Table 5. *Mean cation–oxygen distances* (Å) *in four isostructural compounds of the type* $A^{II}_3 B^{IV} C^{III}_{10} O_{20}$

$Pb_3GeGa_{10}O_{20}$		$Pb_3GeAl_{10}O_{20}$*		$Ba_3SnFe_{10}O_{20}$		$Ba_3TiAl_{10}O_{20}$†	
Pb(1)	2·69	Pb(1)	2·59	Ba(1)	2·79	Ba(1)	2·72
Pb(2)	2·82	Pb(2)	2·81	Ba(2)	2·89	Ba(2)	2·90
Ge	1·93	Al(1)	1·86	Oc(1)	2·05	TiAl(1)	1·90
Ga(1)	1·99	Al(2)	1·94	Oc(2)	2·07	TiAl(2)	1·95
Ga(2)	1·83	Al(3)	1·79	Fe(1)	1·87	Al(3)	1·77
Ga(3)	1·83	Al(4)	1·77	Fe(2)	1·86	Al(4)	1·76

* Vinek *et al.* (1970).
† Cadée *et al.* (1982).

The isotropic temperature factor of Ba(2) in $Ba_3TiAl_{10}O_{20}$, which has an irregular nine-coordination, is high (1,62 Å^2) compared to Ba(1) (0·12 Å^2). This can be explained by the fact that Ba^{2+} favours a more regular coordination. In $Ba_3SnFe_{10}O_{20}$ these differences are not large, probably due to the high temperature of the diffraction measurement, 873 K.

In $Ba_3TiAl_{10}O_{20}$ a slight preference of Ti for the Oc(2) site can be observed from the mean cation–O distances of the octahedral sites (Table 5), opposite to the preference of Sn in $Ba_3SnFe_{10}O_{20}$.

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A Neutron Diffraction Determination of the Structure of Deuterated Aluminium Nitrate Nonahydrate, Al(NO₃)₃.9D₂O

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Abstract. $M_r = 393·26$, monoclinic, $P2_1/c$, $a = 13·8937$ (14), $b = 9·6258$ (7), $c = 10·9127$ (7) Å, $\beta = 95·66$ (1)°, $V = 1452·3$ (2) Å^3, $T = 295$ K [the cell parameters were determined from the refinement of 39 θ values from a Guinier–Hägg X-ray powder film (Cr $K\alpha$ radiation, $\lambda = 2·28975$ Å, using a CoP₃ standard: $a = 7·70778$ Å)], $Z = 4$, $D_x = 1·80$ Mg m^{-3}, final $R_w(F^2) = 0·069$ for all 4480 independent reflections collected out to $\sin\theta/\lambda = 0·69$ Å^{-1}. The crystal structure of Al(NO₃)₃.9D₂O has been studied by three-dimensional neutron diffraction data collected at 295 K. The asymmetric unit contains Al(D₂O)₆³⁺ octahedra, NO₃⁻ ions and three D₂O molecules which are not coordinated to Al³⁺ ions. All nine water molecules in the formula unit are crystallographically independent and the 19 hydrogen bonds donated have O···O distances in the range 2·650 (2)–3·054 (2) Å. The hydrogen bonds donated by the D₂O molecules which are coordinated to Al³⁺ ions are shorter than the other hydrogen bonds. A distinct correlation exists between the O—D and D···O distances.

Introduction. The present room-temperature study was undertaken to obtain a detailed picture of the hydrogen bonding in Al(NO₃)₃.9D₂O prior to a low-temperature electron density study. An earlier determination of the structure of Al(NO₃)₃.9H₂O from film data (Herpin & Sudarsanan, 1965) roused interest in the compound, since the nine H₂O molecules were crystallographically independent and donated hydrogen bonds spanning a wide range of O···O lengths. Errors in the earlier structure determination made it impossible to fit the structure to the neutron diffraction data. A redetermination of the structure was therefore essential, and could most readily be achieved from X-ray data. A low-accuracy X-ray data set was collected and the

correct non-hydrogen-atom positions thus obtained were used as starting values in the refinement of the neutron data.

Experimental. The neutron diffraction study was carried out on the deuterated compound in order to avoid the effect of incoherent scattering obtained from crystals with a high proportion of H atoms.

