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The crystal structure of H_5IO_6.*

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Experimental

H_5IO_6 crystallizes in the monoclinic system, space group $P2_1/n$, with

$$a=5{\cdot}31,\ b=18{\cdot}36,\ c=4{\cdot}95\ \text{Å};\ \beta=111^\circ\ 30'.$$

Assuming 4 molecules per unit cell, the density was calculated to be 3·37 g.cm.$^{-3}$; the experimental density is 3·39 g.cm.$^{-3}$ as determined by the pycnometric method.

Integrated multiple-film Weissenberg photographs taken with Mo $K\alpha$ radiation were used to record the intensities of the $(hk0)$, $(h0l)$ and $(0kl)$ reflections. The intensities were measured densitometrically and corrected for Lorentz and polarization factors.

Determination of the structure

The parameters of the iodine atoms were easily deduced from the [100] and [001] Patterson projections. The position of the oxygen atoms was found by means of the vector convergence method (Beevers & Robertson, 1950). Signs of the structure factors were calculated from the deduced positions, and Fourier syntheses of the [100] and [001] projections were computed. A Fourier synthesis of the [010] projection was of little use, because of the overlap of the oxygen atoms. The parameters obtained from the Fourier syntheses were refined by means of the least-squares method using a Ferranti digital computer (Curtis, 1959). Due to the overlap of the oxygen atoms, it was not possible to refine the [010] projection. The temperature factors were assumed to be isotropic and equal for different atoms of the same kind. The final coordinates and the exponents of the temperature factors are given in Table 1. The values of the disagreement index, R, for the three projections are:

$$R_{hk0}=8{\cdot}3\%,\quad R_{h0l}=12{\cdot}0\%,\quad R_{0kl}=8{\cdot}2\%\ .$$

Table 1

	x	y	z	
I	0·327	0·121	0·463	$B_I=0{\cdot}80$ Å^2
O_1	0·299	0·051	0·722	$B_O=1{\cdot}15$ Å^2
O_2	0·606	0·082	0·419	
O_3	0·090	0·064	0·162	
O_4	0·339	0·196	0·208	
O_5	0·038	0·168	0·504	
O_6	0·543	0·182	0·771	

Note: The exponents of the temperature factors are in good agreement with those of HIO_3: $B_I=0{\cdot}75$ Å^2 and $B_O=1{\cdot}30$ Å^2 (Garrett, 1954).

Discussion of the structure

The structure consists of slightly deformed oxygen octahedra with iodine in its centres. The I–O distances have values between 1·73 and 1·90 Å. The structure may be derived from an ideal model, based on a hexagonal lattice, consisting of double layers of close-packed

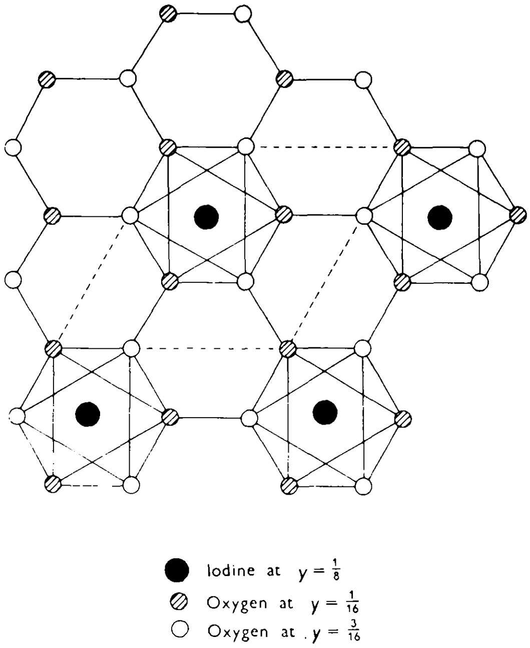

Fig. 1. Ideal double layer of close-packed oxygens, enclosing a layer of iodines in H_5IO_6, based on a hexagonal lattice.

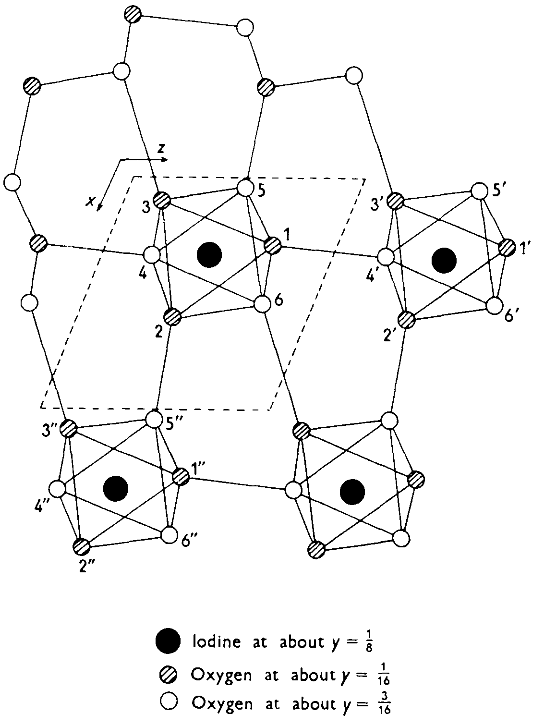

Fig. 2. Actual double layer of oxygens, enclosing a layer of iodines in H_5IO_6.

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oxygens enclosing a layer of iodine, parallel to the (010) plane. The H_5IO_6 structure is found by displacement of the atoms and a slight deformation of the ideal unit cell as shown in Figs. 1 and 2.

