

Data collection

Enraf–Nonius CAD-4 diffractometer	2747 reflections with $l > 2\sigma(I)$
Profile data from $\omega/2\theta$ scans	$R_{\text{int}} = 0.026$
Absorption correction: Gaussian using <i>ABSORB</i> over a $16 \times 16 \times 16$ grid (DeTitta, 1985)	$\theta_{\text{max}} = 25.92^\circ$ $h = 0 \rightarrow 18$ $k = -14 \rightarrow 14$ $l = -14 \rightarrow 14$
$T_{\text{min}} = 0.007$, $T_{\text{max}} = 0.040$	3 standard reflections
9755 measured reflections	frequency: 120 min
4139 independent reflections	intensity decay: -6.4%

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 3.616 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$\Delta\rho_{\text{min}} = -2.369 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.076$	Extinction correction: <i>SHELXL93</i>
$S = 1.076$	Extinction coefficient: 0.000307 (9)
4136 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
254 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pb1—O8	2.226 (13)	Pb5—O7 ⁱⁱⁱ	2.203 (13)
Pb1—O22 ⁱ	2.756 (12)	Pb5—O21 ⁱⁱ	2.408 (14)
Pb1—O24 ⁱⁱ	2.85 (2)	Pb5—O11	2.68 (2)
Pb2—O8	2.275 (13)	Pb6—O8 ⁱⁱⁱ	2.194 (12)
Pb2—O14 ⁱⁱ	2.74 (2)	Pb6—O12	2.44 (2)
Pb2—O13	2.84 (2)	Pb6—O13 ⁱⁱ	2.73 (2)
Pb2—O12 ⁱ	2.86 (2)	Pb6—O23	2.77 (2)
Pb3—O7	2.283 (14)	Pb8—O14	2.71 (2)
Pb3—O11 ⁱ	2.57 (2)	Pb10—O24	2.63 (2)
Pb4—O7	2.263 (13)	Pb10—O22 ⁱ	2.871 (13)
Pb5 ⁱ —O7—Pb4	143.1 (7)	Pb6 ⁱ —O8—Pb1	137.6 (6)
Pb5 ⁱ —O7—Pb3	115.6 (6)	Pb6 ⁱ —O8—Pb2	119.6 (6)
Pb4—O7—Pb3	99.1 (5)	Pb1—O8—Pb2	102.3 (5)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x - 1, y, z$; (v) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Reflection background subtraction, based on the peak profile analysis, and Lorentz and polarization corrections, were performed using programs *REFPK* and *BGLP* (Blessing, 1989). Time-dependent scaling of the measured data with cubic polynomials (*SCALE3*; Blessing, 1989) gave scale factors varying from 1.000 to 0.940 (average 0.979). Multiple-repeated and symmetry-equivalent measurements were averaged, after Gaussian absorption correction using the *SORTAV* program (Blessing, 1995), by a least-squares fit of real spherical harmonic functions (y_{lim} , with an even-order limit of $l_{\text{omax}} = 4$ and an odd-order limit of $l_{\text{imax}} = 1$). The 'relative weighting factor' parameter of the program was set to $w_a = 4.0$. This yielded corrections corresponding to effective transmission factors varying from 0.985 to 1.020 (average 0.999), and improved the residuals for symmetry-equivalent measurements from $R_{\text{int}} = 0.0306$ (using the conventional averaging procedure) to $R_{\text{int}} = 0.0259$. Bayesian statistical treatment was applied using the *BAYES* program (Blessing, 1989) to calculate the estimates of F^2 , $\sigma(F^2)$, F and $\sigma(F)$. Anisotropic displacement parameters were refined for all atoms. The first 25 peaks in the final electron density in the difference Fourier map were found to be ghosts to Pb or Mo atoms at distances less than 1.05 \AA .

Data collection: *CAD-4 Users Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 Users Manual*. Data reduc-

tion: data reduction and error analysis programs (Blessing, 1989, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Neutron Powder Diffraction Study on Highly Deuterated Ca(IO₃)₂.D₂O

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Abstract

Neutron powder diffraction experiments were performed on highly deuterated calcium iodate monohydrate (bruggenite) to examine possible H/D enrich-

ment effects. The title compound is built up of distorted CaO_8 quadratic antiprisms. The iodate ions form layers parallel to (100), revealing relatively short interionic $\text{I}\cdots\text{O}$ distances of 3.02 and 2.90 Å. The water molecules are trigonally planar coordinated (2 IO_3^- , 1 Ca^{2+} , site symmetry C_1), forming asymmetric hydrogen bonds of different strengths to adjacent iodate ions. Deviation from random distribution of the H atoms has been established.