Polycrystalline $Al(NO_3)_3.9D_2O$ was formed from repeated recrystallizations in a dry-box at room temperature. Well shaped crystals were easily obtained by slow evaporation. The final D content in the batch was 97%, on the basis of the relative intensities of the OD and OH stretching bands in the infrared spectrum (assuming an absorption-coefficient ratio of 0·5 for OD and OH stretching bands). The D content was again checked after the data collection by removing a small piece from the crystal used. No change was observed in the D/H ratio. A refinement of the occupancies of the D atoms at the final stage of the least-squares refinement yielded occupancies between 0·988 (3) and 0·997 (4), corresponding to a D content between 99·2 and 99·8%. Two independent methods thus confirm the high degree of deuteration. A plate-like crystal (maximum dimension: 5·8 mm) was glued with Araldite on to an aluminium pin and sealed in a thin-walled quartz-glass bulb. Some experimental details for the data collection are given in Table 1. For a more complete description of the apparatus see, for example, Hermansson, Thomas & Olovsson (1980). The three test reflections were used to obtain a scaling function which was then applied to the whole data set. Integrated intensities were obtained by the peak-profile-analysis technique of Lehmann & Larsen (1974). Lorentz and absorption corrections were also made, the latter using a Gaussian grid of $8 \times 8 \times 8$ points and $\mu = 0.049$ mm⁻¹. This was derived by measuring the intensity attenuation of the primary beam through an $Al(NO_3)_3.9D_2O$ crystal positioned over a small hole in a Cd plate placed at the aperture to the detector.

Structure refinement. The non-hydrogen-atom sites obtained in the X-ray structure determination and refinement were inserted in a difference Fourier synthesis calculation to reveal all 18 D positions. These parameters were then used as input to the full-matrix least-squares refinement program *UPALS* (Lundgren, 1982). The quantity minimized was $\sum w(F_o^2-F_c^2)^2$, where $w^{-1} = \sigma^2_{count}$ $(F_o^2) + (kF_o^2)^2$. The value of k was set empirically to 0·02, on the basis of the weight analysis following the least-squares refinement cycles. In the final cycles of refinement a total of 370 parameters were refined: one scale factor, six anisotropic extinction parameters, positional and anisotropic thermal parameters for all 41 atoms except Al which was fixed at (0,0,0) and $(\frac{1}{2},0,\frac{1}{2})$. Using the definition $F_{o,uncorr.}^2 = \gamma F_{o,ext.corr.}^2$, 16 reflections (out of 4045) had $y < 0.40$ and were excluded from the refinements. 12%

Table 1. *Neutron data collection and R values*

Reactor	R2 at AB Atomenergi, Studsvik, Sweden
Diffractometer	Hilger & Watts four-circle
Temperature (K)	295 (± 1)
λ(Å)	1·210 (4)
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0·69
Scanning mode	ω–2θ step scanning
Scan interval in θ	1·80° for 0° < θ < 50° 2·00° for 50° < θ < 57°
Total No. of independent reflections	4480 (excluding test reflections)
No. of test reflections	3 (600, 040, 006; intensity decrease < 3% for each)
Reflections collected	±hkl
No. of unique reflections	4045 (after removal of extinct and +$hk0$ reflections)
Crystal volume (mm³)	50·9
μ_{obs}(mm⁻¹)	0·0488 (2)
T_{range} absorption-weighted (mm)	2·1–4·6
Transmission range	0·79–0·90
Extinction level ($F_{o,uncorr.}^2 = yF_{o,corr.}^2$)	12% of reflections had $y < 0.85$

$R(F^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2 = 0.056$ (all reflections); 0·046 $[F_o^2 > 3\sigma(F_o^2)]$

$R_w(F^2) = [\sum w(|F_o^2 - F_c^2|)^2/\sum wF_o^4]^{1/2} = 0.069$ (all reflections); 0·062 $[F_o^2 > 3\sigma(F_o^2)]$

$R(F) = \sum ||F_o| - |F_c||/\sum |F_o| = 0.068$ (all reflections); 0·037 $[F_o^2 > 3\sigma(F_o^2)]$

of the whole data set had $y < 0.85$. The extinction correction was made according to the Becker & Coppens (1975) formalism using a type I model with an anisotropic Lorentzian mosaic spread distribution as given by Thornley & Nelmes (1974). Various models for the mosaic spread were tested, but did not change the result significantly. The scattering lengths used in the refinements were $b_{Al} = 3.45$, $b_O = 5.80$, $b_D = 6.674$ and $b_N = 9.36$ fm (Koester & Steyerl, 1977). The R values from the final refinement are listed in Table 1. The standard deviation of unit weight, S, was 1·6 and the δR plot (Abrahams & Keve, 1971) gave a straight line with intercept 0·03 and slope 0·68. No features in the residual map calculated after the final refinement corresponded to more than 2·5% of the maximum peak height in an F_o synthesis map.*

Discussion. The final positional parameters are listed in Table 2. A stereoscopic illustration of a 'representative' part of the unit cell is given in Fig. 1. Interatomic distances and angles are listed in Table 3.

