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The Crystal Structure of a New $KH(IO_3)_2$ Modification

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The crystal structure of a new potassium hydrogendiiodate modification, $KH(IO_3)_2$, has been determined from three-dimensional X-ray data by means of Patterson and Fourier syntheses and refinements by full-matrix least-squares methods, with 580 independent reflexions, to give a conventional R of 0·059. X-ray diffraction patterns establish *Fdd*2 as the exact orthorhombic space group, with the unit-cell parameters a = 39·294 (2), b = 8·157 (3), c = 11·580 (2) Å and 24 formula units per cell. The structure consists of iodate groups; the three covalently bonded O atoms of each group together with three further (weakly bonded) O atoms form highly distorted octahedra around two iodine atoms. However, there is a 'capped-octahedral' environment (sevenfold coordination) around the third iodine atom. The covalent I–O bonds of the iodate groups, which form pseudotrigonal pyramids, lie in the range 1·75–1·84 Å; the I–OH bonds are 1·93 Å and the weaker I–O bonds are 2·39–2·97 Å. The K atoms are surrounded by eight O atoms forming distorted square prisms; the K–O bond lengths are in the range 2·66–3·23 Å. Fluctuations of the bond lengths are caused by a different degree of interaction with adjacent I atoms and by the action of two different kinds of hydrogen bonds.

Introduction

According to the phase diagram of the system KIO_3–HIO_3–H_2O there are two phases at normal conditions (Mellor, 1927): potassium hydrogendiiodate, $KIO_3.HIO_3$, and potassium dihydrogentriiodate, $KIO_3.2HIO_3$. The crystal structure of the first compound was determined by Chan & Einstein (1971). During the present investigation of the same system, but at above room temperature and ambient pressure (Hamid & Kunze, 1976*a*), several new phases were found. One of these, $KH(IO_3)_2$, has strong polar properties and shows more complex IR and Raman spectra than the diiodate polymorph $KIO_3.HIO_3$ (with the nonpolar space group $P2_1/c$), the IR spectrum of which was reported by Dasent & Waddington (1960). To understand the different behaviour (mentioned above) of the two diiodate polymorphs it is necessary to know how both polymorphs are structurally constituted. The purpose of the present paper is, therefore, to elucidate the structure of the new diiodate phase $KH(IO_3)_2$.

Experimental

The synthesis of the orthorhombic $KH(IO_3)_2$ crystals has been reported by Hamid & Kunze (1976*a*); their unit-cell dimensions, calculated from a Guinier powder photograph, and other conventional crystallographic data are listed in Table 1. Buerger precession photographs of reflexions $0kl$, $1kl$, …, $5kl$ and $h0l$, …, $h3l$, together with Weissenberg photographs taken with Mo $K\alpha$ and Cu $K\alpha$ radiation, showed the systematic absences ($I_{hkl} \equiv 0$):

$$\begin{array}{lll} hkl: & h+k, k+l, l+h \neq 2n & \\ 0kl: & k, l \neq 2n \quad \text{and} \quad k+l \neq 4n+2 & \left.\right\} \\ h0l: & h, l \neq 2n \quad \text{and} \quad h+l \neq 4n+2 & \\ hk0: & h, k \neq 2n. & \end{array} \qquad (1)$$

These are characteristic only for the space group *Fdd*2 (C_{2v}^{19}). Intensities I_{hkl} were collected with a crystal 0·12 × 0·03 × 0·02 mm on a Stoe two-circle diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation). The background was counted for half the total scanning time on each side of the reflexions. One standard reflexion, measured periodically, showed no significant change during data collection. In the range of measurements, 2200 reflexions were measured (580 being independent). The $00l$ reflexions were taken from an integrated Buerger precession photograph. An absorption correction was not applied (Table 1). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962); anomalous contributions were ignored.

Table 1. *Principal crystallographic data of the new diiodate crystal at room-temperature*

a = 39·294 (2) Å
b = 8·157 (3)
c = 11·580 (2)
D_x = 4·186 g cm^{-3}
Z = 24
Point group $mm2$ (C_{2v})

FW 389·94
V = 3711·64 Å^3
F(000) 4176
D_m = 4·20 g cm^{-3}
μ(Mo $K\alpha$) = 116·0 cm^{-1}
Space group *Fdd*2 (C_{2v}^{19})

Further details may be obtained from (Hamid & Kunze, 1976*b*).

Structure determination

In spite of the very long lattice period a (Table 1), the structure determination could be started and maintained on the basis of a simple classical treatment. It seems worthwhile describing this, together with some characteristic features of the X-ray patterns upon which the classical treatment was based in the first stage of the determination.

The structure amplitude of the space group $Fdd2$ can be represented by

$$F_{hkl} = \sum_j f_j \phi_j^{(N_j)} \qquad (2a)$$

with $N_j = 16\,(8)$ for the general (special) set of equivalent positions and

$$\begin{aligned}\phi_j^{(16)} &= 4 \times 2[(1 + i^{h+k+l}) \cos 2\pi hx_j \cos 2\pi ky_j \\ &\quad - (1 - i^{h+k+l}) \sin 2\pi hx_j \sin 2\pi ky_j] \\ &\quad \times \exp(i2\pi lz_j) \qquad (2b)\end{aligned}$$

and

$$\phi_j^{(8)} = 4(1 + i^{h+k+l}) \exp(i2\pi lz_j). \qquad (2c)$$

The most striking characteristic of the a axis rotation photographs is the fact that all their layer lines (index h) for which

$$h \equiv 0 (\mathrm{mod}\ 10) \qquad (3a)$$

are particularly marked and occupied by the strongest reflexions, while the adjacent layer lines $h \equiv \pm 1 (\mathrm{mod}\ 10)$ contain only those reflexions with nearly disappearing intensities.

