up to this point but a weighting scheme[4] of the type $w = a^2/[a^2 + (F - b)^2]$ with $a = 48.3$ and $b = 17.9$ was introduced for the final refinement cycles so that $\langle w(\Delta F)^2\rangle$ was invariant with F. R At the completion of refinement was 0.0306. Scattering factors used throughout included the anomalous scattering for iodine and aluminium atoms, and were taken from ref. 5.

TABLE 1

Atomic parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B_{iso}, β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.0	0.0	0.5	0.098(7)	β_{11}	0.0021(5)	$\beta_{11}/2$	0.0	0.0
N	0.0	0.0	0.0	0.0141(23)	β_{11}	0.0038(17)	$\beta_{11}/2$	0.0	0.0
O_N	0.1854(15)	0.0	0.0	0.0175(21)	0.0249(32)	0.0095(19)	$\beta_{22}/2$	$\beta_{23}/2$	−0.0020(16)
I	2/3	1/3	0.11011(7)	1.11(2)					
O_w	0.1434(21)	0.2694(7)	0.3724(5)	1.56(7)					
O_I	0.5398(24)	0.0611(8)	0.2148(6)	1.92(8)					

Anisotropic thermal parameters are for the invariant form exp $-(h_r h_s \beta^{rs})$.

TABLE 2

Interatomic distances (Å) and angles (°)

(*a*) Distances

Al–O_w	1.887(4)	$O_w \cdots I_I^{iv}$	2.554
I–O_I	1.806(5)	$O_w \cdots O_I^{i}$	2.738
N–O_N	1.254(10)	$O_N \cdots O_N^{i}$	2.172
$O_w \cdots O_w^{i}$	2.735	$O_N \cdots O_I$	2.818
$O_w \cdots O_w^{ii}$	2.538	$O_N \cdots I$	3.022
$O_w \cdots O_w^{iii}$	2.661	$O_N \cdots O_I^{v}$	2.818
$O_w \cdots O_N^{i}$	3.127	$O_I \cdots O_I^{vi}$	2.764

(*b*) Angles

$O_I \cdots O_w \cdots O_I^{iv}$	98.2	$O_N \cdots I{-}O_I^{iv}$	81.6
$O_I \cdots I{-}O_I^{iv}$	99.8	$O_N \cdots I{-}O_I^{v}$	165.6
$O_N \cdots I \cdots O_N^{v}$	111.7	$I \cdots O_N{-}I^{vi}$	90.5
$O_N \cdots I{-}O_I$	65.9		

Superscripts denote the following equivalent positions relative to x, y, z:

i $\bar{y}, x - y, z$
ii $y, x, 1 - z$
iii $\bar{z}, y - x, 1 - z$
iv $1 + y - x, 1 - x, z$
v $x - y, \bar{y}, \bar{z}$
vi $1 - y, x - y, z$
vii $y, x - 1, \bar{z}$

Refinement of the structure was carried out by use of a local full-matrix least-squares program RBLS, and Fourier syntheses were computed by use of a modified version of FORDAP. All computations were performed on an IBM 1130 computer.

Table 1 gives final atomic parameters, with the estimated errors. The root-mean-square displacement and direction cosines of the principal axes of the β_{ij} tensors are deposited with final observed and calculated structure factors in Supplementary Publication No. SUP 21357 (4 pp., 1 microfiche).* Interatomic distances and angles are listed in Table 2.

DISCUSSION

The structure (Figure 1) consists of discrete iodate, nitrate, and hydrated aluminium ions, which interact through ionic and weaker forces. The most important of the latter are the hydrogen bonds between the water molecules and the iodate oxygen atoms. Each water molecule is involved in two asymmetric hydrogen bonds with two different iodate ions, the $O_w \cdots O_I$ distances being 2.554 and 2.738 Å and the $O_I \cdots O_w \cdots O_I$ angle 98.2°. Since this angle precludes two linear hydrogen bonds, the curve given by Nakamoto *et al.*[6] cannot be used to predict the expected i.r. OH-stretching frequen-