The structure is seen to comprise $Al(D_2O)_6^{3+}$ octahedra, NO_3^- ions and D_2O molecules linked together by hydrogen bonds to form a three-dimensional network.

The NO_3^- ions are roughly parallel to the ac plane and act as hydrogen-bond acceptors to connect $Al(D_2O)_6^{3+}$ octahedra from adjacent layers as well as to join octahedra within the same layer. There are three independent D_2O molecules which are not coordinated to an Al^{3+} ion; two of these, $D_2O(7)$ and $D_2O(8)$, are situated close to the $Al(D_2O)_6$ layers and participate in the bonding between octahedra in the same layer, whereas the third, $D_2O(9)$, is situated between the layers and links together three NO_3^- ions and two $D_2O(7)$ molecules. All atoms belonging to the three independent D_2O molecules around $Al(1)^{3+}$ [*i.e.* $D_2O(1)$, $D_2O(2)$ and $D_2O(3)$] have their counterparts in the coordination octahedron around $Al(2)^{3+}$ [*i.e.* $D_2O(4)$, $D_2O(5)$ and $D_2O(6)$] such that the vectors relating corresponding atoms are all close to $(\frac{1}{2}, 0, \frac{1}{2})$. The surroundings of the corresponding D_2O molecules are very similar in the two octahedra, with the exception of D(31) and D(61) (see Fig. 3), where the interatomic vector in fractional coordinates is (0·538, 0·003, 0·551). In the same way, the $NO_3(1)^-$ and $NO_3(2)^-$ ions and the $D_2O(7)$ and $D_2O(8)$ molecules, respectively, are almost related by a B-centring translation but small deviations exist due to differences in the immediate surroundings.

Table 2. *Atomic coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* (*expressed as average r.m.s. amplitudes*)

	x	y	z	$\bar{U}$ (Å)
Al(1)	0	0	0	0·123
Al(2)	50000	0	50000	0·131
O(1)	−9324 (8)	14218 (13)	−503 (12)	0·147
O(2)	−6740 (9)	91481 (14)	−13694 (12)	0·154
O(3)	−7161 (9)	89528 (14)	10555 (12)	0·154
O(4)	40294 (9)	13749 (15)	49948 (13)	0·169
O(5)	43034 (9)	90892 (15)	36852 (12)	0·160
O(6)	43277 (10)	89011 (16)	60810 (12)	0·165
O(7)	−3365 (9)	62175 (15)	12984 (13)	0·168
O(8)	45115 (10)	61394 (16)	63062 (13)	0·174
O(9)	14398 (11)	52637 (18)	4961 (15)	0·190
D(11)	−14706 (9)	14983 (14)	−6914 (13)	0·190
D(12)	−10360 (9)	19900 (14)	6685 (13)	0·188
D(21)	−5145 (9)	91519 (14)	−22245 (12)	0·185
D(22)	−12550 (9)	85689 (14)	−13313 (12)	0·185
D(31)	−13433 (9)	92289 (15)	12980 (13)	0·194
D(32)	−5893 (9)	79558 (15)	11947 (12)	0·190
D(41)	35090 (9)	14770 (15)	43248 (13)	0·194
D(42)	38766 (10)	18943 (15)	57197 (13)	0·198
D(51)	43954 (9)	90933 (15)	28053 (12)	0·190
D(52)	36604 (9)	86865 (15)	37702 (12)	0·190
D(61)	40403 (10)	91948 (16)	68094 (14)	0·203
D(62)	44545 (10)	78965 (17)	61548 (13)	0·200
D(71)	−7649 (11)	57073 (16)	6967 (14)	0·206
D(72)	3138 (11)	60181 (17)	11007 (14)	0·214
D(81)	40060 (11)	56733 (18)	57872 (14)	0·215
D(82)	51068 (11)	56624 (21)	61992 (15)	0·231
D(91)	18199 (14)	47671 (28)	11058 (20)	0·284
D(92)	18818 (12)	58516 (20)	1120 (17)	0·230
N(1)	−20156 (5)	31140 (8)	20716 (7)	0·152
O(11)	−23725 (10)	16550 (18)	−19567 (12)	0·187
O(12)	−11407 (9)	28590 (17)	20593 (13)	0·186
O(13)	25454 (9)	81326 (16)	39381 (12)	0·170
N(2)	28520 (5)	21283 (8)	21941 (7)	0·160
O(21)	25757 (10)	34017 (18)	81405 (14)	0·193
O(22)	37202 (10)	23821 (19)	21382 (15)	0·205
O(23)	−22517 (10)	75765 (16)	−13034 (13)	0·181
N(3)	30616 (5)	50930 (8)	37286 (7)	0·158
O(31)	38405 (10)	95334 (18)	83529 (14)	0·196
O(32)	30172 (12)	48723 (21)	48291 (14)	0·220
O(33)	23196 (10)	49602 (17)	30043 (14)	0·189