Regarded as a whole, the a axis rotation photographs – and this is in agreement with the rotation photographs of other layer or layer-like structures – create *a priori* the impression that the $KH(IO_3)_2$ crystals also exhibit a layer or layer-like structure and, if so, that according to (3a) the mass (nuclei), at least that of the heaviest atoms, is concentrated on planes perpendicular to x, being separated by about $a/10 = 3{\cdot}93$ Å parallel to x:

$$\Delta x = 1/10. \qquad (3b)$$

Especially on the layer lines, given by (3a), the reflexions can be subdivided into two groups

$$I_{hkl} = \left\{ \begin{matrix} \text{(very) strong} \\ \text{(very) weak} \end{matrix} \text{ for } h + k + l \begin{matrix} = 4n \\ = 4n + 2 \end{matrix} \right\}. \qquad (4a)$$

This subdivision of the reflexions may be understood in terms of expression (2b) for the general set of equivalent positions. Note in particular that restricting further consideration to the atoms with the higher and highest scattering powers, K and I, which make the chief contributions to the structure amplitude, and replacing (4a) by the 'radical', sharpened approximation (for K and I atoms)

$$\hat{I}_{hkl} = \left\{ \begin{matrix} \text{(maximal) strong} \\ 0 \end{matrix} \text{ for } h + k + l = \begin{matrix} 4n \\ 4n + 2 \end{matrix} \right\}, \qquad (4b)$$

requires the second term in parentheses of (2b) to disappear. For this there are several possibilities, in so far as (4b) can be fulfilled throughout by the condition

$$y_j = 0, \qquad (5a)$$

through which the term concerned of course disappears for all layer lines, or by

$$x_j = n_j/10, \qquad (5b)$$

with $n_j = 0, 1, \ldots, 9$, through which the second requirement of (4b) is fulfilled only for layer lines of type (3a); or it may be that both (5a) and (5b) are satisfied. However, (5a) satisfies the first requirement of (4b) as well as the second, which suggests a high probability that (5a) is valid at least as a first approximation. Then (2b) will be reduced to

$$\phi_j^{(16)} = 8(1 + i^{h+k+l}) \cos 2\pi hx_j \exp(i2\pi lz_j), \qquad (6)$$

and (2c) remains unchanged. The first requirement of (4b), applied to equations (6) and (2c), demands finally that z_j is also zero. Therefore

$$y_j = 0, \quad z_j = 0, \quad j = 1, 2, \ldots, 5 \qquad (7a)$$

and

$$\phi_j^{(16)} = 8(1 + i^{h+k+l}) \cos 2\pi hx_j, \quad j = 2, \ldots, 5 \quad (7b)$$

$$\phi_j^{(8)} = 4(1 + i^{h+k+l}), \quad j = 1, \qquad (7c)$$

with $j = 1, 2$ as indices for the two nonequivalent K atoms, and $j = 3, 4, 5$ as indices for the three nonequivalent I atoms [because of their smaller scattering power the nine nonequivalent O atoms with indices $j = 6, \ldots, 14$ were excluded from equation (4b) onwards]. Concluding in the same manner, it is necessary that each of the possible coordinates x_j (with $j = 1, \ldots, 5$) takes a discrete value from the set (5b), for only then is $\cos 2\pi hx_j = 1$ and only in this way can (7b), for the layer lines of type (3a), provide a maximal contribution to the structure amplitude through the K and I atoms (by superimposing their partial amplitudes without phase shifts). It should be emphasized at this point that all the (very weak) reflexions of the second group of (4a), for which $h + k + l = 4n + 2$, will be produced preponderantly by the O atoms, which cannot be subjected to the rigorous requirement (4b) with the same simple checks as can the K and I atoms.

Now let (x_j, y_j, z_j) be the (representative) position of the jth set of equivalent points in the space group, *viz* the position of one atom, which represents the whole set of (crystallographic) equivalent atoms. Transferring (3b) to the representative atoms of the five sets ($j = 1, \ldots, 5$) (mentioned above) and selecting the first five values of (5*b*) for occupation by these atoms, one obtains four possible combinations, as listed in Table 2. With the extremely simplified equations (7*a*–*c*) the work involved in the calculation of the scattering amplitudes was reduced to a minimum. Such calculations, carried out for several *hkl* of different layer lines, immediately allowed the exclusion of the combinations β and γ (Table 2). The classical results, as described here, were confirmed by a three-dimensional Patterson synthesis; the positions of its maxima correspond to those which can be derived by space-group operations from the K and I atom positions (listed in Table 2). Deciding between the two remaining combinations, α and δ, required some further calculations. In connexion with this, it was interesting to observe that the conventional discrepancy index, defined as

$$R = \sum_{hkl} (|F_o| - |F_c|)/\sum_{hkl} |F_o|, \tag{8}$$

and at first calculated with only the contributions from the K and I atoms (to the amplitude F_c), in the initial stage was indeed smaller for combination α, namely $R_\alpha = 0{\cdot}35 < 0{\cdot}41 = R_\delta$. But attempts to refine the initial combination α were unsuccessful: R_α did not decrease enough.

Table 2. *Classical isolated* x_j, y_j, z_j *parameters for the nonequivalent* K *and* I *atoms*

$y_j = z_j = 0$, according to equation (7*a*).

			10 x_j			
j		N_i	α	β	γ	δ
1	K(1)	8	0	0	0	0
2	K(2)	16	4	3	2	1
3	I(1)	16	3	2	1	4
4	I(2)	16	2	1	4	3
5	I(3)	16	1	4	3	2

Table 4. *The final positional parameters for iodine and potassium*

	x	y	z
K(1)	0·0	0·5	0·5
K(2)	0·0973 (2)	0·4968 (6)	0·512 (1)
I(1)	0·0926 (1)	0·4748 (2)	0·002 (1)
I(2)	0·0504 (1)	0·7551 (2)	0·256 (1)
I(3)	0·0500 (1)	0·2551 (2)	0·243 (1)

Table 5. *The final atomic parameters for oxygen*

	x	y	z	B(Å^2)
O(11)	0·099 (1)	0·318 (2)	0·108 (2)	1·1 (4)
O(12)	0·096 (1)	0·343 (2)	0·877 (3)	0·6 (1)
O(13)	0·046 (1)	0·478 (2)	0·008 (2)	0·4 (3)
O(21)	0·084 (1)	0·719 (3)	0·160 (3)	2·1 (6)
O(22)	0·050 (1)	0·563 (4)	0·337 (2)	1·4 (5)
O(23)	0·017 (1)	0·700 (3)	0·146 (2)	1·4 (3)
O(31)	0·049 (1)	0·064 (3)	0·166 (2)	1·0 (4)
O(32)	0·085 (1)	0·224 (4)	0·345 (2)	2·2 (6)
O(33)	0·014 (1)	0·213 (4)	0·352 (3)	1·1 (4)

Refinement of the atom positions by the method of least squares applied to the structure factors (Busing, Martin & Levy, 1962) reduced the R value of the combination δ (Table 2) from 0·41 to 0·21. Ignoring the K atoms of the combination δ the same factor would be 0·42 before and 0·23 after the refinement.

