

A Single-Crystal Neutron Diffraction Study of HIO₃ at 295 and 30 K and of DIO₃ at 295 K

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The crystal structures of hydrogen iodate, HIO₃, and its deuterated form, DIO₃, have been refined from single-crystal neutron data, $\lambda = 1.215(1)$ Å, $P2_12_12_1$, $Z = 4$, HIO₃: 295 K; $a = 5.5400(2)$, $b = 5.8768(3)$, $c = 7.7370(4)$ Å, $R(F) = 0.022$ from 377 unique reflections and at 30 K; $a = 5.492(3)$, $b = 5.841(3)$, $c = 7.660(8)$ Å, $R(F) = 0.021$ from 375 unique reflections and DIO₃: $a = 5.5402(3)$, $b = 5.8746(4)$, $c = 7.7351(5)$ Å, $R(F) = 0.024$ from 375 unique reflections.

The iodate group forms a pyramid with iodine as one apex. Including oxygens at distances shorter than the sum of van der Waals radii the I–O coordination can be described as a distorted bicapped trigonal prism and the structure as of the antimentite type. The iodate groups are connected through hydrogen bonding, forming chains along the b -axis, H \cdots O, 1.725(3) Å and O–H \cdots O 173.5(2)°. The only significant difference between HIO₃ and DIO₃ is a longer [1.747(2) Å] D \cdots O distance. At 30 K, HIO₃ shows decreased intermolecular distances and O–I–O angles.

HIO₃ belongs to the simple iodates, MIO₃, $M = H/D^+$, NH_4^+ , Tl^+ and alkali ions, in some cases in solid solution. These materials have received a great interest in the search for optically non-linear materials. With the exception of NaIO₃ they have all been shown to be non-centric and second-harmonics generators,¹ and LiIO₃ and HIO₃, for instance, are widely used in optical applications. However, a full understanding and quantitative modelling of their properties will depend on our obtaining accurate structure data. In order to improve the accuracy of the structure determinations of HIO₃ by Rogers and Helmholtz² and Garret,³ and to compare the structure of HIO₃ with that of DIO₃, a neutron powder diffraction study was recently made.⁴ As this investigation left some ambiguities concerning differences between the HIO₃ and DIO₃ structures it was decided to carry on with a single-crystal neutron diffraction study, which is reported herein.

Experimental

An HIO₃ crystal, 3×4×4 mm³, bound by {001} and {110}, was cut from a larger crystal grown from slow evaporation of a water solution. A DIO₃ crystal, 2.5×2.5×4 mm³, bound by {111} and {001}, was obtained after five times repeated recrystallizations with slow evaporation at 323 K from D₂O with addition of DNO₃, starting with HIO₃. The room-temperature unit cells were refined from 110 accurately measured and absorption-corrected⁵ 2 θ -values in the

range 40–50° with well resolved α_1 – α_2 peaks, collected on a Huber diffractometer with graphite monochromatized MoK α radiation using 0.30 mm ground spheres of HIO₃ and DIO₃. The unit cell at 30 K was determined from ten 2 θ -values measured on the single-crystal diffractometer beam line at the Studvik Research Reactor, Sweden [$\lambda = 1.215(1)$ Å], also used for the data collections. The low temperature, 30(2) K, was attained with a CTI Cryogenics

Table 1. Data reduction and refinement data for DIO₃ at 295 K and HIO₃ at 295 and 30 K; space group $P2_12_12_1$, $Z = 4$.