Table 3. *Interatomic distances* (Å) *and angles* (°) *for* $Al(NO_3)_3.9D_2O$

(*a*) $Al(D_2O)_6^{3+}$ octahedra

Al(1)–O(1)	1·881 (1)	O(1)–Al(1)–O(2)	90·38 (6)
–O(2)	1·873 (1)	O(1)–Al(1)–O(3)	90·20 (5)
–O(3)	1·886 (1)	O(2)–Al(1)–O(3)	90·06 (6)
Al(2)–O(4)	1·889 (1)	O(4)–Al(2)–O(5)	90·62 (6)
–O(5)	1·868 (1)	O(4)–Al(2)–O(6)	90·15 (6)
–O(6)	1·897 (1)	O(5)–Al(2)–O(6)	91·93 (6)

(*b*) NO_3^- ions

N(1)–O(11)	1·234 (1)	O(11)–N(1)–O(12)	121·4 (1)
–O(12)	1·242 (1)	O(11)–N(1)–O(13)	119·9 (1)
–O(13)	1·263 (1)	O(12)–N(1)–O(13)	118·7 (1)
N(2)–O(21)	1·246 (2)	O(21)–N(2)–O(22)	120·2 (1)
–O(22)	1·238 (2)	O(21)–N(2)–O(23)	120·1 (1)
–O(23)	1·249 (2)	O(22)–N(2)–O(23)	119·7 (1)
N(3)–O(31)	1·247 (2)	O(31)–N(3)–O(32)	120·0 (1)
–O(32)	1·227 (2)	O(31)–N(3)–O(33)	120·9 (1)
–O(33)	1·242 (2)	O(32)–N(3)–O(33)	119·1 (1)

(*c*) D_2O molecules and hydrogen bonds: distances

	O–D	O···O	D···O
O(1)–D(11)···O(11)	0·975 (2)	2·750 (2)	1·777 (2)
O(1)–D(12)···O(12)	0·979 (2)	2·726 (2)	1·752 (2)
O(2)–D(21)···O(7)	0·980 (2)	2·656 (2)	1·692 (2)
O(2)–D(22)···O(23)	0·985 (2)	2·670 (2)	1·685 (2)
O(3)–D(31)···O(33)	0·972 (2)	2·722 (2)	1·766 (2)
O(3)–D(32)···O(7)	0·985 (2)	2·693 (2)	1·711 (2)
O(4)–D(41)···O(21)	0·981 (2)	2·723 (2)	1·742 (2)
O(4)–D(42)···O(22)	0·977 (2)	2·699 (2)	1·731 (2)
O(5)–D(51)···O(8)	0·981 (2)	2·650 (2)	1·675 (2)
O(5)–D(52)···O(13)	0·986 (2)	2·650 (2)	1·666 (2)
O(6)–D(61)···O(31)	0·966 (2)	2·703 (2)	1·764 (2)
O(6)–D(62)···O(8)	0·985 (2)	2·680 (2)	1·701 (2)
O(7)–D(71)···O(9)	0·974 (2)	2·761 (2)	1·791 (2)
O(7)–D(72)···O(9')	0·969 (2)	2·851 (2)	1·901 (2)
O(8)–D(81)···O(32)	0·968 (2)	2·782 (2)	1·814 (2)
O(8)–D(82)···O(31)	0·963 (2)	2·757 (2)	1·849 (2)
O(9)–D(91)···O(23)	0·938 (2)	3·054 (2)	2·339 (3)
O(9)–D(91)···O(33)		2·900 (2)	2·127 (3)
O(9)–D(92)···O(13)	0·961 (2)	2·854 (2)	1·918 (2)