Electron density maps, calculated with three-dimensional Fourier syntheses and phased with the I atoms alone, indicated (in addition to the already known K atom positions) three O atom positions. By phasing the Fourier syntheses with both I and K atoms, the positions of two further O atoms appeared with weak contours. Taking into account only the contributions of the I and K atoms, the discrepancy index decreased after two least-squares cycles to $R = 0{\cdot}20$. This value seems to be the lowest limit of the refinements without the O atoms.

Including five of the nine nonequivalent O atoms in the refinements lowered R to 0·170. To localize the remaining O atoms, it was necessary to calculate a difference synthesis. With the following synthesized electron density difference

$$\Delta\tilde{\rho}(\mathbf{x}) = \frac{1}{V}\sum_{\mathbf{h}} \Delta\tilde{F}_{\mathbf{h}} \exp(i2\pi\mathbf{hx}), \tag{9a}$$

with the difference amplitude

$$\Delta\tilde{F}_{\mathbf{h}} = (F_o - \tilde{F}_c)_{\mathbf{h}} \rightarrow (|F_o| - |\tilde{F}_c|)_{\mathbf{h}} \exp(i\tilde{\alpha}_{\mathbf{h}}), \tag{9b}$$

and the partial amplitude $\tilde{F}_c$ with phase $\tilde{\alpha}_{\mathbf{h}}$ as the (calculated) contribution of the K and I atoms alone, the last unknown O positions were discovered. R now decreased to 0·120 and, after further least-squares refinements, involving isotropic Debye–Waller factors for all atoms, to 0·081. Carrying out the last four refinement cycles with isotropic (for O) and anisotropic (for K and I) Debye–Waller factors yielded $R = 0{\cdot}059$ as the final discrepancy index. The observed and calculated absolute structure amplitudes $|F_o|$ and $|F_c|$, listed in Table 3, formed the basis of the calculations.* Table 4 contains the final positional parameters of the K and I atoms, and Table 5 those of the O atoms.

Description of the structure and discussion

To ensure an unequivocal description and to avoid obscurities during the discussion it is useful to introduce, by the space-group operation

$$\Omega^{\lambda\nu}_{Fdd2}\mathbf{r}_j = \mathbf{r}_j^{\lambda\nu}, \quad \lambda, \nu = 1, \ldots, 4, \tag{10}$$

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* Table 3 and the anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32573 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

with $\mathbf{r}_j^{11} \equiv \mathbf{r}_j$ as the vector for the initial position of an atom of the (crystallographic and/or chemical) kind j (Tables 4 and 5), a simple scheme to identify the atoms and to locate them in the unit cell. The meaning of the two (space-group) indices $\lambda\nu$ can be taken from Table 6. By putting

$$A(\mathbf{r}_j^{\lambda\nu}) \equiv A_j^{\lambda\nu}, \qquad (11a)$$

with A representing (the cations) H, K and I, the indices can be directly transferred to the different cations A. For the O atoms (anions) it is necessary to use two indices, m and n, instead of the one, j. Thus

$$\mathrm{O}(\mathbf{r}_{mn}^{\lambda\nu}) \equiv \mathrm{O}_{mn}^{\lambda\nu}, \qquad (11b)$$

with $m, n = 1, 2, 3$, indicates the nth O atom in the first coordination sphere of the central iodine atom $\mathrm{I}(\mathbf{r}_m^{\lambda\nu}) \equiv \mathrm{I}_m^{\lambda\nu}$. However to remain in agreement with accepted nomenclature, the (space-group) index pair $\lambda\nu$ may be replaced by roman numerals, as signified by

$$\begin{array}{cccccccc} 11 & 12 & 13 & 14 & 21 & 22 & 23 & 24 \\ & \mathrm{i} & \mathrm{ii} & \mathrm{iii} & \mathrm{iv} & \mathrm{v} & \mathrm{vi} & \mathrm{vii} \end{array}, \qquad (12)$$

for the first 8 of 16 index pairs. Moreover, the (lower) indices may be set in parentheses, *e.g.* $\mathrm{O}_{mn}^{11} = \mathrm{O}_{mn} \equiv \mathrm{O}(mn)$ or $\mathrm{K}_j^{22} \equiv \mathrm{K}(j^{\mathrm{v}})$ and $\mathrm{O}_{mn}^{23} \equiv \mathrm{O}(mn^{\mathrm{vi}})$ as the complete sign for the nth oxygen atom in the first coordination sphere of the iodine atom $\mathrm{I}_m^{23} \equiv \mathrm{I}(m^{\mathrm{vi}})$. In the illustrations of the structure (Figs. 1, 2 and 3), for reasons of space, the atom indices could not be set in parentheses; therefore, $\mathrm{I}(m^{\mathrm{vi}}) \rightarrow \mathrm{I}_m^{\mathrm{vi}}$, $\mathrm{O}(mn^{\mathrm{vi}}) \rightarrow \mathrm{O}_{mn}^{\mathrm{vi}}$, *etc.*

According to Figs. 1 and 2 the structure is built up from highly distorted oxygen octahedra around iodine atoms. The distortion of the octahedra is a consequence of (in the main) two types of chemical-bond

