Table 1. *Fractional atomic coordinates and B_{eq} values (B_{iso} for H) according to Hamilton (1959), with e.s.d.'s in parentheses*

m is the site-occupation factor.

	m	*x*	*y*	*z*	B_{eq}(Å^2)
La	$\frac{1}{6}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	1·42 (2)
Cl	$\frac{1}{2}$	0·7600 (4)	0	0	3·7 (1)
O	1	0·4358 (12)	0·2520 (11)	0·0149 (9)	3·3 (3)
Aq	$\frac{1}{2}$	0·5574 (19)	0·5798 (17)	$\frac{1}{4}$	3·5 (5)
H	1	0·560	0·659	0·153	2·3

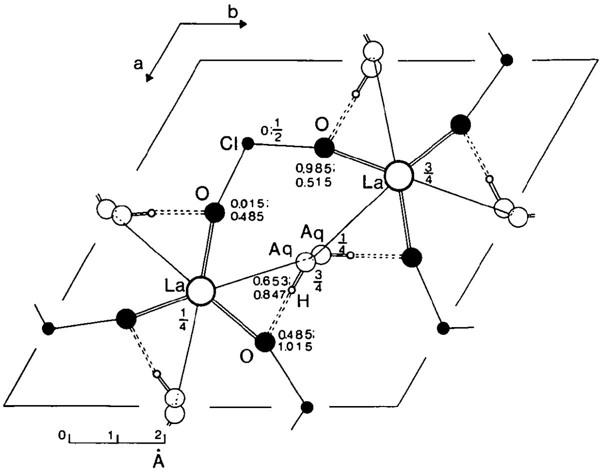

Fig. 1. Projection of one cell along **c**. The double lines denote two superimposed bonds running upwards and downwards respectively. Similarly each of the double-dashed lines represents a pair of hydrogen bonds.

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°), *e.s.d.'s in parentheses*

La—O	2·547 (7)	Aq(—H···)—O^{iii}	2·89 (1)
La—Aq	2·550 (11)	Aq—H	1·02
Cl^{i}—O	1·540 (8)	H—Aq—H^{iv}	104·0
O—Cl^{i}—O^{ii}	114·0 (7)	Aq—H—O^{iii}	176·1

Symmetry code

(i) $1 - x, y - x + 1, \bar{z}$

(ii) $y, x, \bar{z}$

(iii) $y - x + 1, 1 - x, z$

(iv) $x, y, \frac{1}{2} - z$

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The Deuterium-Atom Positions in Deuterated Molybdic Acid, $MoO_3.2D_2O$, by Powder Neutron Diffraction

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Abstract. $M_r = 184·0$, monoclinic, $P2_1/n$, $a = 10·487$ (1), $b = 13·850$ (1), $c = 10·617$ (1) Å, $\beta = 91·62$ (9)°, $V = 1541·5$ Å^3, $Z = 16$, $D_x = 3·17$ g cm^{-3}, $\lambda = 1·909$ Å, $\mu = 0·032$ cm^{-1}, $T = 298$ K. The D-atom positions in $MoO_3.2D_2O$ have been obtained from profile analysis of powder neutron diffraction data. The profile, arising from 1530 overlapping reflections, was refined to $R_{wp} = 9·8$ using the Rietveld method. It was not found necessary to apply a linear absorption correction.

Introduction. $MoO_3.2H_2O$ is one of three stoichiometric hydrates of MoO_3 collectively known as molybdic acids. The two remaining phases are the yellow and white forms of the monohydrate, $MoO_3.H_2O$.

Single-crystal X-ray studies on $MoO_3.2H_2O$ (Krebs, 1972; Åsbrink & Brandt, 1971) have shown that the structure consists of infinite layers of distorted MoO_6 octahedra, each sharing four vertices with neighbouring octahedra. Of the two terminal O atoms in each octahedron, one is replaced by a coordinated

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H_2O group giving the layer composition $[MoO_{4/2}O(H_2O)]_n$. The remaining water molecules are not bonded to Mo but are present as hydrate water between the layers, participating in an extensive network of hydrogen bonding with both coordinated H_2O groups and layer O atoms. A diagram illustrating the structure has been deposited* [see also Fig. 4 in Krebs (1972)].

Both previous single-crystal X-ray studies of $MoO_3.2H_2O$ attempted to refine the H-atom positions but with limited success leading to chemically unreasonable parameters for the water-molecule geometries and poor agreement of the calculated NMR second moment with the experimentally determined value (Jarman, Dickens & Slade, 1981). This paper reports the determination of the D-atom positions in $MoO_3.2D_2O$ by powder neutron diffraction.