(*d*) D_2O molecules and hydrogen bonds: angles

|			
D(11)–O(1)–D(12)	111·7 (2)	O(1)–D(11)···O(11)	174·8 (1)
D(21)–O(2)–D(22)	107·8 (2)	O(1)–D(12)···O(12)	173·2 (1)
D(31)–O(3)–D(32)	112·1 (2)	O(2)–D(21)···O(7)	166·9 (2)
D(41)–O(4)–D(42)	110·4 (2)	O(2)–D(22)···O(23)	178·6 (2)
D(51)–O(5)–D(52)	107·5 (2)	O(3)–D(31)···O(33)	166·7 (2)
D(61)–O(6)–D(62)	107·8 (2)	O(3)–D(32)···O(7)	174·6 (1)
D(71)–O(7)–D(72)	105·7 (2)	O(4)–D(41)···O(21)	178·0 (2)
D(81)–O(8)–D(82)	106·9 (2)	O(4)–D(42)···O(22)	170·7 (2)
D(91)–O(9)–D(92)	105·7 (2)	O(5)–D(51)···O(8)	171·8 (2)
		O(5)–D(52)···O(13)	175·5 (2)
O(11)···O(1)···O(12)	117·88 (6)	O(6)–D(61)···O(31)	162·9 (2)
O(7)···O(2)···O(23)	100·00 (6)	O(6)–D(62)···O(8)	172·3 (2)
O(33)···O(3)···O(7)	118·09 (6)	O(7)–D(71)···O(9)	173·8 (2)
O(21)···O(4)···O(22)	116·05 (6)	O(7)–D(72)···O(9')	166·1 (2)
O(8)···O(5)···O(13)	105·31 (6)	O(8)–D(81)···O(32)	177·1 (2)
O(31)···O(6)···O(8)	99·76 (6)	O(8)–D(82)···O(31)	156·2 (2)
O(9)···O(7)···O(9')	93·02 (6)	O(9)–D(91)···O(23)	132·7 (3)
O(32)···O(8)···O(31)	113·25 (8)	O(9)–D(91)···O(33)	138·8 (3)
O(23)···O(9)···O(13)	116·79 (6)	O(9)–D(92)···O(13)	164·0 (2)
O(33)···O(9)···O(13)	114·53 (7)		
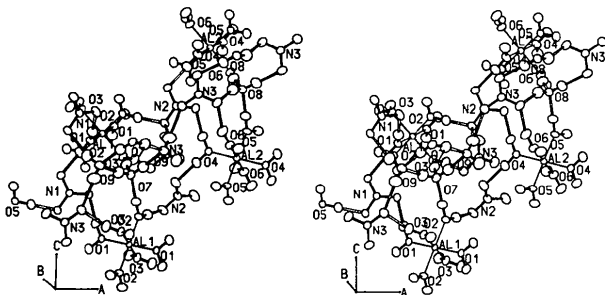
Fig. 1. A stereoscopic picture of the structure of $Al(NO_3)_3.9D_2O$. The thermal ellipsoids are drawn to include 50% probability.

The occurrence of the $NO_3(3)^-$ ions and the $D_2O(9)$ molecules in the structure destroys the B-centring; these two species are located in 'corresponding' regions of the structure, however, and their respective roles as hydrogen-bond acceptors in the bonding scheme are quite similar.

Thermal parameters. The thermal vibrational tensors are highly anisotropic for many of the atoms; in general, the U_{22} value is greater than the U_{11} and U_{33} values.

The isotropic r.m.s. amplitudes of vibration are given in Table 2. D(91) has a large average vibrational amplitude of 0·284 (2) Å. The isotropic r.m.s. amplitudes of vibration for the D atoms show a fair correlation with the O—D distances. This result is connected to the observed correlation between O—D and D···O distances, which will be discussed further below (and is displayed in Fig. 4).

The Al^{3+} ions. Both independent Al^{3+} ions coordinate six D_2O molecules to form almost regular octahedra. The Al^{3+}—O distances lie in the range 1·868 (1)—1·897 (1) Å with average values 1·880 and 1·885 Å for the $Al(1)^{3+}$ and $Al(2)^{3+}$ octahedra, respectively. In a limited literature survey of recently published X-ray diffraction studies nine different AlO_6 groups were found where the standard deviations of the individual Al—O distances were less than 0·02 Å. The average Al—O distance for each AlO_6 group was in the range 1·75—1·92 Å and the overall mean over all groups was 1·877 Å.

The NO_3^- ions. The environments around the three crystallographically independent NO_3^- ions are shown in Fig. 2. The $NO_3(1)^-$ and $NO_3(2)^-$ ions are almost related by a B-centring translation and the surroundings of the two ions are very similar. The $NO_3(1)^-$ and $NO_3(2)^-$ ions both accept four hydrogen bonds.