	DIO ₃	HIO ₃	HIO ₃
T/K	295(1)	295(1)	30(2)
M_r	176.91	175.91	175.91
$D_x/g\text{ cm}^{-3}$	4.67	4.64	4.76
μ/cm^{-1}	0.38(2) ^a	0.72 ^b	0.74 ^b
Transmission factors	0.941–0.946	0.754–0.818	0.754–0.818
$a/\text{Å}$	5.5402(3)	5.5400(2)	5.492(3)
$b/\text{Å}$	5.8746(4)	5.8768(3)	5.841(3)
$c/\text{Å}$	7.7351(5)	7.7370(4)	7.660(8)
$V/\text{Å}^3$	251.75(2)	251.89(1)	245.7(4)
No. of reflections in final LS cycle	375	377	375
No. of parameters	52	52	52
$R(F)$	0.0241	0.0217	0.0207
$R(F^2)$	0.0317	0.0335	0.0335
$R_w(F^2)$	0.0449	0.0488	0.0456
S	1.0361	1.1129	0.9734
c_1^c	0.025	0.033	0.040
c_2^c	0.006	0.002	0.003

^aMeasured. ^bCalculated. ^cIn weighting function, $w = [\sigma^2(F_o^2) + (c_1 F_o^2)^2 + c_2]^{-1}$.

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Table 2. Final fractional coordinates ($\times 10^4$) and isotropic mean values of the temperature factor coefficients (in \AA^2), $B_{av} = 4\pi \sum \beta_j (a_i \cdot a_j) / 3$, with estimated standard deviations for DIO₃ at 295 K and HIO₃ at 295 and 30 K.

	x	y	z	$B_{av}/\text{\AA}^2$
DIO ₃ , 295 K				
I	20 359(24)	-8 612(22)	15 741(14)	0.77(2)
O(1)	-6 778(23)	2 499(22)	25 671(16)	1.18(3)
O(2)	33 530(25)	19 590(25)	8 351(16)	1.36(3)
O(3)	9 494(25)	-15 857(23)	-5 207(15)	1.32(3)
D	23 922(30)	32 201(27)	13 301(22)	2.88(4)
HIO ₃ , 295 K				
I	20 395(19)	-8 538(17)	15 737(12)	1.13(2)
O(1)	-6 832(20)	2 425(17)	25 690(13)	1.56(2)
O(2)	33 409(21)	19 685(20)	8 399(13)	1.79(2)
O(3)	9 469(20)	-15 837(19)	-5 215(12)	1.73(2)
H	23 752(46)	32 350(37)	13 452(31)	3.07(5)
HIO ₃ , 30 K				
I	20 671(17)	-8 559(14)	15 872(11)	0.28(2)
O(1)	-6 992(16)	2 471(14)	25 747(11)	0.51(2)
O(2)	33 631(17)	19 626(15)	8 303(11)	0.56(2)
O(3)	9 743(16)	-16 010(14)	-5 357(11)	0.54(2)
H	23 823(35)	32 593(28)	13 421(24)	1.68(4)

two-step closed He cooler. The intensity data sets were collected for $4 \leq 2\theta \leq 108^\circ$ ($0 \leq h \leq 7$, $0 \leq k \leq 7$, $-10 \leq l \leq 0$, $\sin \theta / \lambda < 0.66 \text{ \AA}^{-1}$) using ω - 2θ step scans. The outer 10% of a scan was used for background calculations. The intensities of three standard reflections measured every 30 reflections showed no systematic variations during any of the three data collections. Each data set was corrected for absorption and the Lorentz effect.

Refinements

The full matrix least-squares refinement minimized $\sum w(F_o^2 - F_c^2)^2$, where $w = [\sigma^2(F_o^2) + (c_1 F_o^2)^2 + c_2]^{-1}$ with $\sigma(F_o^2)$ from counting statistics and c_1 and c_2 adjusted to give as constant a value of $\langle w \Delta F^2 \rangle$ in different $\sin \theta$ and F_o^2 intervals as possible. The refinements were started with parameters from Ståhl and Szafranski.⁴ 52 parameters were refined in the final cycles for each data set, included one scale factor, six anisotropic extinction parameters (type I, Lorentzian mosaicity)⁶ and fractional coordinates and anisotropic temperature factor coefficients of all atoms. Reflections having extinction correction factors > 3.0 (on

Table 3. Selected distances (in \AA) and angles (in $^\circ$) in HIO₃ and DIO₃.