Comment

In contrast to the halate monohydrates of the heavy bivalent metal ions Sr^{2+} , Ba^{2+} and Pb^{2+} , which crystallize in $\text{Ba}(\text{ClO}_3)_2\cdot\text{H}_2\text{O}$ -type structures [$I2/c$; coordination number of metal ions > 8 (Kartha, 1952; Sikka *et al.*, 1968)], $\text{Ca}(\text{IO}_3)_2\cdot\text{H}_2\text{O}$ (Alici *et al.*, 1992) is isostructural with $\text{Ca}(\text{BrO}_3)_2\cdot\text{H}_2\text{O}$ (Rocchiccioli, 1960), crystallizing in the monoclinic space group $P2_1/c$. The structure refined from the neutron powder diffraction data presented in this work resembles that obtained from X-ray single-crystal data of the protonated compound (Alici *et al.*, 1992). The heavy-atom positions refined here, however, are less precise than those of the single-crystal data.

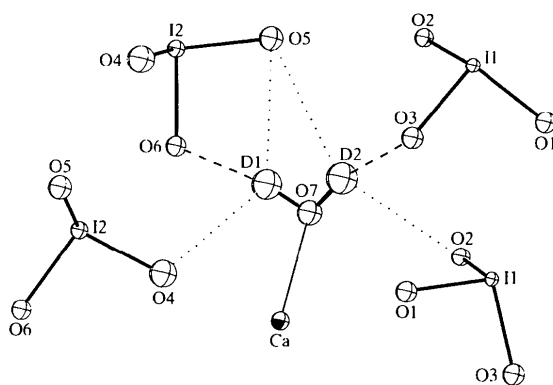


Fig. 1. Coordination of the water molecules in $\text{Ca}(\text{IO}_3)_2\cdot\text{D}_2\text{O}$, with hydrogen bonds indicated by dashed lines. Displacement ellipsoids are drawn at 50% probability.

The water molecules form two different, nearly linear, hydrogen bonds to adjacent iodate ions. The hydrogen-bond distances are $\text{D1}\cdots\text{O6}$ 1.963 (8) and $\text{D2}\cdots\text{O3}$ 2.067 (9) Å, respectively. For further details of the structure, especially the bond lengths between the heavy atoms, see Alici *et al.* (1992). The O–D stretching modes of isotopically diluted samples are 2558 and 2509 cm^{-1} [IR spectra, 295 K (Alici *et al.*, 1992)]. The structural geometry fits the $r(\text{O}\cdots\text{O})$ and $r(\text{H}\cdots\text{O})$ versus $\nu(\text{O}–\text{D})$ correlation diagrams (Mikenda, 1986), as well as the correlation of Brown's bond valences s versus $\nu(\text{O}–\text{D})$ (Brown, 1981; Lutz *et al.*, 1995; Lutz & Jung, 1997). The expected intramolecular O–D distances calculated from Brown's bond valences are $\text{O7}–\text{D1}$ 0.966 and $\text{O7}–\text{D2}$ 0.960 Å [experimental

bond lengths 0.965 (10) and 0.967 (9) Å, respectively]. By analogy with other highly deuterated hydrates (Lutz & Möller, 1993; Lutz *et al.*, 1994), we expected an enrichment of the H atoms at the position of the stronger, more linear, $\text{D1}\cdots\text{O6}$ hydrogen bond. The opposite was found for $\text{Ca}(\text{IO}_3)_2\cdot\text{D}_2\text{O}$, *viz.* 33% of the H atoms present are localized on the position of the stronger $\text{D1}\cdots\text{O6}$ hydrogen bond [occupancy factor 0.06 (2)], with 66% [0.12 (2)] being on the position of the weaker $\text{D2}\cdots\text{O3}$ hydrogen bond. The total refined hydrogen content (9 mol%, with 91 mol% D) is approximately equal to that used in the experimental preparation (10 mol%).

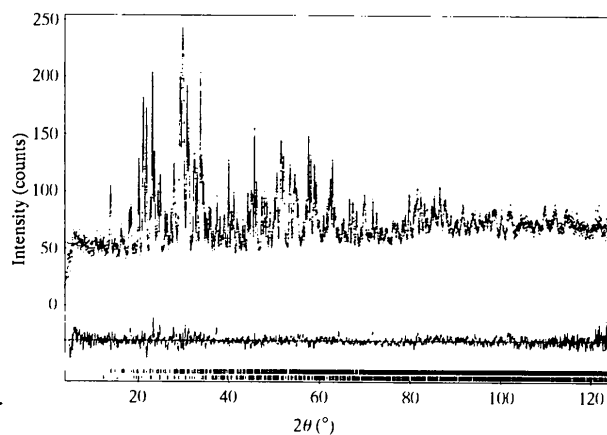


Fig. 2. Neutron diffraction pattern for $\text{Ca}(\text{IO}_3)_2\cdot\text{D}_2\text{O}$: ++++ observed, — fitted. The difference profile is shown underneath. The top row of tick marks indicates reflection positions for $\text{Ca}(\text{IO}_3)_2\cdot\text{D}_2\text{O}$, the second row those for $\text{Ca}(\text{IO}_3)_2\cdot 6\text{D}_2\text{O}$.

