

verged at $R = 0.075$ for 1760 observed reflexions ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$). In the final cycle all shifts in parameters were less than their standard deviations. Atomic parameters are given in Table 1 and the molecular geometry in Table 2.*

Discussion. As part of a study of sesquiterpenoid transformations the crystal structure of (I) was undertaken to check the stereochemistry of the products from epoxidation of humulene (Parker, Roberts & Mitra, 1977). The observed structure (Fig. 1) is consistent with NMR data and has a very similar conformation to the related 1,2–8,9 diepoxide (Cradwick, Cradwick & Sim, 1973) from which it can be synthesized. The two molecules of (I) in the asymmetric unit have identical conformations and differ only slightly from the diepoxide [see Table 2(c)] and from the silver nitrate adduct of humulene (McPhail & Sim, 1966). This constancy of conformation supports the suggestion of Cradwick, Cradwick & Sim (1973) that humulene, although a liquid at room temperature, has a preferred conformation.

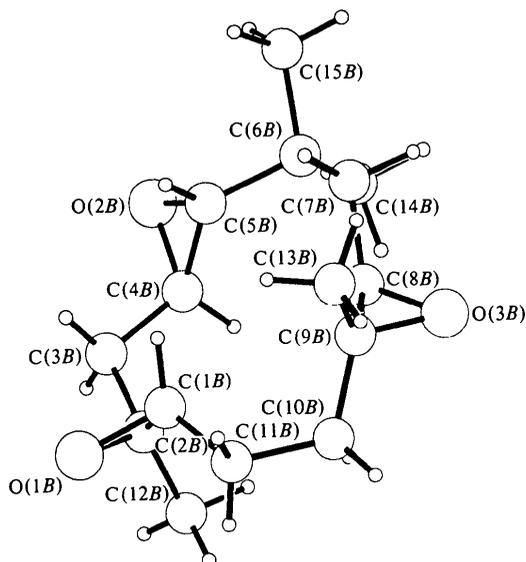


Fig. 1. General view of the molecule.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32936 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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A Neutron Diffraction Study of Lanthanum Magnesium Nitrate $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$

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Abstract. $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, trigonal, $R\bar{3} (C_{3i}^2)$, $a = 13.172(3) \text{ \AA}$, $\alpha = 49.29^\circ$, 23°C , FW 1527.18, $Z = 1$, $V = 1207 \text{ \AA}^3$, $D_c = 2.101 \text{ g cm}^{-3}$ [hexagonal, $a = 10.989(2)$, $c = 34.63(1) \text{ \AA}$, $Z = 3$, $V = 3621(2) \text{ \AA}^3$]. The non-hydrogen atom positions were similar to

those found in the corresponding cerium double salt whereas some differences were found with the H positions. A hydrogen-bonding scheme is proposed in which seven H atoms form single bonds and one forms a weak bifurcated bond.

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Introduction. Lanthanum magnesium nitrate hydrate (LMN) is of great importance as a proton spin-polarized target in both nuclear physics and polarized

neutron diffraction. In this experiment we set out to determine the accurate positions and temperature factors of the H atoms.

Several authors have assumed that the LMN structure is isostructural with the cerium salt, CMN, whose structure was determined by Zalkin, Forrester & Templeton (1963). Although their determination was by X-ray diffraction they were able to locate all eight crystallographically inequivalent H atoms and refine their positions with isotropic temperature factors. The estimated standard deviations on the H positional parameters were, understandably, high at about 0.2 Å. De Beer, de Boer, van't Hof & van Ormondt (1973) assumed LMN and CMN to be isostructural and attempted to refine the metal-complex H atom positions by doping the Mg sites in LMN with Mn^{2+} and studying the ENDOR of the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ion. More recently, Hayter, Jenkin & White (1974) have reported results of a polarized neutron diffraction experiment on a proton spin-polarized sample of LMN. Their results were incompatible with the proton positions given in the X-ray determination of CMN, and hence a determination of the structure of LMN by neutron diffraction was thought necessary.

A single crystal of LMN was grown by slow evaporation from aqueous solution at a reduced temperature of 15–18°C. The crystal, whose approximate dimensions were 3.0 × 4.0 × 7.5 mm, was defined by six faces, and careful measurements of its morphology were made with an optical goniometer. These were required for calculating the pseudo-absorption caused by the incoherent scattering of the H atoms.

1933 integrated intensity measurements with $\sin \theta/\lambda \leq 0.65$ were made, of which 1662 were non-systematically absent and inequivalent, in the hkl sextant. The intensity measurements were made, at room temperature, with a Ferranti Mk II four-circle automated neutron diffractometer at the PLUTO reactor, AERE, Harwell. Monochromation of the neutron beam was by reflexion from the (110) planes of a beryllium crystal which gave a wavelength of 1.136 Å at a take-off angle of 60°. The lattice parameters were refined by least-squares analysis of the 2θ settings of 26 reflexions.