Table 1. *Final parameters for* $MoO_3.2D_2O$ *at* 298 K

E.s.d.'s of refined parameters are in parentheses. The parameters quoted for atoms other than D are those of Krebs (1972). For the purposes of bond-length/angle calculations the e.s.d.'s of the O-atom parameters are taken from Krebs as 0·0003 for *x* and *z*, and 0·0002 for *y*.

	x	*y*	*z*	B_{iso}(Å^2)
Mo(1)	0·11729	0·24968	0·14710	0·99
Mo(2)	0·39389	0·25528	0·35964	0·98
Mo(3)	−0·13721	0·25189	0·39802	1·04
Mo(4)	0·15387	0·24499	0·61827	1·01
O(1)	0·0216	0·2543	−0·0255	1·20
O(2)	0·2313	0·2085	0·2661	1·14
O(3)	0·2635	0·2087	0·0192	1·21
O(4)	−0·0266	0·2438	0·2287	1·39
O(5)	0·4812	0·2623	0·2190	1·46
O(6)	0·2716	0·2094	0·5116	1·15
O(7)	−0·2695	0·2958	0·2652	1·20
O(8)	0·0146	0·2539	0·4779	1·50
O(9)	0·1520	0·3685	0·1431	1·65
O(10)	0·3423	0·3727	0·3770	1·60
O(11)	−0·1723	0·1334	0·3897	1·78
O(12)	0·1737	0·3662	0·6288	1·86
O(13)	0·0838	0·0889	0·1107	1·47
O(14)	0·4146	0·0910	0·3514	1·59
O(15)	−0·0884	0·4106	0·3610	1·40
O(16)	0·0920	0·0857	0·6003	1·35
O(17)	0·3593	0·5011	0·1288	2·07
O(18)	0·3612	0·5119	0·6243	2·52
O(19)	0·1426	0·5035	0·3762	1·89
O(20)	−0·1339	0·4896	0·1234	2·07
D(1)	0·0040 (13)	0·0588 (12)	0·1223 (13)	4·3 (3)
D(2)	0·1061 (13)	0·0666 (12)	0·0313 (12)	2·9 (3)
D(3)	0·3905 (12)	0·0610 (12)	0·2786 (12)	3·6 (3)
D(4)	0·4931 (14)	0·0604 (13)	0·3648 (13)	3·4 (3)
D(5)	−0·0027 (12)	0·4339 (10)	0·3779 (11)	3·3 (3)
D(6)	−0·1132 (14)	0·4333 (13)	0·2774 (12)	3·4 (3)
D(7)	0·1124 (12)	0·0582 (11)	0·5219 (13)	3·8 (3)
D(8)	0·0051 (14)	0·0624 (14)	0·6192 (13)	3·4 (3)
D(9)	0·2859 (14)	0·4587 (11)	0·1324 (13)	5·4 (4)
D(10)	0·3455 (16)	0·5606 (14)	0·1685 (14)	4·6 (4)
D(11)	0·2925 (14)	0·4643 (14)	0·6293 (13)	4·8 (3)
D(12)	0·3566 (13)	0·5442 (11)	0·7029 (13)	3·9 (4)
D(13)	0·2112 (13)	0·4636 (11)	0·3837 (13)	4·7 (3)
D(14)	0·1414 (18)	0·5361 (14)	0·4525 (13)	5·2 (5)
D(15)	−0·2069 (16)	0·5388 (14)	0·1159 (14)	4·8 (3)
D(16)	−0·1501 (14)	0·4445 (12)	0·0669 (12)	4·3 (4)

Experimental. Sample of $MoO_3.2D_2O$ prepared by Freedman's (1959) method using fully deuterated reagents. The IR spectrum of the product showed it to be completely deuterated and thermogravimetric analysis gave the composition as $MoO_3.(2\cdot00 \pm 0\cdot01)D_2O$. Neutron powder diffraction measurements on the sample (~10 g), contained in a thin-walled vanadium can, performed at 298 K and atmospheric pressure using a wavelength of 1·909 Å on the D1A high-resolution diffractometer at the High Flux Reactor, ILL, Grenoble. Data collected in steps of 0·05° between 6 and 154° in 2θ; scan took about 18 h. The powder neutron profile for $MoO_3.2D_2O$ could be indexed in space group $P2_1/n$ (No. 14, non-standard orientation) using the lattice parameters of Krebs (1972), which were later refined. The least-squares refinement program used was a modification of the AERE (Harwell) version (Hewat, 1973) of the Rietveld (1969) method implemented on the ICL 2980 computer at Oxford. $M = \sum_i w_i[y_i(\text{obs.}) - cy_i(\text{calc.})]^2$ minimized, where w_i is the weighting function, y_i is the number of counts at the point $2\theta_i$ (after subtracting the background) and c is the scale factor. Background estimated at 10° intervals on the profile, other values by interpolation. Weighting function: $w_i = 1/Y_i$, where Y_i is the number of counts at $2\theta_i$ before correction for background. Scattering lengths: Mo 6·90, O 5·80, D 6·67 fm (Bacon, 1975). The asymmetric unit of $MoO_3.2D_2O$ contains 40 atoms. Only positional and isotropic thermal parameters of the 16 D atoms, the scale factor, three half-width parameters, the zero-point correction and the lattice parameters, *i.e.* a total of 73 parameters, varied [in line with the recent recommendation of Albinati & Willis (1982) concerning the number of parameters which may realistically be refined]. Mo- and O-atom parameters, including isotropic thermal parameters, fixed at the values determined by Krebs (1972) [use of the values of Åsbrink & Brandt (1971) produced no significant differences in the D positions obtained in the refinement]. Starting parameters of the D atoms obtained from the H-atom positions of Krebs (1972). All site occupancies fixed at unity. Regions of the profile from $2\theta_i = 6$ to 30° and 140 to 154° excluded from refinement; the former to avoid an asymmetry correction to the peak shape and the latter due to deterioration in the quality of the profile. Inclusion of a preferred-orientation parameter found to be unnecessary. Final $R_{wp} = 100\{\sum_i w_i[y_i(\text{obs.}) - cy_i(\text{calc.})]^2/w_i[y_i(\text{obs.})^2]\}^{1/2} = 9\cdot8$.* The final atom parameters are given in Table 1. The parameter shifts in the last refinement cycle were $\le 0\cdot05\sigma$ [as calculated according to the original Rietveld formulation (Sakata & Cooper,

