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A Combined Neutron Powder and X-Ray Single Crystal Diffraction Study of Anhydro-Iodic Acid, $DIO_3 \cdot I_2O_5$, at 293 K

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The crystal structure of deuterated anhydro-iodic acid, $DIO_3 \cdot I_2O_5$, at 293 K has been determined from neutron powder and X-ray single crystal diffraction data. $DIO_3 \cdot I_2O_5$ is monoclinic, space group $P2_1/n$, with $a = 7.581(2)$, $b = 7.713(1)$, $c = 11.405(1)$, $\beta = 90.20(1)°$, and $Z = 4$. This work confirms that the compound often written HI_3O_8 is an addition compound of HIO_3 and I_2O_5. The DIO_3 molecule is pyramidal with I–O bond distances of 1.795(2), 1.799(2), and 1.890(2) Å, the latter also bonded to D. The I_2O_5 molecule has approximate mirror symmetry. The four terminal I–O distances are in the range 1.787(2)–1.800(20 Å, while the two central I–O distances are 1.957(2) and 1.959(2) Å, with an I–O–I angle of 126.0(1)°. The DIO_3 and I_2O_5 molecules are linked by a hydrogen bond (D · · · O 1.81(2) Å and O · · · O 2.755(2) Å). The three-dimensional structure is described as built from edge and corner-sharing bicapped trigonal prisms of oxygen atoms around iodine and its lone pair electrons.

Introduction

As part of an on-going study of the structures and properties of simple iodates we have determined the crystal structure of $DIO_3 \cdot I_2O_5$ at 293 K by means of both X-ray single crystal and neutron powder diffraction data. The topics of other investigations in this series include the structure and properties of $Co(IO_3)_2$, the relationships among α-$LiIO_3$ type structures (*1*), the γ-$LiIO_3$ structure (*2*), the temperature dependence of the structure and properties of α-$LiIO_3$ (*3*, *4*), the structures of $Li_2NH_4(IO_3)_3$ (*5*) and $NaIO_3$ (*6*), measurement and interpretation of the ultraviolet absorption of alkaline iodates, bromates, and chlorates (*7*), and the structures of HIO_3 and DIO_3 (*8*). Feikema and Vos earlier determined the structure of HI_3O_8 (*9*), which should be written $HIO_3 \cdot I_2O_5$, from X-ray data. Their results were not of high precision, and they could only find indirect evidence for the position of the hydrogen atom. The present work confirms their structural solution in general and resolves any ambiguities about the hydrogen atom position and the hydrogen bonding in the compound.

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Experimental

Starting from commercially available HIO_3 (Analar quality, BDH Chemicals Ltd. Poole, England) crystals of $DIO_3 \cdot I_2O_5$ were obtained by fivefold recrystallization through slow evaporation at 50°C from D_2O with the addition of D_2SO_4 (*10*).

X-ray single crystal data. The crystal used was a thick (101) plate with approximate dimensions 0.07 × 0.15 × 0.20 mm. It was mounted on a Huber four-circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda(K\alpha_1)$ = 0.70926 Å). Unit cell dimensions were determined from accurately measured Bragg angles of 26 reflections with $22° < 2\theta < 40°$. Three-dimensional intensity data cover the complete reciprocal sphere up to $2\theta = 62°$ ($-10 \le h \le 10$, $-11 \le k \le 11$, $0 \le l \le 16$). One further quadrant of data with $62° < 2\theta < 80°$ ($-13 \le h \le 13$, $0 \le k \le 13$, $0 \le l \le 20$) was measured. Scan widths in the $\omega - 2\theta$ scans were calculated from $\Delta\omega = 0.68° + 0.4° \tan\theta$ with a scan rate of 2° min^{-1}. The rate was lowered to 0.4° min^{-1} in a second scan if initially $1 \le I/\sigma(I) \le 10$. The continuous scans were divided into 256 steps by a high-speed multichannel scaler. Peak widths were assigned with the Lehmann–Larsen method (*11*) and all steps outside the peak were used as background. The intensities of three standards measured every 2 hr decreased by a total of 3% during the 111 hr of exposure time. They were fitted by a function linear in time, which was used to rescale all intensities. The 10,648 intensities were corrected for Lp and absorption effects (Gaussian integration). With a linear absorption coefficient of 139.2 cm^{-1} the range of transmission factors was 0.24–0.39.