Table 6. *Equivalent atom coordinates in the space group Fdd*2

	$\lambda \backslash \nu$	1	2	3	4
				*dd*2	
		x	$\bar{x}$	$0{\cdot}25-x$	$0{\cdot}25+x$
	1	y	$\bar{y}$	$0{\cdot}25+y$	$0{\cdot}25-y$
		z	z	$0{\cdot}25+z$	$0{\cdot}25+z$
		x	$\bar{x}$	$0{\cdot}25-x$	$0{\cdot}25+x$
	2	$0{\cdot}5+y$	$0{\cdot}5-y$	$0{\cdot}75+y$	$0{\cdot}75-y$
F		$0{\cdot}5+z$	$0{\cdot}5+z$	$0{\cdot}75+z$	$0{\cdot}75+z$
		$0{\cdot}5+x$	$0{\cdot}5-x$	$0{\cdot}75-x$	$0{\cdot}75+x$
	3	y	$\bar{y}$	$0{\cdot}25+y$	$0{\cdot}25-y$
		$0{\cdot}5+z$	$0{\cdot}5+z$	$0{\cdot}75+z$	$0{\cdot}75+z$
		$0{\cdot}5+x$	$0{\cdot}5-x$	$0{\cdot}75-x$	$0{\cdot}75+x$
	4	$0{\cdot}5+y$	$0{\cdot}5-y$	$0{\cdot}75+y$	$0{\cdot}75-y$
		z	z	$0{\cdot}25+z$	$0{\cdot}25+z$

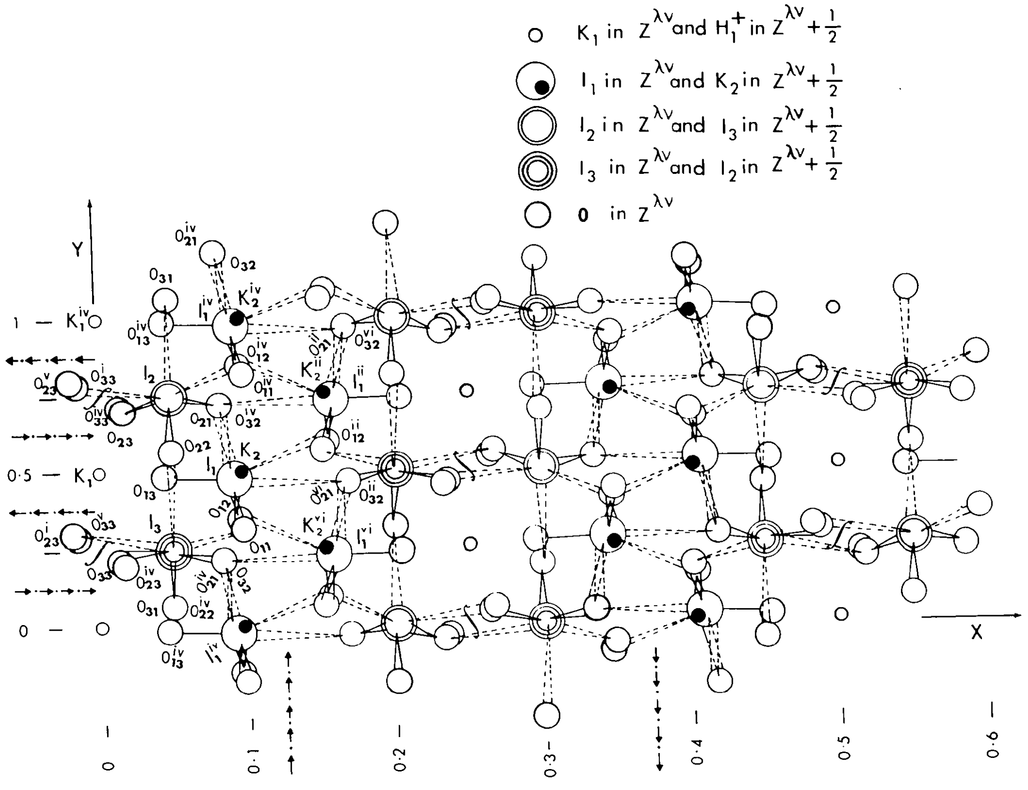

Fig. 1. The crystal structure of $KH(IO_3)_2$ viewed down the z axis. Unbroken lines indicate covalent I–O bonds, broken lines indicate weak I···O interactions. Symbols such as $z^{\lambda\nu}$ and $\mathrm{I}_1^{\mathrm{vi}}$ are explained in equations (10)–(12).

interactions, by which three of the six octahedral oxygen atoms approach the central iodine atom. Similar environments around the iodine atoms were also found in the α modification of iodic acid (Rogers & Helmholz, 1941) and in the diiodate polymorph $HIO_3.KIO_3$ (Chan & Einstein, 1971), and other crystals of iodate compounds. The I—O bond lengths of the three covalently bonded oxygen atoms of the IO_3 groups (each of these again forms a distorted pyramidal arrangement) vary from 1·759 to 1·929 Å, while the distances of the weaker I···O interactions are from 2·396 to 2·972 Å (Table 7*a*). It may be pointed out that there are some (at least) fine differences between the environments of the three (crystallographic) nonequivalent iodine atoms I(1), I(2) and I(3) – not only with regard to the variation in the bond lengths, but also with regard to the average bond distances of both oxygen groups, the one with strong and the other with weak bonds (Table 7*a*). Thus, it is noteworthy that the average I—O distance of the strongly bonded oxygen atoms around I(1) is shorter than that of those around I(2) and I(3). Conversely, however, the average I···O distance of the weakly bonded oxygen atoms around I(1) is longer than that of those around I(2) and I(3). Otherwise the variation of the interionic distances is smaller for the strong I(1)—O bonds (0·050 Å) than for the I(2)—O bonds (0·114 Å) and for the I(3)—O bonds (0·136 Å). The corresponding values for the weak I···O interactions are in the same order: 0·243, 0·383 and 0·374 Å. These facts require some consideration.