Before the equivalent reflexions were averaged, a pseudo-absorption correction was applied with $\mu = 3.210 \text{ cm}^{-1}$, the linear absorption coefficient, calculated from the incoherent cross-section of hydrogen ($81.5 \times 10^{-24} \text{ cm}^2$). Thus the corrected intensities, I_{COR} , were related to the observed intensities, I_{OBS} , by:

$$I_{\text{OBS}} = I_{\text{COR}} \frac{1}{V} \int_V \exp[-\mu(p+q)] dV$$

where p and q are the incident and reflected path lengths of the beam in the crystal and the integration is over the whole crystal volume. The integration was performed with the *ABSCOR* program of XRAY 73.

The atomic coordinates of all non-hydrogen atoms of the CMN structure were used as a trial structure. The scattering lengths used were La 0.83, Mg 0.52, N 0.94, O 0.580 and H $-0.374 \times 10^{-12} \text{ cm}$ (Bacon, 1972). A three-dimensional difference Fourier synthesis was computed in order to locate the H atom positions. These positions were refined, and anisotropic temperature factors were then introduced. An isotropic secondary extinction parameter was included in the refinement whereby the corrected values of F_c were given by:

$$F_c^* = KF_c[1 + 0.301\beta(2\theta)F_c^2]^{-1/4}$$

(Larson, 1967). The final weighted agreement index, $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega F_o^2]^{1/2}$, was 0.065 where the weights, ω , were given by $\omega = \sigma F_o^{-2}$. The final atomic parameters are given in Table 1.†

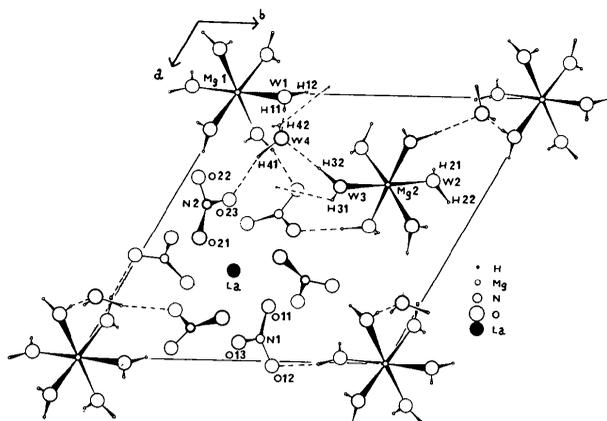
Discussion. The crystal is made up of two types of ion, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{La}(\text{NO}_3)_6]^{3-}$, which are linked together by hydrogen bonds from both the 'free' water molecules and those from the water molecules of the

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32909 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Parameters derived from the final least-squares refinement

	x	y	z
La(1)	0.0000*	0.0000*	0.2496 (2)
Mg(1)	0.0000*	0.0000*	0.0000*
Mg(2)	0.0000*	0.0000*	0.4279 (2)
N(1)	0.0316 (3)	0.2457 (3)	0.3003 (1)
N(2)	0.2517 (4)	0.2157 (4)	0.2020 (1)
O(11)	-0.0546 (6)	0.1239 (6)	0.3091 (2)
O(12)	0.0450 (6)	0.3456 (6)	0.3190 (2)
O(13)	0.1084 (6)	0.2638 (5)	0.2716 (2)
O(21)	0.1274 (7)	0.1784 (7)	0.1922 (2)
O(22)	0.3504 (7)	0.3032 (8)	0.1849 (2)
O(23)	0.2668 (6)	0.1549 (7)	0.2300 (2)
W(1)	0.0140 (7)	0.1587 (7)	0.0346 (2)
W(2)	0.1592 (6)	0.0166 (8)	0.3935 (2)
W(3)	0.1553 (7)	0.1563 (7)	0.4610 (2)
W(4)	0.1668 (7)	0.2271 (7)	0.1037 (2)
H(11)	0.0664 (12)	0.1877 (11)	0.0587 (3)
H(12)	-0.0058 (15)	0.2252 (15)	0.0251 (4)
H(21)	0.5024 (11)	0.6037 (13)	0.0585 (4)
H(22)	0.5144 (13)	0.7289 (15)	0.0355 (4)
H(31)	0.3934 (17)	0.5148 (17)	0.1460 (4)
H(32)	0.2797 (11)	0.4127 (11)	0.1177 (3)
H(41)	0.2333 (16)	0.1951 (16)	0.1058 (3)
H(42)	0.1210 (16)	0.2011 (16)	0.1282 (4)

* Special-position parameter.