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* See deposition footnote.

* A list of each measured point on the profile for $MoO_3.2D_2O$ and a figure illustrating the structure have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39354 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1979)]. The agreement between observed and calculated profiles is shown in Fig. 1.

Discussion. The hydrogen-bonded water network in $MoO_3.2D_2O$ is illustrated in Fig. 2. Bond distances and angles for the water molecules and the network of hydrogen bonds are given in Table 2. The system of atom labelling used in Table 2 is shown in Fig. 3 which schematically illustrates the essential arrangement of water molecules and hydrogen bonds.

A coordinated D_2O group in a particular layer participates in a single hydrogen bond with each of two interlayer water molecules. Each interlayer water molecule participates in single hydrogen bonds with two coordinated D_2O groups in adjacent layers and a terminal O atom. The interlayer water molecule is further involved in a bifurcated hydrogen bond with a coordinated D_2O group and a bridging O atom. Groups of four D_2O units consisting of two coordinated D_2O groups in adjacent layers together with two interlayer water molecules are linked *via* single hydrogen bonds to form an approximate square such that neither type of water is hydrogen bonded to another of the same type. There is no contact between the squares *via* single hydrogen bonds.

Reference to a recent review of the geometries and environments of water molecules in crystalline hydrates studied by neutron diffraction (Chiari & Ferraris, 1982) shows that the values quoted in Table 2 are in agreement with those typically found in hydrates with the single exception of the bond angle in the coordinated group D(3)—O(14)—D(4) [however, it should be noted that the D-atom positions found for this molecule represent definite minima in the refinement which remain unchanged when either the atom coordinates of Åsbrink & Brandt (1971) or different initial parameters for the D atoms are used].

A check on the overall accuracy of the D-atom positions found in the refinement is provided by the good agreement of the rigid-lattice NMR second moment of $MoO_3.2H_2O$ calculated on the basis of the D positions in Table 2 (40 ± 3 G^2) (1 G = 10^{-4}T) compared with the experimental value (36 ± 1 G^2) (Jarman *et al.*, 1981). The slightly high value of the calculated second moment is caused by the anomalously small value of the D···D separation in the coordinated group D(3)—O(14)—D(4).

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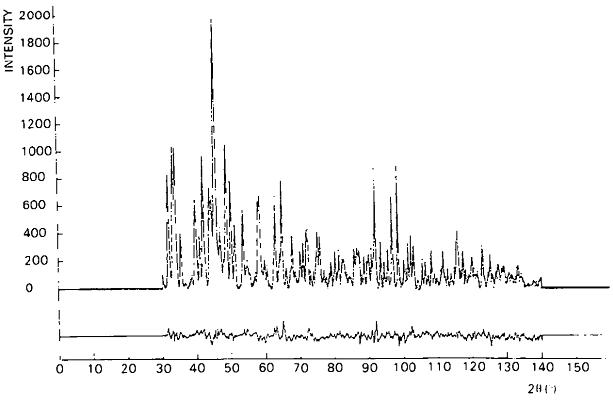

Fig. 1. Observed (points), calculated (line) and difference profiles for $MoO_3.2D_2O$ at 298 K and 1·909 Å.