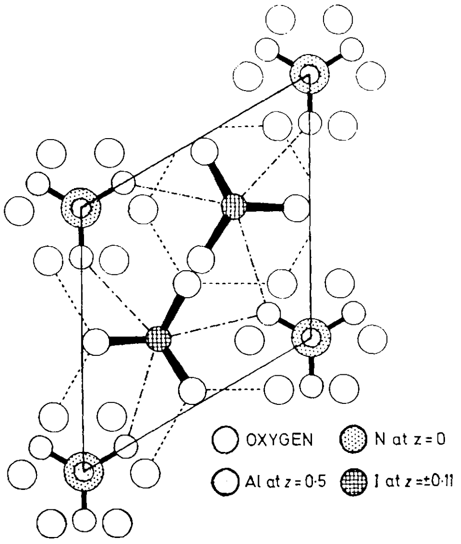

FIGURE 1 Projection of unit cell on (001) plane. H bonds involving one IO_3^- are shown as dashed lines, $I \cdots NO_3$ interactions as dash-dot lines

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[4] O. S. Mills and J. S. Rollet, in ' Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon, Oxford, 1961, p. 117.

[5] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

cies of both hydrogen bonds. In fact, the i.r. spectrum shows a single broad band at 2 963 cm^{-1} which is consistent with the stretching vibration of O–H involved in a linear hydrogen bond with O · · · O 2.7 Å; consequently the shorter hydrogen bond is probably non-linear. The other weak interaction which contributes to the stability of the structure involves the iodine atom and the nitrate ion. The I · · · O_N separation of 3.022 Å provides the iodine atom with a distorted octahedral environment, a common feature of iodine in high oxidation states.[7-11]

In the iodate ion, iodine generally forms three equal bonds of 1.80 Å, considerably less than the 1.99 Å which would be expected on the basis of the covalent single-bond radii.[12] This reduction is generally attributed to d_π–p_π bonding,[13] and to the fact that the iodine *d* orbitals concerned in the weak interactions (with O_N in the present structure) are made more diffuse as a result of repulsion by the iodate σ bonds and the iodine lone-pair, thus precluding a stronger I–O_N interaction.

Each nitrate oxygen is 3.0 Å from two iodine atoms and at the van der Waals distance (2.8 Å) from two iodate oxygen atoms. There is therefore no tendency for the nitrate to become disordered, but since these interactions are weak, this ion is associated with the highest thermal motion parameters. The N–O_N bond length [1.254(10) Å] is within σ of those in structures with symmetrical nitrate ions, *e.g.* 1.267(21) in $Pb(NO_3)_2$ (ref. 14) and 1.25 Å in $NaNO_3$.[15]

The arrangement of water molecules about the aluminium ion is based on the trigonal antiprism (D_{3d}) and the minor distortions from ideal symmetry can be seen when dihedral angles between adjacent faces are calculated.[16] The dihedral angles associated with the edges b_1, b_2, and b_3 (Figure 2) are 68.7, 75.4, and 69.1° whereas in a regular trigonal antiprism (*i.e.* an octahedron) all dihedral angles are 70.5°.[16] The observed values can be rationalized as a twisting of the two triangular faces of a trigonal prism by 55.8°, compared with 60° for a regular antiprism. The compression ratio has been defined [17] as the ratio of the edge length of the triangle to the intertriangle separation, and for an ideal trigonal antiprism is 1.225. In the present structure this ratio is 1.32, which is best interpreted as an expansion of the triangular edges by *ca.* 0.2 Å because of hydrogen-bond formation with the iodate oxygen atoms. The twist of the antiprism is probably due to repulsion of the water molecules by the nitrate oxygen atoms, since, apart from the nitrate oxygen atom, the electrostatic environment of the water molecules is symmetrical.

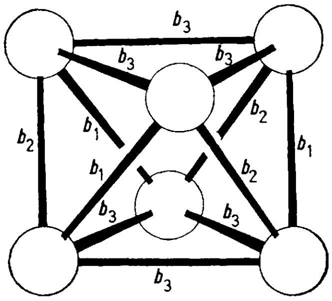

FIGURE 2 Water co-ordination antiprism. The *c* axis is normal to the faces defined by the edges b_3

The crystal structure analysis has established that this compound is not a double salt of aluminium iodate and aluminium nitrate, but a mixed-anion salt. The double salt would have to contain three unit cells of the solved structure, each with minor differences. The only axis which can be tripled is *c*, and a long exposure photograph taken with the crystal rotating about this axis failed to show any sign of axis tripling.

We thank the crystallography section of the Chemistry Department of the University of Aberdeen for the use of their diffractometer and, in particular, B. G. Cooksley for the collection of intensity data.

[5/154 *Received, 22nd January,* 1975]

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