	DIO ₃ T/K = 295	HIO ₃ 295	HIO ₃ 30
I-O(1)	1.810(2)	1.812(1)	1.815(2)
I-O(2)	1.889(2)	1.896(1)	1.895(2)
I-O(3)	1.780(2)	1.783(1)	1.787(2)
I-O(1) ^a	2.495(2)	2.504(1)	2.481(2)
I-O(2) ^b	3.365(2)	3.372(1)	3.324(4)
I-O(2) ^c	3.490(2)	3.492(1)	3.436(2)
I-O(3) ^d	2.759(2)	2.760(1)	2.731(2)
I-O(3) ^b	2.892(2)	2.889(1)	2.841(2)
O(1)-I-O(2)	97.61(8)	97.63(7)	97.55(6)
O(1)-I-O(3)	101.04(9)	100.92(7)	100.63(7)
O(2)-I-O(3)	93.70(8)	93.86(6)	93.48(7)
O(2)-H/D	0.989(2)	0.996(3)	1.000(2)
H/D...O(1) ^e	1.747(2)	1.725(3)	1.700(2)
O(2)-H/D-O(1) ^e	173.0(2)	173.5(2)	173.4(2)
I-O(2)-H/D	109.3(1)	109.4(2)	109.3(1)

^a-x, y-1/2, 1/2-z; ^b1/2-x, 1-y, 1/2+z; ^c1-x, y-1/2, 1/2-z; ^d1/2+x, -1/2-y, -z; ^e-x, 1/2+y, 1/2-z.

F_o^2) were excluded in the final cycles (four for HIO₃ at 295 K, three for HIO₃ at 30 K and eight for DIO₃). The refinements were considered converged when the maximum shift per e.s.d. was < 0.01 . The final difference Fourier maps showed maximum peak heights corresponding to $< 3\%$ of the O(1) peak. Neutron scattering lengths were taken from Koester *et al.*⁷ The computer programs used have been described by Lundgren.⁸ Additional information on data reductions and refinements is given in Table 1, and the final fractional coordinates and isotropic mean values of the temperature factor coefficients are given in Table 2. Lists of observed and calculated structure factor amplitudes and anisotropic temperature factor coefficients can be obtained from one of the authors (K.S.).

Discussion

The geometric details of the HIO₃ and DIO₃ structures are given in Table 3. The iodate ion forms a pyramid (Fig. 1), with the iodine lone pair as the fourth vertex of a tetrahedron. The H/DIO₃ molecules are connected through hydrogen bonds, O(2)-H/D...O(1), forming chains directed along the b-axis. By including next-nearest neighbours at distances shorter than the sum of the van der Waals radii

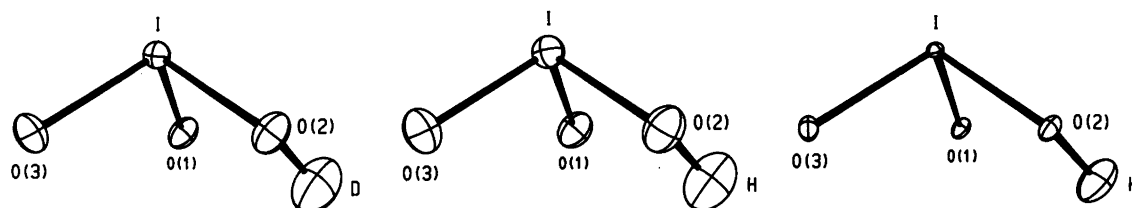


Fig. 1. Thermal ellipsoid drawings scaled to include 50% probability for (from left to right) DIO₃ at 295 K, HIO₃ at 295 K and HIO₃ at 30 K.