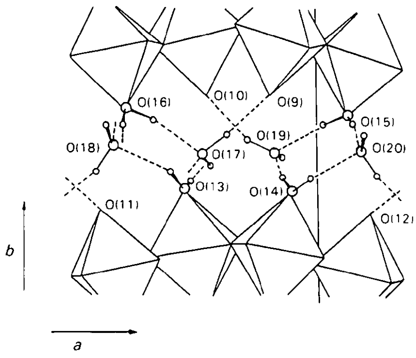

Fig. 2. The water network in $MoO_3.2D_2O$. For clarity the bifurcated hydrogen bonds are not shown (after Krebs, 1972).

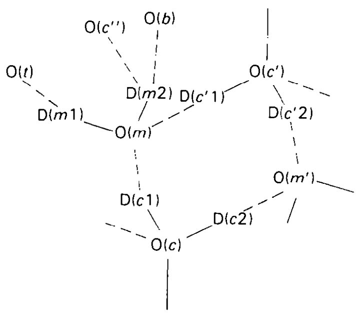

Fig. 3. Schematic diagram of the water network in $MoO_3.2D_2O$. The labels c (also c' and c'') refer to coordinated D_2O (with $c = 13$ to 16) while m (and m') refer to interlayer D_2O (with $m = 17$ to 20). O(t) is a terminal oxygen (with $t = 9$ to 12) and O(b) is a bridging oxygen (with $b = 2, 3, 6$ or 7).

Table 2. *Bond distances* (Å) *and angles* (°) *for the water network in* $MoO_3.2D_2O$ *at* 298 K

E.s.d.'s are in parentheses. The atom labelling corresponds to that used in Fig. 3.

(*a*) Originating from the coordinated D_2O groups

	*c*1	O(*c*) – D(*c*1)		*m*	O(*c*) – O(*m*)	D(*c*1) – O(*m*)	O(*c*) – D(*c*1) – O(*m*)
c			D(*c*1) – O(*c*) – D(*c*2)				
	*c*2	O(*c*) – D(*c*2)		*m'*	O(*c*) – O(*m'*)	D(*c*2) – O(*m'*)	O(*c*) – D(*c*2) – O(*m'*)
	1	0·95 (3)		18^{i}	2·73 (1)	1·79 (3)	170·4 (15)
13			102·5 (15)				
	2	0·93		18^{ii}	2·79	1·86	174·1
	3	0·91		19^{ii}	2·75	1·85	174·1
14			98·4				
	4	0·93		20^{ii}	2·70	1·77	172·2
	5	0·97		19	2·74	1·80	163·3
15			106·6				
	6	0·97		20	2·78	1·82	169·6
	7	0·95		17^{ii}	2·76	1·82	175·9
16			106·2				
	8	0·99		17^{iii}	2·75	1·77	166·7

(*b*) Originating from the interlayer D_2O molecules

	*m*1	O(*m*) – D(*m*1)		*t*	O(*m*) – O(*t*)	D(*m*1) – O(*t*)	O(*m*) – D(*m*1) – O(*t*)
m			D(*m*1) – O(*m*) – D(*m*2)				
	*m*2	O(*m*) – D(*m*2)		*c''*	O(*m*) – O(*c''*)	D(*m*2) – O(*c''*)	O(*m*) – D(*m*2) – O(*c''*)
				b	O(*m*) – O(*b*)	D(*m*2) – O(*b*)	O(*m*) – D(*m*2) – O(*b*)
	9	0·97 (3)		9	2·85 (1)	1·89 (3)	175·6 (15)
17			112·4 (15)				
	10	0·94		13^{iv}	3·06	2·47	121·3
				2^{iv}	3·23	2·32	166·2
	11	0·98		12	2·82	1·84	174·0
18			102·4				
	12	0·95		16^{v}	3·12	2·22	158·9
				7^{vi}	3·08	2·42	125·6
	13	0·91		10	2·77	1·87	171·3
19			104·5				
	14	0·93		15^{vi}	3·10	2·20	163·6
				3^{iv}	3·20	2·60	122·2
	15	1·03		11^{vii}	2·85	1·82	175·0
20			106·8				
	16	0·88		14^{i}	3·15	2·46	136·5
				6^{i}	3·15	2·35	150·8

Roman numerals attached to atom labels refer to the following transformations of the coordinates given in Table 1. (i) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $-x, 1-y, 1-z$; (vii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

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The Structure of Barium Aluminate, $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$

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Abstract. $M_r = 675\cdot8$, $P6_3/mmc$, $a = 5\cdot582$ (2), $c = 22\cdot715$ (3) Å, $V = 612\cdot9$ (1) Å^3, $Z = 2$, $D_x = 3\cdot662$ (1) g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 42\cdot14$ cm^{-1}, $F(000) = 646\cdot45$, $T = 293$ K, $R = 0\cdot025$ for 317 observed reflections. The compound almost has the sodium aluminate structure. Instead of BaO layers, layers are found in which one of every four Ba's is replaced by an O to obtain, in combination with the

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