These latter interactions, primarily effected by electrostatic attraction and supported by van der Waals forces, are able to balance the ions with fluctuating distances, as indicated by the variations described above. The strong I—O bonds of the iodate groups, however, act with much more sensitivity. They are extremely inflexible; very small changes in their bond

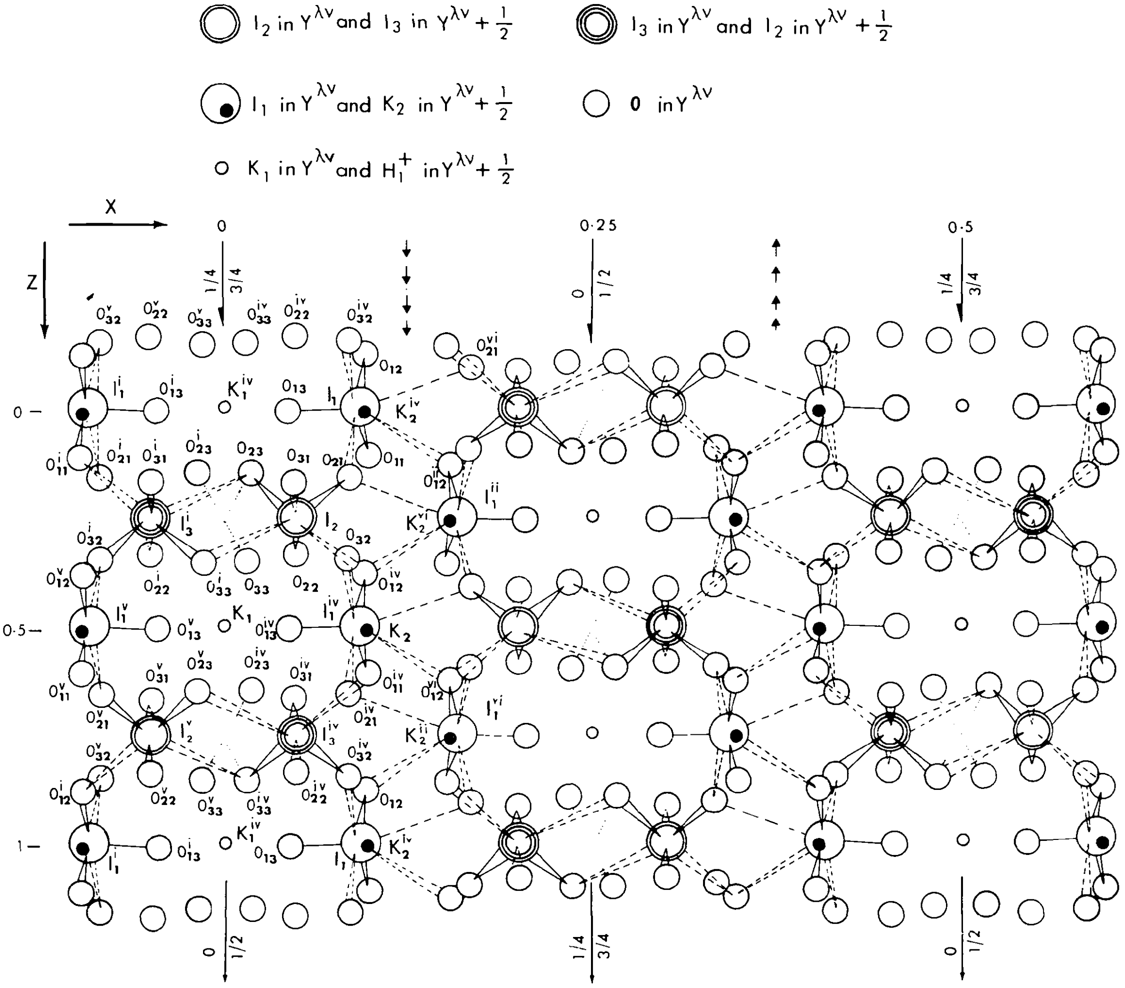

Fig. 2. The crystal structure of $KH(IO_3)_2$ viewed down the y axis. Unbroken lines indicate covalent I—O bonds, broken lines indicate weak I···O interactions, dotted lines indicate hydrogen bonds. Symbols such as $Y^{\lambda v}$ and O^{iv}_{11} are explained in equations (10)–(12).

Table 7. *Interionic distances and bond lengths* (*in* Å)

(*a*) I–O			
I(1)–O(11)	1·794 (3)	I(2)–O(21)	1·759 (4)
O(12)	1·807 (4)	O(22)	1·823 (4)
O(13)	1·844 (3)	O(23)	1·873 (3)
Average	1·815	Average	1·818
I(1)···O(21)	2·729 (4)	I(2)···O(12^{iv})	2·396 (4)
O(32^{iv})	2·742 (4)	O(31)	2·727 (3)
O(12^{ii})	2·972 (4)	O(33^{i})	2·779 (5)
Average	2·814	Average	2·634
I(1)···O(21^{vi})	3·066 (4)	I(2)···O(13^{iv})	3·435 (5)
I(3)–O(31)	1·793 (3)		
O(32)	1·834 (4)		
O(33)	1·929 (5)		
Average	1·852		
I(3)···O(11)	2·523 (3)		
O(22)	2·736 (4)		
O(23^{i})	2·897 (3)		
Average	2·719		
I(3)···O(13)	3·279 (5)		
(*b*) K···O			
K(1)···O(22)	2·764 (4)	K(2)···O(31^{iv})	2·660 (3)
O(22^{i})		O(22)	2·814 (4)
O(31^{iv})	2·778 (3)	O(11^{ii})	2·827 (3)
O(31^{v})		O(32^{ii})	2·835 (4)
O(33)	2·951 (5)	O(11^{iv})	2·845 (3)
O(33^{i})		O(21^{iv})	2·889 (4)
O(23^{iv})	3·055 (3)	O(32)	2·985 (4)
O(23^{v})		O(12^{iv})	3·229 (3)
Average	2·887	Average	2·886
(*c*) K···I			
K(1)···I(3^{iv})	4·010 (2)	K(2)···I(1^{iv})	3·783 (2)
I(3^{v})		I(3^{iv})	3·878 (2)
I(2)	4·026 (2)	I(2^{iv})	3·912 (2)
I(2^{i})		I(3^{ii})	4·042 (2)
I(2^{iv})	4·090 (2)	I(2)	4·072 (2)
I(2^{v})		I(3)	4·130 (2)
I(3)	4·091 (2)	I(1^{ii})	4·255 (2)
I(3^{i})		I(1^{vi})	4·268 (2)
Average	4·054	Average	4·043
		K(2)···I(1^{iv})*	4·264 (2)
(*d*) K···K			
K(1)···K(2)	3·826 (1)	K(2)···K(2^{ii})	4·157 (1)
K(2^{i})		K(2^{vi})	
(*e*) I···I			
I(1)···I(3)	3·714 (2)	I(1)···I(3^{iv})	4·127 (2)
I(3)···I(2)	4·082 (2)	I(2^{ii})···I(3^{iii})	3·949 (2)
I(2)···I(1)	4·084 (2)	I(1^{iv})···I(2^{ii})	4·212 (2)
I(1)···I(2^{iv})	3·746 (2)	I(1)···I(1^{ii})	4·362 (2)