Experimental

By reaction of stoichiometric amounts of DIO_3 and CaCO_3 in a mixture of about 90 mol% D_2O and 10 mol% H_2O at 350 K, polycrystalline samples of highly deuterated $\text{Ca}(\text{IO}_3)_2\cdot\text{D}_2\text{O}$ were obtained. Surplus DIO_3 was removed by repeated washing with hot D_2O (pH > 6). DIO_3 was prepared by treating HIO_3 with D_2O several times. All preparations were performed in an Ar glove box.

Compound

Crystal data

$\text{Ca}(\text{IO}_3)_2\cdot\text{D}_2\text{O}$
 $M_r = 409.91$
 Monoclinic
 $P2_1/c$
 $a = 8.5161$ (4) Å
 $b = 10.0390$ (4) Å
 $c = 7.5138$ (3) Å
 $\beta = 95.372$ (3)°
 $V = 639.56$ (5) Å³
 $Z = 4$
 $D_x = 4.257$ Mg m⁻³
 D_m not measured

Neutron radiation (Ge
 monochromator)
 $\lambda = 1.2272$ Å
 Cell parameters from 2020
 reflections
 $\theta = 4.15–62.46^\circ$
 $\mu = 0.03313$ mm⁻¹
 $T = 293$ (2) K
 Specimen shape: cylinder
 $50 \times 8 \times 8$ mm
 Specimen prepared at
 293 (2) K
 White

Data collection

3T2 high resolution neutron powder diffractometer, LLB, Saclay (France)
Debye-Scherrer scans
Specimen mounting: vanadium can

Specimen mounted in reflection mode
Absorption correction: none
 $2\theta_{\min} = 4.0$, $2\theta_{\max} = 125.7^\circ$
Increment in $2\theta = 0.05^\circ$

Refinement

$R_p = 0.040$
 $R_{wp} = 0.046$
 $R_{exp} = 0.034$
 $R_B = 0.057$
 $2\theta_{\min} = 5.0$, $2\theta_{\max} = 125.0^\circ$
Increment in $2\theta = 0.05^\circ$
Wavelength of incident radiation: 1.2272 Å
Background fitted by a polynomial function

Profile function: pseudo-Voigt
70 parameters
All H atoms refined
Preferred orientation correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O4—D1	2.859 (9)	D1—O5 ⁱⁱ	2.668 (8)
O7—D1	0.965 (10)	D2—O3 ⁱⁱⁱ	2.067 (9)
O7—D2	0.967 (9)	D2—O2 ⁱ	2.690 (9)
D1—O6 ⁱ	1.963 (8)	D2—O5 ⁱⁱ	2.936 (9)
D1—O7—D2	103.7 (14)	O7—D2—O3 ⁱⁱⁱ	158 (4)
O7—D1—O6 ⁱ	165(5)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, y, 1+z$; (iii) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The neutron powder diffraction experiment on highly deuterated Ca(IO₃)₂.D₂O (91 mol% D according to structure refinement) was performed at ambient temperature. Starting values of Ca, I, O and D/H were taken from the positional parameters of the X-ray single-crystal data (Alici *et al.*, 1992). Altogether, 70 parameters were refined: lattice constants a , b , c and β , instrumental resolution parameters u , v and w , scale factor, zero point, asymmetry parameters, pseudo-Voigt function (ratio Gaussian:Lorentzian), fractional coordinates, isotropic atomic displacement factors, and D/H site occupancy. Reflections from the hexahydrate, Ca(IO₃)₂.6D₂O [< 1 weight%;

neutron single-crystal data (Suchanek *et al.*, 1997)], were considered in the structure refinement. The scattering lengths used for Ca, I, O, D and H were 4.700, 5.280, 5.803, 6.671 and -3.7409 fm, respectively (*International Tables for Crystallography*, Vol. C, 1992).

Data collection: 3T2 diffractometer local software. Cell refinement: *FULLPROF* (Rodriguez-Carvajal, 1990). Program(s) used to refine structure: *FULLPROF*. Molecular graphics: *ORTEP* (Johnson, 1965).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1201). Services for accessing these data are described at the back of the journal.

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