The $NO_3(3)^-$ ion accepts altogether five hydrogen bonds. In addition to its function as a link between $Al(1)(D_2O)_6^{3+}$ and $Al(2)(D_2O)_6^{3+}$ octahedra the $NO_3(3)^-$ ion bonds to one $D_2O(9)$ molecule and also participates in a ring system with two $D_2O(8)$ molecules:
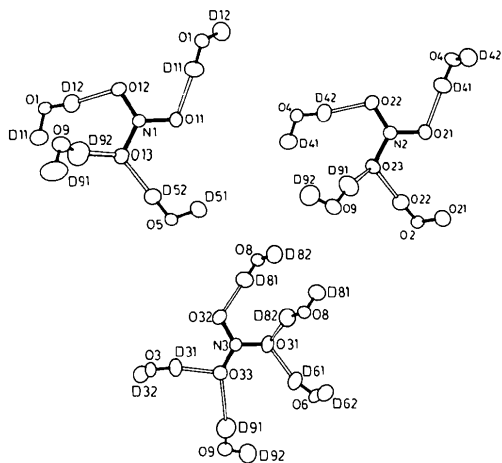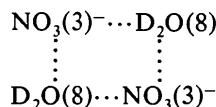
$$NO_3(3)^- \cdots D_2O(8)$$
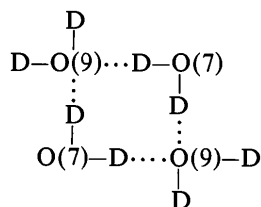$$\vdots \qquad \qquad \vdots$$
$$D_2O(8) \cdots NO_3(3)^-$$

The NO_3^- ions are planar. The N—O distances range from 1·227 (2) to 1·263 (1) Å. In general, the N—O distances are longer if the O atom is an acceptor of two hydrogen bonds instead of one. There is also a tendency towards longer N—O distances for shorter hydrogen bonds.

The hydrogen bonds accepted by the NO_3^- ions lie approximately in the planes of the ions [except for the D(92)···O(13), D(91)···O(23) and D(82)···O(31) bonds].

D_2O molecules and hydrogen bonds. The coordinations around each of the nine D_2O molecules are seen in Fig. 3. The six D_2O molecules bonded to Al^{3+} ions [*i.e.* $D_2O(1)$–$D_2O(6)$] have trigonal surroundings, which is the most common environment found for water molecules bonded to M^{3+} ions (Falk & Knop, 1973). Three D_2O molecules do not participate in $Al(D_2O)_6^{3+}$ octahedra: the $D_2O(7)$ and $D_2O(8)$ molecules which are tetrahedrally surrounded by hydrogen bonds and the $D_2O(9)$ molecule with a fivefold coordination.

All water molecules except $D_2O(9)$ donate *two* hydrogen bonds to two NO_3^- ions, two D_2O molecules or to one NO_3^- ion and one D_2O molecule. The $D_2O(9)$ molecule, however, is involved in a bifurcated bond scheme and donates *three* hydrogen bonds to $NO_3(1)^-$, $NO_3(2)^-$ and $NO_3(3)^-$ ions.

The $D_2O(9)$ molecule also participates as a deuteron acceptor in a ring system of the type

$$\begin{array}{ccc} & D & \\ & | & \\ D-O(9)\cdots D-O(7) \\ \vdots & & | \\ D & & D \\ | & & \vdots \\ O(7)-D\cdots O(9)-D \\ & | & \\ & D & \end{array}$$

The hydrogen bonds donated by $D_2O(7)$, $D_2O(8)$ and $D_2O(9)$ have O···O distances in the range 2·757 (2)—2·854 (2) Å, while the O···O distances for the six D_2O molecules belonging to the $Al^{3+}(D_2O)_6$ octahedra lie in the range 2·650 (2)—2·750 (2) Å with a mean value of 2·69 Å. This value agrees well with the value of 2·68 Å given by Falk & Knop (1973) for the mean distance of hydrogen bonds donated by water molecules coordinated to M^{3+} ions. The hydrogen bonds donated by the $Al(D_2O)_6^{3+}$ water molecules are shorter than those donated by the other three water molecules since the polarizing influence of the Al^{3+} ions on the D_2O molecules favours the formation of strong hydrogen bonds. A comparison of mean O···O distance with Al—O distance for each of these six water molecules shows a tendency for the hydrogen bond to become shorter the shorter the Al—O distance; *cf.* the decrease of O···O distances with shorter Cr^{3+}—O