* This iodine atom lies in the neighbouring unit cell.

lengths can therefore signify a change in the bond type. From this point of view the different IO_3 groups may be considered as follows: The iodate groups with I(1) at the top of nearly undistorted pyramids involve a chemical bond uniformly of one type, while the more distorted pyramids of the other iodate groups [those with I(2) and I(3)] appear to involve a second type of chemical bond (in addition to the acting covalent bond). In a free ion the three covalent I–O bonds of the IO_3 group would form the equivalent edges of a regular trigonal pyramid with the point-group symmetry $3m(C_{3v})$. Taking into account, however, the site symmetry of the IO_3 units in the space group $Fdd2$, it is expected that the symmetry of these units will be reduced: on easy terms only, to that of the subgroup $m(C_s)$, otherwise total, to $1(C_1)$. A cursory glance at the I–O bond lengths (Table 7*a*) and the calculated geometric proportions of all three IO_3 pyramids (Table 8) confirms the expectation: the differing IO_3 pyramids show a lower symmetry [close to $m(C_s)$] – in fact, the lowest possible: $1(C_1)$.

None of the groups of three atoms in the basal plane of the different IO_3 pyramids form equilateral triangles nor are the covalent-bond angles (O–I–O) equal within each pyramid. Analysing the shape of the different pyramids with the data of Tables 7(*a*) and 8 one finds, as previously pointed out, that the pyramid with I(1) at the top, $O_3I(1)$, is the iodate unit with the smallest distortions; the covalent-bond angles [O(1*j*)–I(1)–O(1*k*)] at 96·7 ± 0·2° do not exceed the standard-deviation limit. Nevertheless, this pyramid does not exhibit trigonal symmetry, since the three angles of the triangle O(1*i*)–O(1*j*)–O(1*k*) depart from 60° by more than the standard deviation; however, two of these angles are equal (up to or within this limit). Thus in losing the trigonal axis, the $O_3I(1)$ pyramid does not totally reduce its symmetry; rather, one of the three free-ion mirror planes is kept. For the other iodate units, $O_3I(2)$ and $O_3I(3)$, the departure from trigonal (or only monoclinic) symmetry is markedly larger. In summary, in addition to the monoclinic pseudotrigonal iodate complexes, given by the $O_3I(1)$ units, the structure of the $KH(IO_3)_2$ crystals contains triclinic pseudotrigonal iodate complexes, given by the $O_3I(2)$ and $O_3I(3)$ units. The latter have an unequal (but low) degree of triclinic character.

Table 8. *Interatomic distances* (Å) *and bond angles* (°)

Standard deviations for distances and angles are $\sigma < 0{\cdot}01$ Å and σ 0·2°.

O(11)···O(12)	2·69	O(11)–I(1)–O(12)	96·6	O(11)···O(12)···O(13)	60·4
O(11)···O(13)	2·72	O(11)–I(1)–O(13)	96·9	O(11)···O(13)···O(12)	59·1
O(12)···O(13)	2·73	O(12)–I(1)–O(13)	96·5	O(12)···O(11)···O(13)	60·5
O(21)···O(22)	2·77	O(21)–I(2)–O(22)	101·1	O(21)···O(22)···O(23)	56·8
O(21)···O(23)	2·63	O(21)–I(2)–O(23)	92·9	O(22)···O(21)···O(23)	61·8
O(22)···O(23)	2·78	O(22)–I(2)–O(23)	97·4	O(21)···O(23)···O(22)	61·4
O(31)···O(32)	2·82	O(31)–I(3)–O(32)	102·2	O(31)···O(32)···O(33)	60·6
O(31)···O(33)	2·83	O(31)–I(3)–O(33)	99·1	O(32)···O(33)···O(31)	60·3
O(32)···O(33)	2·79	O(32)–I(3)–O(33)	95·6	O(32)···O(31)···O(33)	59·1

The heterogeneous distortion of these building units (described above) gives rise to the complexity of the IR and Raman spectra of the $KH(IO_3)_2$ crystals (concerning both the number and sharpness of the spectral lines, their shift and profile deformation); this is especially the case when the symmetry degeneracy of the vibration modes is removed nonuniformly and with different degrees of completeness, due to unequal and incomplete lowering of the symmetry of single building units.

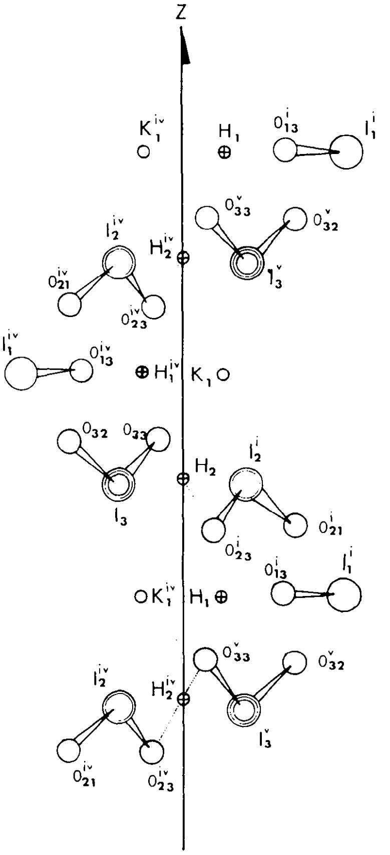

Fig. 3. A cross-section of Fig. 2, close to a twofold screw axis. The symbols are explained in Figs. 1 and 2.