The symmetry is monoclinic with systematic extinctions corresponding to $P2_1/n$. After exclusion of extinct reflections, 10,271 remained. The internal agreement factor ($R_{int} = \Sigma(\Sigma|F_0^2 - F_{aver}^2|)/\Sigma F_0^2$) when symmetry equivalent reflections were averaged was 0.034.

Neutron powder data. The powder sample was ground and packed by vibrations in an ultrasonic bath into a vanadium sample holder with an 11 mm diameter and a 50 mm height. The neutron powder data set was collected at the powder diffraction beam line at The Studsvik Neutron Research Laboratory, Sweden, using λ = 1.470(1) Å, $9.80° < 2\theta < 123.4°$, in steps of 0.08°, and each step was measured for approximately 2 min (monitor controlled) with an array of 10 detectors.

Refinements

X-ray single crystal data. The iodine positions were solved with MULTAN80 (*12*) and the oxygen and deuterium positions were located in consecutive difference Fourier maps. The coordinate set used was chosen to make the asymmetric part a connected $DIO_3 \cdot I_2O_5$ unit, and it does not conform with the coordinate set used by Feikema and Vos (*9*). $\Sigma w_i(F_0^2 - F_c^2)^2$ was full-matrix least-squares minimized with weights calculated from $w^{-1} = \sigma_c^2(F_0^2) + (0.05\,F_0^2)^2 + (0.012\,\langle F_0^2\rangle)^2$. The unaveraged data set was used in the refinements. The 105 parameters refined included one scale factor, one isotropic extinction parameter, positional parameters, anisotropic thermal parameters for I and O atoms, and an isotropic thermal parameter for the D atom. Data with $\sin\theta/\lambda < 0.3$ Å^{-1} were excluded in the final cycles in order to diminish problems with multiple diffraction and extinction. In addition, all reflections with an extinction correction factor greater than 1.3 (on F_0^2) were rejected, leaving a final number of 9637 (3969 unique) reflections. The isotropic extinction parameter (type I, Lorentzian mosaicity (*13*)) was 1.02(3) × 10^4. The largest (parameter shift)/(parameter ESD) in the final cycle was less than 0.01. The largest residuals in the difference Fourier map were −1.24 and +0.92 eÅ^{-1}. Scattering factors for neutral atoms and

TABLE I

DATA COLLECTION AND REFINEMENT DATA FOR $DIO_3 \cdot I_2O_5$ AT 293 K, SPACEGROUP $P2_1/n$, $Z = 4$, $M_r = 510.72$, $D_x = 5.08$ g/cm^3

	Neutron powder	X-rays, single crystal
Max sin θ/λ (Å^{-1})	0.599	0.906
No. of steps	1421	—
No. of reflections	—	10,271
unique	1289	3,969
No. of param. ref.	61	105
μ (cm^{-1})	0.1	139.0
a (Å)	7.5871(9)	7.5802(15)
b (Å)	7.7210(8)	7.7126(8)
c (Å)	11.4165(12)	11.4048(10)
β (°)	90.195(9)	90.202(10)
V (Å^3)	669.8(2)	666.8(1)
R_p or $R(F^2)$ (%)	4.46	4.67
R_{wp} or $R_w(F^2)$ (%)	5.96	7.76
S	2.32	0.99
$R(F)$ (%)	1.56	3.67

anomalous dispersion corrections were taken from (*14*).

Neutron powder data. The Rietveld analysis program used in this study is essentially the LHMP1 program described in (*15*), modified to use Chebyshev polynomials in background refinements and to fit the local I/O formats. The program minimizes the quantity $\Sigma w_i(Y_{io} - Y_{ic})^2$ with $w_i = 1/Y_{io}$. A pseudo-Voigt function was used with a Lorentzian component $\gamma = \gamma_1 + \gamma_2 2\theta$, where γ_1 and γ_2 were refined. The FWHM was defined as $(U \tan^2\theta + V \tan\theta + W)^{1/2}$, where U, V, and W were refined. The peaks were truncated at three half widths from the peak position. The 2θ zero point was refined as well as one asymmetry parameter for $2\theta \leq 40°$ and one preferred orientation parameter. Six background parameters (type I Chebyshev polynomials of order 0 to 5) were refined in the initial cycles and then kept constant through the final refinements. The data were corrected for absorption according to (*16*) with μR of 0.02. One overall scale factor, four unit cell parameters, and fractional coordinates and independent isotropic temperature factor coefficients of all atoms were refined. The maximum (parameter shift)/(parameter ESD) in the final cycle was less than 0.1. The refinements were started with I and O parameters from the X-ray refinements and D located in a difference Fourier map. Neutron scattering lengths were taken from (*17*). R-values given for the Rietveld analysis are defined as $R_p = \Sigma|Y_{io} - Y_{ic}|/\Sigma Y_{io}$, $R_{wp} = (\Sigma w_i(Y_{io} - Y_{ic})^2/\Sigma w_i Y_{io}^2)^{1/2}$, $S = (\Sigma w_i(Y_{io} - Y_{ic})^2/(N - P))^{1/2}$, and the derived Bragg R-value, $R_F = \Sigma|F_{ko} - F_{kc}|/\Sigma F_{ko}$.