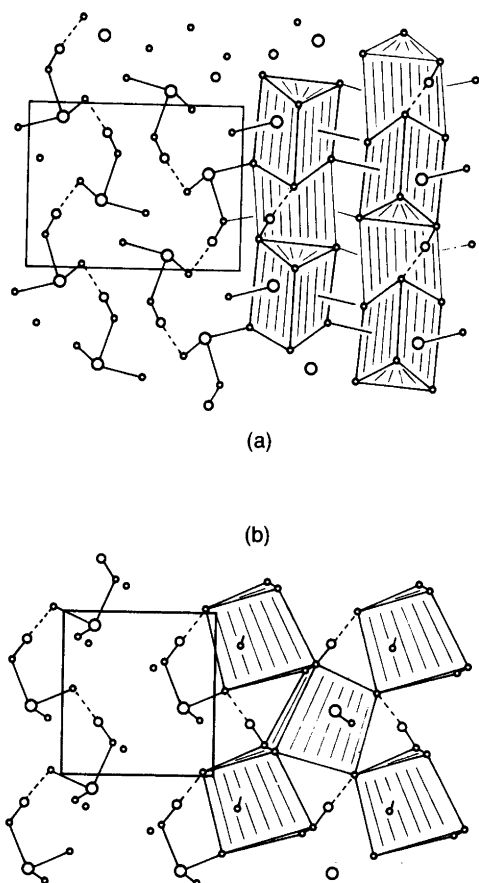


Fig. 2. The crystal structure of HIO_3 and DIO_3 . (a) Projected on the bc -plane. To the left are the molecular geometry with hydrogen bonds (broken lines) and the unit cell. The atomic positions are extended to the right-hand side, where the connected bicapped prisms are shown. (b) A section projected on the ab -plane. A view perpendicular to the sheets of connected capped prisms. The large circles are iodine, the intermediate are hydrogen/deuterium and the small circles oxygen.

(3.6 Å), the I–O coordination can be described as a distorted bicapped trigonal prism, with the iodine approximately on one of the capped rectangular faces of the prism. The iodine lone pair is approximately at the centre of the prism, giving lone pair to oxygen distances in the range 2.2–2.9 Å. The HIO_3 and DIO_3 structures are of the antimentite type⁹ (Fig. 2), isostructural with XeO_3 ^{9,10} and related to the NaIO_3 structure,^{9,11} with H/D on a face of the octahedral interstice (empty in cementite, occupied by Na in NaIO_3).

The structural parameters are not significantly different from those obtained from powder diffraction data,⁴ but e.s.d.s are now on average a factor of five smaller and a factor of eight to ten smaller than obtained by Garret.³ The only significant difference between HIO_3 and DIO_3 is a 0.022(3) Å shorter hydrogen-bonding distance in HIO_3 . Based on NQR data, the O–D distance was predicted to be 0.005 Å shorter than the O–H distance.¹² The observed difference, 0.007(3) Å, is consistent with the prediction, but barely significant at the present level of accuracy. The

differences between the HIO_3 structures at 295 and 30 K are essentially in the molecular packing, where the decrease in thermal motions at 30 K allows shorter intermolecular distances and on average 0.25(5)° smaller O–I–O angles (cf. Table 3).

The effect of hydrogen bonding on the molecular geometry can be seen in a comparison with $\text{DIO}_3 \cdot \text{I}_2\text{O}_5$,¹³ where the hydrogen-bond acceptor is an oxygen of the I_2O_5 molecule. The DIO_3 molecule has one long I–O(D) distance, 1.890(2) Å, and two short I–O distances, 1.795(2) and 1.799(2) Å, while the latter distances in pure DIO_3 are differentiated, with a longer I–O distance for the hydrogen-bond accepting oxygen. Also the bond angles are affected, with generally smaller O–I–O angles in $\text{DIO}_3 \cdot \text{I}_2\text{O}_5$: 95.26(9) [O(D)], 93.53(9) [O(D)] and 99.12(9)°. A comparison with the isostructural XeO_3 ¹⁰ reveals the effect on molecular packing: The ratio of diagonals of the projected rhombic 'holes' (cf. Fig. 2b) is 1.8 in XeO_3 , while the contraction caused by hydrogen bonding gives a ratio of 2.1 in HIO_3 and DIO_3 . The packing efficiency is also higher in HIO_3 and DIO_3 ; expressed as the inverse quantity volume per oxygen or iodine lone pair,¹⁴ it is 16.36 Å³ in XeO_3 and 15.74 Å³ in HIO_3 and DIO_3 , despite shorter covalent oxygen distance and a higher formal valence of Xe.

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