The structure exhibits several significant peculiarities. So it is surprising that only seven of the nine nonequivalent oxygen atoms are common corner atoms of neighbouring octahedra, *e.g.* like the oxygen atoms in the chain ···I(3)···O(11)–I(1)···O(21)–I(2)···O(31)–I(3)··· (Figs. 1 and 2) or in the chains of Fig. 3. Two of the nonequivalent oxygen atoms, however, do not follow this building principle: one is O(12), which is the common corner atom of three oxygen octahedra, *i.e.* those around I(1), I(1^{vi}) and I(2^{vi}); the other is O(13), which belongs only to the octahedron with I(1) at its centre. It may be pointed out that the three oxygen atoms mentioned, O(11), O(12) and O(13), are on the one hand members (common corner atoms) of two, three and one different octahedra, respectively, and that on the other hand they belong to the same pyramidal iodate unit, $O_3I(1)$; nevertheless (as described above) this unit is the least distorted. The other two units, $O_3I(2)$ and $O_3I(3)$, are much more distorted, though their covalently bonded oxygen atoms are, throughout, common corner atoms for two neighbouring octahedra. Therefore, the unequal membership of the covalently bonded oxygen atoms to different octahedra cannot be the main reason for the departure of the pyramidal iodate units from trigonal symmetry.

Another peculiarity of the structure, as can be seen in Figs. 1 and 2, is the fact that the adjacent oxygen octahedra around I(2) and I(3^i) share the edge O(23)–O(33^i) with a length of 2·78 Å (Table 9); there is no further type of (octahedral) edge bonding. However, a new situation, also with regard to such edge sharings, arises from the inclusion of a further weakly bonded oxygen atom in the octahedral environment around the

Table 9. *Distances* (Å) *between* O *atoms of different octahedra* (2·65–3·5 Å)

O(11)···	O(32)	2·90	O(21)···	O(12^{iv})	2·75	O(31)···	O(11)	2·92
	O(31)	2·92		O(12^{ii})	2·95			
	O(12^{ii})	3·13		O(13)	3·05		O(21)	3·13
	O(21)	3·38		O(31)	3·13		O(23)	3·23
				O(11)	3·38		O(23^{i})	3·26
O(12)···	O(21^{iv})	2·75	O(22)···	O(12^{iv})	2·96	O(32)···	O(11)	2·90
	O(21^{vi})	2·95						
	O(22^{iv})	2·96						
	O(11^{vi})	3·13		O(32)	3·09		O(22)	3·09
	O(32^{iv})	3·16		O(33^{i})	3·10		O(13^{iv})	3·15
				O(33)	3·18		O(12^{iv})	3·16
O(13)···	O(23)	2·66	O(23)···	O(13)	2·66	O(33)···	O(23^{i})	2·78
	O(33^{iv})	2·91		O(33^{i})	2·78		O(13^{iv})	2·91
	O(21)	3·05		O(31)	3·23		O(22^{i})	3·10
	O(32^{iv})	3·15		O(31^{i})	3·26		O(22)	3·18
	O(23^{i})	3·29		O(13^{i})	3·29		O(13^{v})	3·34
	O(35^{v})	3·34		O(33^{iv})	3·41		O(23^{iv})	3·41

iodine atoms (sevenfold coordination). Table 7(*a*) (which gives the distances between these seventh oxygen atoms and the central iodine atoms) shows that the extension from sixfold to sevenfold coordination is justified in any case for I(1), but is less justified for I(2) and I(3) because of the relatively large jump in the interionic distances from the sixth to the seventh oxygen atom. A similar extension of octahedra to so-called 'capped octahedra' was also observed by Chan & Einstein (1971) in the structure of the diiodate polymorph $\mathrm{HIO_3.KIO_3}$. The weak interactions between I(1) and the seventh oxygen atom $\mathrm{O}(21^{\mathrm{vi}})$ are indicated in Figs. 1 and 2 by broken lines. Now, as shown by these figures, there are new contacts by edge bonding: the capped octahedron around $\mathrm{I}(1^{\mathrm{vi}})$ and the octahedron around $\mathrm{I}(2^{\mathrm{iv}})$ share the edge O(12)–$\mathrm{O}(21^{\mathrm{iv}})$, with a length at 2·75 Å (Table 9).

For decisive estimations in the further discussion of the structure it is desirable to introduce the following empirical bond lengths: (*a*) a hydrogen bond: [–O–H···O–] = 2·75 ± 0·03 Å; (*b*) a covalent I–O bond: [I–O] = 1·78 ± 0·02 Å; (*c*) a (covalent) I–OH bond: [I–O–H] = 1·93 ± 0·02 Å, if O acts as a hydrogen-bond donor; and (*d*) a (covalent) I–OH bond: [I–O···H] = 1·87 ± 0·02 Å, if O acts as a hydrogen-bond acceptor. Each (*b*)–(*d*) length is taken between the iodine and the oxygen atom; in (*a*) the first oxygen atom plays the part of a hydrogen-bond donor, the second that of a hydrogen-bond acceptor.

A review of the inter-octahedral O···O distances, given in Table 9, allows, by applying (*a*), the immediate selection of those O···O pairs which are possibly involved in hydrogen bonding. According to this selection only O(12)···$\mathrm{O}(21^{\mathrm{iv}})$ and O(23)···$\mathrm{O}(33^{\mathrm{i}})$ remain as such pairs with O···O distances of 2·75 and 2·78 Å respectively. All the other O···O pairs, including O(23)···O(13) with the shortest O···O distance (2·66 Å), can be excluded unambiguously by (*a*). Besides the criterion (*a*) as a necessary (but not yet sufficient) condition for an O···O pair to be hydrogen-bond active, however, the two conditions (*c*) and (*d*) must also be fulfilled by one atom of each O···O pair. Reviewing Table 7(*a*) from this point of view demands the exclusion of the pair O(12)···$\mathrm{O}(21^{\mathrm{iv}})$, because neither I(1)–O(12) = 1·81 Å nor $\mathrm{I}(2^{\mathrm{iv}})$–$\mathrm{O}(21^{\mathrm{iv}})$ = 1·76 Å fulfils one of the conditions (*c*) or (*d*). On the contrary, both are within the limits of pure I–O bonds, given by (*b*), and indicate that both I(1)–O(12) and I(2)–O(21) are pure covalent I–O bonds.