Programs other than the diffractometer control, MULTAN80, and Rietveld programs have been described by (*18*). Additional information on data collection and refinement is given in Table I and the final fractional coordinates and isotropic mean values of the temperature factor coefficients are given in Table II.[1] The powder diffraction pattern with the final difference pattern is shown in Fig. 1.

Discussion

The two structure refinements using X-ray single crystal data and neutron powder data are in good agreement, with the higher precision in the X-ray investigation except for the deuterium atom parameters (cf. Table III). The neutron wavelength value is probably the main reason for the differences in cell parameters from X-ray and neutron data. Differences in atomic pa-

[1] See NAPS Document No. 04982 for 52 pages of supplementary material. Order from ASIS/NAPS Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or, for photocopy, $7.75 for up to 20 pages plus $.30 for additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling for the first 20 pages, and $1.00 for each additional 10 pages of material, $1.50 for postage of any microfiche orders.

TABLE II

FINAL FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTOR COEFFICIENTS FOR $DIO_3 \cdot I_2O_5$

	x	y	z	B(Å^2)
I(1)	0.74161(2)	0.22780(2)	0.09527(1)	0.797(3)
I(1)	0.737(2)	0.228(2)	0.093(1)	0.6(3)
I(2)	0.66226(2)	0.23619(2)	0.39633(1)	0.770(3)
I(2)	0.660(2)	0.240(2)	0.397(1)	0.3(2)
I(3)	0.24412(2)	0.54737(2)	0.30866(1)	0.811(3)
I(3)	0.244(2)	0.537(2)	0.309(1)	0.3(2)
O(1)	0.9580(3)	0.3010(3)	0.0537(2)	1.33(3)
O(1)	0.958(2)	0.299(2)	0.052(1)	1.3(3)
O(2)	0.6300(3)	0.4315(3)	0.0870(2)	1.40(3)
O(2)	0.624(2)	0.435(2)	0.081(1)	0.4(2)
O(3)	0.8284(3)	0.3225(3)	0.4917(2)	1.28(3)
O(3)	0.830(2)	0.321(2)	0.489(1)	0.8(3)
O(4)	0.5595(3)	0.4404(2)	0.3636(2)	1.31(3)
O(4)	0.556(2)	0.440(2)	0.363(1)	0.9(3)
O(5)	0.8168(3)	0.2454(3)	0.2592(2)	1.06(3)
O(5)	0.812(2)	0.239(1)	0.257(1)	0.8(3)
O(6)	0.2835(3)	0.4549(3)	0.1575(2)	1.42(4)
O(6)	0.268(2)	0.455(2)	0.158(1)	1.4(3)
O(7)	0.1969(3)	0.3424(3)	0.3762(2)	1.41(3)
O(7)	0.195(2)	0.346(2)	0.377(1)	0.8(2)
O(8)	0.0225(2)	0.6144(3)	0.2746(2)	1.29(3)
O(8)	0.026(2)	0.612(1)	0.279(1)	0.9(3)
D	0.383(10)	0.452(9)	0.143(6)	1.5(1.1)
D	0.409(2)	0.438(2)	0.138(2)	3.7(4)

Note. The first line gives the X-ray single crystal and the second line the neutron powder diffraction results. The mean B values of the x-ray anisotropic temperature factors were calculated by $B = 4/3 \cdot \Sigma_i\Sigma_j\beta_{ij}(\mathbf{a}_i\mathbf{a}_j)$.