Fig. 2. The surroundings of the three NO_3^- ions. The ions are in the plane of the paper.
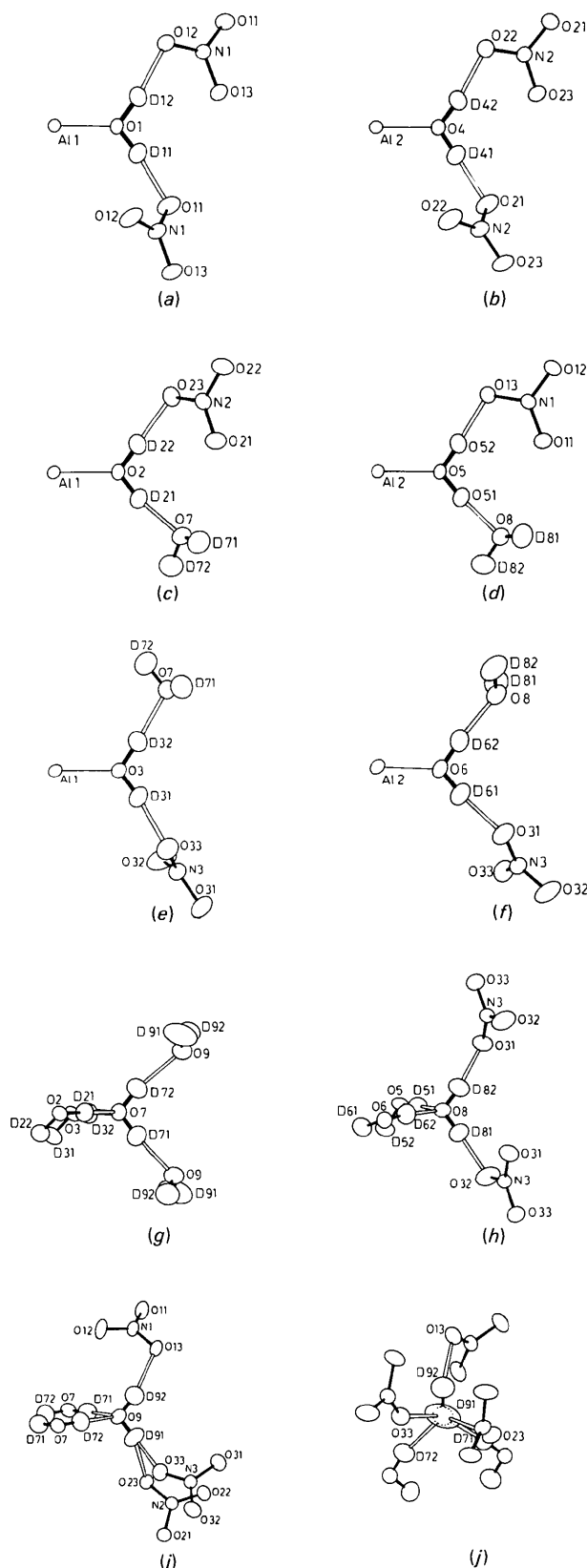
Fig. 3. The surroundings of the nine D_2O molecules. The D_2O molecules are in the plane of the paper, except in (j) where the view is given along the D(91)—O(9) direction.

distance in $Cr_4H_2(SO_4)_7.24H_2O$ (Gustafsson, Lundgren & Olovsson, 1980).

As for the internal geometries of the D_2O molecules the O—D distances range from 0·961 (2) to 0·986 (2) Å with (again) the exception of the O(9)—D(91) distance which is only 0·938 (2) Å. The D(91) atom has very large thermal motion with a marked anisotropy $(U_{11}:U_{22}:U_{33} \approx 1:2·5:1·4)$. The largest principal axis is roughly perpendicular to the O(9)—D(91) bond and close to the plane containing D(91) and its two hydrogen-bond acceptors (see Fig. 3i,j). The short O—D distance observed in the $D_2O(9)$ molecule is most probably an artifact of an improper vibrational model.

The large thermal ellipsoid of D(91) may be due to positional disorder rather than large vibrational motion. In order to test this hypothesis, a disordered model for the D(91) atom was introduced involving two anisotropically vibrating D atoms each with occupancies 0·5. The midpoint between these two half-atoms was constrained to correspond to the position obtained for the ordered model; the thermal parameters were constrained to be equal, i.e. the number of refined parameters was the same as for the ordered model. The refinement converged and gave the same R values as for the ordered model. The positions of the two half-atoms were 0·25 (2) Å apart and their equivalent isotropic r.m.s. amplitudes of vibration were 0·24 (1) Å. It is thus not possible with the present data to distinguish between an ordered and a disordered model for the $D_2O(9)$ molecule. The tables and figures in this paper refer to the ordered model.