Applying the same criteria to the (not yet excluded) pair O(23)···$\mathrm{O}(33^{\mathrm{i}})$ shows that this, and only this, pair is hydrogen-bond active. O(23) especially proves to be a hydrogen-bond acceptor, whilst $\mathrm{O}(33^{\mathrm{i}})$ is a hydrogen-bond donor. This may be elucidated from Table 7(*a*) by comparing the bond lengths I(2)–O(23) = 1·87 Å and I(3)–O(33) = 1·93 Å with the corresponding lengths (*c*) and (*d*). The hydrogen bonds are drawn in Figs. 2 and 3 as dotted lines. Unlike the arrangements of bifurcated hydrogen bonds in the structures of α-$\mathrm{HIO_3}$ (Rogers & Helmholz, 1941) and the diiodate polymorph $\mathrm{KIO_3.HIO_3}$ (Chan & Einstein, 1971) the hydrogen-bond system of the $\mathrm{KH(IO_3)_2}$ structure does not exhibit any bifurcation of this type. Fig. 3 shows clearly the single unbifurcated hydrogen bonds, among which that with the symbol –O(33)–H(2)···$\mathrm{O}(23^{\mathrm{i}})$– stands for all symmetry-equivalent bonds of this kind. Since the hydrogen atoms H(2) occupy general positions of the space group (with multiplicity 16) there are 16 hydrogen bonds in each unit cell. These bonds operate along the above-mentioned common edges of adjacent oxygen octahedra (Fig. 2) and cause a strengthening of the weak interaction forces between these octahedra, *e.g.* between those around I(3) and $\mathrm{I}(2^{\mathrm{i}})$, as shown by Fig. 3.

Table 10. *Interatomic distances* $\mathrm{H^+}$(1)–O (<2·6 Å)

H(1)···O(13), $\mathrm{O}(13^{\mathrm{i}})$	1·81 Å
H(1)···O(23), $\mathrm{O}(23^{\mathrm{i}})$	2·45
H(1)···$\mathrm{O}(33^{\mathrm{iv}})$, $\mathrm{O}(33^{\mathrm{v}})$	2·50

Besides the 16 H(2) atoms there are eight further H(1) atoms in the unit cell at special positions for the space group. These H(1) atoms act between oxygen atoms of the type O(13) and are primarily responsible for the elongation of the covalent I(1)–O(13) bonds (Table 7*a*) [by which the symmetry of the $\mathrm{O_3I(1)}$ pyramids will be reduced from 3*m* to *m*]. The action of H(1) between two O(13) atoms (Figs. 1 and 2) justifies the location of H(1) in the special position (0,0,*z*) with $z \sim 0$ (Fig. 3). Tables 10 and 11 give details of the environment of H(1) with regard to oxygen and iodine atoms (coordination numbers, bond lengths). Unlike the operation of hydrogen bonds –O–H(2)···O– with two distinguishable oxygen atoms (either a hydrogen-bond donor or acceptor) the operation of the H(1) atoms does not allow a distinction between the two cooperating oxygen atoms. This appears to be plausible on consideration of the following chain: ···$\mathrm{I}(1^{\mathrm{iv}})$–$\mathrm{O}(13^{\mathrm{iv}})$–$\mathrm{H}(1^{\mathrm{iv}})$–$\mathrm{O}(13^{\mathrm{v}})$–$\mathrm{I}(1^{\mathrm{v}})$··· (Fig. 2), in which H(1) is flanked on both sides by crystallographically equivalent, and therefore indistinguishable, oxygen atoms $\mathrm{O}(13^{\mathrm{iv}})$ and $\mathrm{O}(13^{\mathrm{v}})$. This indistinguishability justifies the introduction of –O–H(1)–O– as the symbol for a second kind of hydrogen bond, in which each oxygen atom acts with equal probability as a hydrogen-bond donor and acceptor. So, it may be pointed out that the structure of the new diiodate,

Table 11. *Interatomic distances* $\mathrm{H^+}$(1)···I (<4·2 Å)

H(1)···I(1), $\mathrm{I}(1^{\mathrm{i}})$	3·64 Å
H(1)···I(3), $\mathrm{I}(3^{\mathrm{i}})$	3·97
H(1)···$\mathrm{I}(2^{\mathrm{iv}})$, $\mathrm{I}(2^{\mathrm{v}})$	3·98
H(1)···I(2), $\mathrm{I}(2^{\mathrm{i}})$	4·13
H(1)···$\mathrm{I}(3^{\mathrm{iv}})$, $\mathrm{I}(3^{\mathrm{v}})$	4·13

$KH(IO_3)_2$, consists of $O_3I(j)$ units ($j = 1, 2, 3$), which are held together on the one hand by hydrogen bonds of two types and on the other hand electrostatically by positively charged potassium ions.

Considering the projections of Figs. 1 and 2 from the standpoint of structural chemistry and structural physics one cannot but recognize, *expressis verbis*, that the $KH(IO_3)_2$ structure is marked by a strong bonding anisotropy. Cleavage experiments to prove this could not be carried out, however, because of the small size of the crystals. However, the phenomenon is specified in so far as the glide reflexion planes at $x = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$ are only penetrated by weak interaction forces – as is often the case in layer-like structures and as was already expected from several characteristics of the X-ray rotation photographs.

The different coordination polyhedra of the structure show similar distortions to those involving the oxygen octahedra around the iodine atoms. Thus, the eight oxygen atoms around a potassium atom (Table 7*b*) form a distorted square prism with varying (K···O) bond lengths. The variation of these lengths can be taken as a measure of the degree of distortion. For a perovskite-type structure the variation of these bond lengths would disappear, likewise that of the interionic distances: K···I (Table 7*c*), K···K (Table 7*d*), or I···I (Table 7*e*). Another effect of the distortions is the change of coordination numbers, as is the case in the iodine coordination spheres around the potassium atoms (Table 7*c*): K(1) has eightfold coordination; K(2), however, has ninefold coordination or, by analogy with the term 'capped octahedron', 'capped eightfold coordination'.

If the $KH(IO_3)_2$ crystal had been a substitutionally mixed crystal with the formula $(K,H)IO_3$, each hydrogen atom would be coordinated with the same number of oxygen atoms as a potassium atom. Comparing the oxygen coordinations of K(1) and H(1) with the aid of Tables 7(*b*) and 10 shows that there is no similarity between the coordinations mentioned. A substitutional replacement of H(1) by K(1), and *vice versa*, is therefore entirely impossible. The shorter bond lengths H(1)···O and the higher density of oxygen atoms close to the hydrogen atoms reveal that the hydrogen atoms are responsible for nearly all the distortions of the structure discussed above, and likewise for the excellent polar properties of the $KH(IO_3)_2$ crystals.

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