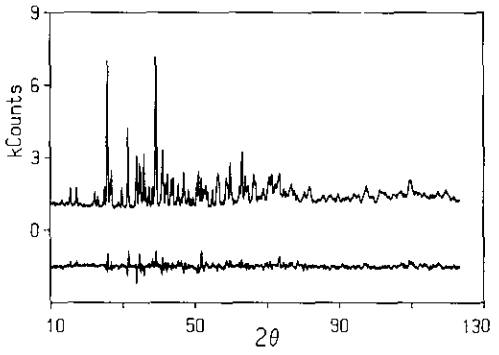

FIG. 1. Observed neutron powder diffraction pattern and final difference pattern on the same scale for $DIO_3 \cdot I_2O_5$.

TABLE III

SELECTED DISTANCES (Å) AND ANGLES (°) IN $DIO_3 \cdot I_2O_5$ COMPARED TO INTRAMOLECULAR DISTANCES AND ANGLES REPORTED FOR I_2O_5 (*20*) AND DIO_3 (*8*)

	Neutron powder	X-ray single crystal	Published values
I(1)–O(1)	1.82(2)	1.800(2)	1.78(3)[a]
–O(2)	1.82(2)	1.787(2)	1.77(3)[a]
–O(5)	1.96(2)	1.957(2)	1.92(2)[a]
–O(7)	2.55(2)	2.577(2)	
–O(8)	2.63(2)	2.645(2)	
–O(4)	2.76(2)	2.720(2)	
–O(3)	3.32(2)	3.322(2)	
–O(3)	3.33(2)	3.366(2)	
O(1)–I(1)–O(2)	98.6(9)	98.18(9)	100(1)[a]
–O(5)	88.3(8)	88.11(8)	96(1)[a]
O(2)–I(1)–O(5)	99.7(8)	97.20(9)	102(1)[a]
I(2)–O(3)	1.78(2)	1.790(2)	1.83(3)[a]
–O(4)	1.78(2)	1.790(2)	1.79(3)[a]
–O(5)	1.96(2)	1.959(2)	1.95(3)[a]
–O(1)	2.37(2)	2.392(2)	
–O(8)	2.64(2)	2.573(2)	
–O(2)	2.88(2)	2.835(2)	
–O(6)	3.44(2)	3.445(2)	
–O(1)	3.57(2)	3.525(2)	
O(3)–I(2)–O(4)	98.2(9)	95.96(9)	95(1)[a]
–O(5)	93.4(9)	92.89(8)	93(1)[a]
O(4)–I(2)–O(5)	95.1(8)	93.58(9)	98(1)[a]
I(1)–O(5)–I(2)	127(1)	126.0(1)	139(1)[a]
I(3)–O(6)	1.84(2)	1.890(2)	1.889(2)[b]
–O(7)	1.71(2)	1.795(2)	1.810(2)[b]
–O(8)	1.79(2)	1.799(2)	1.780(2)[b]
–O(3)	2.61(2)	2.550(2)	
–O(4)	2.55(2)	2.603(2)	
–O(7)	3.23(2)	3.135(2)	
–O(6)	3.25(2)	3.174(2)	
–O(1)	3.42(2)	3.371(2)	
O(6)–I(3)–O(7)	98.6(9)	95.26(9)	97.61(8)[b]
–O(8)	91.6(8)	93.53(9)	93.79(8)[b]
O(7)–I(3)–O(8)	99.4(9)	99.12(9)	101.04(9)[b]
O(6)–D	1.04(2)	0.77(8)	0.989(2)[b]
I(3)–O(6)–D	110(2)	111(5)	109.3(1)[b]
D · · · O(2)	1.81(2)	1.99(8)	
O(6)–D · · · O(2)	170(2)	173(7)	
O(6) · · · O(2)	2.84(2)	2.755(3)	

[a] Ref. (*20*).
[b] Ref. (*8*).

rameters may be caused by the fundamental difference in the origin of the scattering. On the other hand, the two sets of coordinates for all 12 atoms were compared in a half-normal δp plot (*19*). The 30 points with $\delta p < 3.0$, out of a total of 36 points, fall approximately on a straight line with slope 2.01(5) and intercept $-0.03(2)$. The pooled standard deviations are essentially equal to

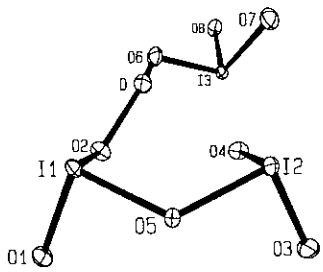

FIG. 2. A perspective view of a set of hydrogen-bonded DIO_3 and I_2O_5 molecules in $DIO_3 \cdot I_2O_5$. The projection is onto the plane through I(1)–O(5)–I(2) of the I_2O_5 molecule.

the standard deviations from neutron refinement, so it might be reasoned that the coordinate sets are equal assuming that the neutron standard deviations are underestimated by a factor of 2. In the discussion below we refer to the X-ray results except when structural parameters involving deuterium are mentioned.