A higher-cumulant refinement (Johnson, 1969) was also made for D(91) (ordered model). The refined third-order cumulants were all smaller than 3σ, however, and the second-order cumulants did not change significantly.

In a literature survey of 97 different hydrates studied by neutron diffraction Chiari & Ferraris (1982) found that, for 142 water molecules donating hydrogen bonds to two O atoms, the O···O···O angle subtended at the water O atom varied between 69 and 148° while the internal H—O—H angle only varied between 101 and
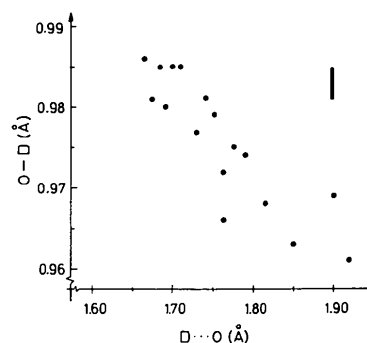

Fig. 4. A plot of O—D distances versus D···O distances for the nine D_2O molecules in $Al(NO_3)_3.9D_2O$. The D(91) atom is not included in the plot. The rectangle in the upper-right corner of the plot indicates $\pm 1\sigma$.

114° with an average H—O—H angle of 107·2°. The corresponding geometrical parameters for the D$_2$O molecules in Al(NO$_3$)$_3$.9D$_2$O lie within these ranges. The D—O—D angles range from 105·7 (2) to 112·1 (2)° with a mean value of 108·4°, and the O···O···O angles vary between 93·02 (6) and 118·09 (6)°.

Fig. 4 gives a plot of O—D versus D···O distances. It shows the same trend as other correlation curves published for O—H···O hydrogen bonds (see, for example, Olovsson & Jönsson, 1976) and gives an indication of the quality of the present results.

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The Structure and Electron Deformation Density of LiNO$_2$.H$_2$O at 295 K

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Abstract. $M_r = 70·959$, monoclinic, $P2_1/c$, $Z = 4$, $a = 3·3387$ (3), $b = 14·2980$ (10), $c = 6·3961$ (5) Å, $\beta = 105·10$ (1)°, $V = 294·79$ (4) Å^3, $D_x = 1·60$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu_{calc} = 0·154$ mm^{-1}, $T = 295$ K, $F(000) = 144$. Two data sets were collected out to $\sin\theta/\lambda = 0·91$ Å^{-1}: one on a twinned crystal, the other on a single crystal. Positional and thermal parameters from the two data sets show only random deviations. Somewhat high $R_w(F^2)$ values of 0·084 and 0·081, respectively, resulted from the refinement of a spherical-atom model. This reflects the inadequacies of such a model. Introduction of multipolar deformation functions for the single-crystal data set brought the $R_w(F^2)$ value down to 0·029. The crystal contains one independent Li$^+$ ion with fivefold coordination, a tetrahedrally coordinated H$_2$O molecule and an NO$_2^-$ ion which accepts two medium-strength hydrogen bonds [O—H···O 2·755 (1); O—H···N 2·890 (1) Å] and has three Li$^+$—O contacts. The static deformation density for the NO$_2^-$ ion shows N—O bond maxima of 0·50 e Å^{-3}; O lone-pair maxima of 0·20–0·30 e Å^{-3} are situated in the molecular planes at approximately 90° to the N—O bonds. The lone-pair density associated with the water O is markedly asymmetric; no support for this effect has been found in theoretical model calculations, however.

Introduction. Electron density studies of a series of hydrates are underway at this Institute. LiNO$_2$.H$_2$O has a high valence/core electron ratio, $V/\sum n^2_{core} = 3·7$ (Stevens & Coppens, 1976) and is, at least in this respect, well suited to electron density study. Moreover, its constituent ions and molecules are similar to those of LiNO$_3$.3H$_2$O, previously studied in this project (Hermansson, Thomas & Olovsson, 1977).

Two X-ray data sets were collected. Twinned crystals are readily formed and, unwittingly, our first data set was collected on such a crystal. The structure was solved from these data. The results from this refinement were, in fact, of the same quality (judged on the basis of R values, σ's, etc.) as those from a second untwinned data set which was collected later. Tables of coordinates and distances refer to the untwinned data set.