In the ideal structure half of the oxygens are in the position $y=1/16$ and the other half in the position $y=3/16$. The iodine atoms lie in the plane $y=1/8$. In the actual structure these values are:

$$\begin{aligned}&\mathrm{I}:\ y=1/8-0{\cdot}004; && \mathrm{O}_1:\ y=1/16-0{\cdot}012;\\ &\mathrm{O}_2:\ y=1/16+0{\cdot}019; && \mathrm{O}_3:\ y=1/16+0{\cdot}001;\\ &\mathrm{O}_4:\ y=3/16+0{\cdot}008; && \mathrm{O}_5:\ y=3/16-0{\cdot}020;\\ &\mathrm{O}_6:\ y=3/16-0{\cdot}006.\end{aligned}$$

The unit cell contains four of these double layers of oxygen perpendicular to the b-axis, connected by the symmetry elements. As the structure of $Al(OH)_3$ is also derived from the same ideal model, the crystal structure of H_5IO_6 is closely related to that of $Al(OH)_3$ (Megaw, 1934). In $Al(OH)_3$ two of the three oxygen octahedra are filled by aluminium. In H_5IO_6 only one of the three octahedra contains an iodine atom. The shortest distances between oxygen in neighbouring octahedra are shown in Table 2. These distances give the impression that an oxygen octahedron in a double layer is linked by three hydrogen bonds to octahedra in the same layer and by two hydrogen bonds to octahedra of adjacent layers. An attempt will be made to determine the positions of the hydrogen atoms from neutron diffraction data.

Table 2

$O_1(x, y, z)$-O_3' (x, y, z) = 2·76 Å
$O_6(x, y, z)$–O_4' (x, y, z) = 2·79
$O_2(x, y, z)$–$O_5''(x, y, z)$ = 2·69
$O_1(x, y, z)$–O_2 $(\bar{x}, \bar{y}, \bar{z})$ = 2·64
$O_6(x, y, z)$–$O_4(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ = 2·81 Å

Note: The parameters in brackets give the symmetry relation between the oxygen atoms and the primes refer to an oxygen atom in neighbouring unit cells (see Fig. 2).

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References

Beevers, C. A. & Robertson, J. H. (1950). *Acta Cryst.* **3**, 164.
Curtis, A. R. (1959). AERE-R 3134.
Garrett, B. S. (1954). ORNL-1745.
Megaw, H. D. (1934). *Z. Kristallogr.* **87**, 185.

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Lattice constants and space group of sodium tungstate dihydrate.*

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The crystallographic properties of $Na_2WO_4.2\,H_2O$ have only been superficially investigated. Marignac (1863) found that the crystalline substance is orthorhombic bipyramidal. His goniometric measurements indicate that

$$a:b:c=0{\cdot}8002:1:0{\cdot}6470\;.$$

Baker's Analyzed Reagent grade $Na_2WO_4.2\,H_2O$ was used in the present investigation. The company's analysis is as follows: insoluble matter 0·002%; alkalinity (as Na_2CO_3) 0·08%; chloride (as Cl) 0·001%; nitrogen compounds (as N) 0·0003%; sulfate (as SO_4) 0·003%; arsenic (as As) 0·0001%; heavy metals (as Pb) 0·0002%; iron (as Fe) 0·0001% and molybdenum (as Mo) 0·0001%. The substance was used without further purification.

Under the microscope the crystals have the appearance of basal tablets, elongated parallel to a or b, with a perfect {001}, and less perfect {110} and {120} cleavages. The optic plane is (010); $r<v$ strong. The refractive indices for NaD light are

$$n_x=1{\cdot}5530\pm0{\cdot}001,\ n_y=1{\cdot}5535\pm0{\cdot}001,$$
$$n_z=1{\cdot}5650\pm0{\cdot}001;\ n_z-n_x=0{\cdot}012;$$
$$(+)2V=26^\circ;\ X=a,\ Y=b,\ Z=c\;.$$

The X-ray powder diffraction pattern of finely ground $Na_2WO_4.2\,H_2O$ at 25 °C. was obtained in a Norelco high angle recording diffractometer, using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) and a Ni filter. The scanning speed was $1/8^\circ$ (2θ) per min. High-purity sodium chloride was used as an internal standard.

The assignment of the peaks was made with the aid of some runs emphasizing preferred orientation, and by using the goniometric value for $a:b:c$. All of the observed diffraction peaks could be satisfactorily assigned as being due to an orthorhombic lattice with the following unit-cell dimensions, obtained by a least-squares treatment:

$$a_0=8{\cdot}456\pm0{\cdot}005,\ b_0=10{\cdot}601\pm0{\cdot}005,$$
$$c_0=13{\cdot}842\pm0{\cdot}005\ \text{Å}\;.$$

The present axial ratio,

$$a_0:b_0:c_0=0{\cdot}7978:1:2(0{\cdot}6530)\;,$$

agrees reasonably well with the goniometric value (Marignac, 1863).

The calculated density of $Na_2WO_4.2\,H_2O$ at 25 °C., assuming 8 molecules per unit cell, is 3·532 g.cm.$^{-3}$. Clarke & Davis (1877) found that the pycnometric density at 19 °C. is 3·2314 g.cm.$^{-3}$. However, according to Zambonini (1923) this value is too low. His pycnometric measurements on carefully selected material gave a density at 15 °C. of 3·50 g.cm.$^{-3}$, which is in fair agreement with X-ray density.

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