The structure determination clearly shows that the unit cell of the compound commonly written DI_3O_8 contains four formula units of $DIO_3 \cdot I_2O_5$. Each set of molecules is linked by a hydrogen bond, as shown in Fig. 2, from O(6) of DIO_3 to O(2) of I_2O_5. The D $\cdots$ O(2) and O(6) $\cdots$ O(2) distances are 1.81(2) and 2.755(2) Å. Both the DIO_3 and the I_2O_5 molecules deviate slightly from C_s symmetry. The DIO_3 parts form pyramids, with a significantly longer I–O distance to the O(6)–D group. The O(6)–I–O(7) and O(6)–I–O(8) angles are also correspondingly smaller than O(7)–I–O(8). The molecular geometry of the DIO_3 part differs from that of pure DIO_3, where O(7) is a hydrogen bond acceptor, in that pure DIO_3 has longer I–O(7) distances and larger O–I–O(7) angles (*8*); cf. Table III. The deviations of the I_2O_5 molecule from C_s symmetry might be accounted for by the hydrogen bond accepted by O(2), which has the shortest I–O distance of 1.787(2) Å, but more significant are the differences in bond angles with O(2)–I–O(5) and O(2)–I–O(1) of 97.20(9)° and 98.18(9)° compared to O(1)–I–O(5) of 88.11(8)°. In the other half of the I_2O_5 molecule bond angle differences are smaller. In the crystal structure of pure I_2O_5 (*20;* cf. Table III) the conformation of the molecule is quite different, due to completely different molecular packing and the lack of hydrogen bonding. The most notable difference otherwise is the 13(1)° larger I–O–I angle in pure I_2O_5.

All I–O distances shorter than the sum of the van der Waals radii, 3.60 Å, are given in Table III. Each iodine atom has eight oxygen neighbors. We describe the polyhedron formed as a bicapped trigonal prism around the iodine atom and its lone pair of electrons, analogously to the description of the structures of HIO_3 (*8, 21*), $NaIO_3$ (*6, 21*), and a number of other iodates related to the α-$LiIO_3$ type (*1*). The position of the iodine atom is close to a rectangular face of the prism with one of its three closest oxygens capping the prism. The lone pair of electrons protrudes toward the center of the prism. The bicapped trigonal prisms are distorted so that the edges further away from the iodine are progressively longer. The left part of Fig. 3 shows a double strand of prisms linked along *b*. The backbone of this strand is formed by the I_2O_5 molecules. The two halves of the strand are related by a 2_1 screw axis along the middle of it, close to the O(5) atoms. The right part of Fig. 3 shows a chain of prisms, centered by iodine atoms of the DIO_3 molecules, along a 2_1 axis close to the I(3) atoms. This chain is linked in a similar manner to the way tricapped trigonal prisms are connected in one direction in $Y(OH)_3$ (*21*). The coordination polyhedra described are linked in three dimensions by edge and corner-sharing into a fairly dense structure. The unit cell volume divided by the number of oxygen atoms and iodine lone pairs is 15.2 $Å^3$, which is at the low end of the range that is normal for simple oxides (*21*). The corresponding volumes for

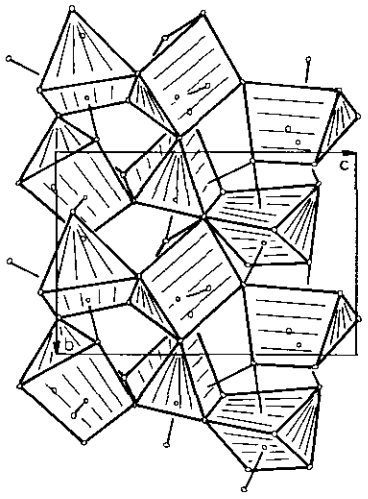

FIG. 3. A parallel projection of the structure of $DIO_3 \cdot I_2O_5$ along [100]. All atoms except deuterium within approximately $0.5 \leq x \leq 1.0$ are shown. The structure is described in terms of linked bicapped trigonal prisms.

crystals of DIO_3 and I_2O_5 are 15.9 and 15.5 Å^3, respectively.

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