Fig. 1. A view of the structure down c .

metal complex. Fig. 1 shows a view along the c axis illustrating how the structure is formed from layers of Mg(1) type ions at the C_{3i} symmetry sites interleaved with layers of Mg(2) and La type ions at sites with C_3 symmetry. The Mg ion is smaller than the La ion, and the packing within the latter layer type is completed by surrounding the smaller ion by three 'free' water molecules. The bond lengths and angles of these ions (Table 2) are similar to those of CMN.

Each of the metal complex's water molecules acts as donor of one short and almost linear (strong) hydrogen bond and one long and bent (weak) hydrogen bond. The 'free' water molecule is four-coordinated by hydrogen. Its oxygen atom, $W(4)$, acts as an acceptor for two strong hydrogen bonds, H(11) and H(32), from different metal complexes (Table 3). Of the two hydrogen bonds donated by $W(4)$, one is strong and the other is weak and bifurcated. Apart from $W(4)$, the acceptors of the hydrogen bonds are all O atoms of the nitrate groups.

The three-dimensional network of hydrogen bonds is built up as follows. Strong hydrogen bonds [H(11)] are formed between the Mg(1) type complex and its six surrounding 'free' water molecules which are subsequently strongly hydrogen-bonded [H(32)] to Mg(2) type complexes. The six weak hydrogen bonds [H(12)] are formed between the Mg(1) complex and O(12) of the six neighbouring La complexes generated by the C_{3i} site symmetry at Mg(1). At the Mg(2) complex sites the remaining three strong hydrogen bonds [H(21)] bond to O(13) atoms and the six weak bonds [H(22) and H(31)] to O(11) and O(22) atoms, all of different La complexes. The final links are those from the hydrogens of the 'free' water which bond strongly [H(41)] to O(23) atoms of a La complex and weakly [H(42)] to an O(22) atom of a further two La complexes (bifurcated bond).

It is always difficult with very weak 'hydrogen bonds' [H(42) and H(31)], whose geometry is poor, to say

Table 2. Bonded and non-bonded distances (\AA) and angles ($^\circ$)

$[\text{La}(\text{NO}_3)_6]^{3-}$ ion			
La-N(1)	3.093 (5)	O(11)-N(1)-O(12)	122.2 (5)
La-O(11)	2.696 (9)	O(12)-N(1)-O(13)	120.5 (4)
La-O(13)	2.693 (6)	O(13)-N(1)-O(11)	117.3 (5)
N(1)-O(11)	1.231 (6)	O(21)-N(2)-O(22)	122.3 (6)
N(1)-O(12)	1.218 (8)	O(22)-N(2)-O(23)	120.8 (6)
N(1)-O(13)	1.253 (7)	O(23)-N(2)-O(21)	116.9 (5)
La-N(2)	3.073 (5)	N(1)-La-N(2)	88.0 (1)
La-O(21)	2.649 (8)	N(1)-La-N(1)*	91.0 (2)
La-O(23)	2.642 (6)	N(2)-La-N(2)*	93.9 (2)
N(2)-O(21)	1.262 (8)		
N(2)-O(22)	1.187 (7)		
N(2)-O(23)	1.236 (8)		

$[\text{Mg}(1)(\text{H}_2\text{O})_6]^{2+}$ ion			
Mg(1)- $W(1)$	2.058 (8)	Mg(1)- $W(1)$ -H(11)	124 (1)
$W(1)$ -H(11)	0.971 (13)	Mg(1)- $W(1)$ -H(12)	121 (1)
$W(1)$ -H(12)	0.921 (21)	H(11)- $W(1)$ -H(12)	112 (1)
		$W(1)$ -Mg(1)- $W(1)$ *	89.6 (2)
		$W(1)$ -Mg(1)- $W(1)$ †	90.4 (2)

$[\text{Mg}(2)(\text{H}_2\text{O})_6]^{2+}$ ion			
Mg(2)- $W(2)$	2.048 (8)	Mg(2)- $W(2)$ -H(21)	116 (1)
$W(2)$ -H(21)	0.935 (19)	Mg(2)- $W(2)$ -H(22)	122 (1)
$W(2)$ -H(22)	0.959 (15)	H(21)- $W(2)$ -H(22)	109 (1)
Mg(2)- $W(3)$	2.063 (8)	Mg(2)- $W(3)$ -H(31)	132 (1)
$W(3)$ -H(31)	0.895 (15)	Mg(2)- $W(3)$ -H(32)	117 (1)
$W(3)$ -H(32)	1.005 (13)	H(31)- $W(3)$ -H(32)	108 (1)
		$W(2)$ -Mg(2)- $W(2)$ *	89.8 (4)
		$W(2)$ -Mg(2)- $W(3)$	86.2 (3)
		$W(3)$ -Mg(2)- $W(3)$ *	92.0 (4)

$[\text{H}_2W(4)]$			
$W(4)$ -H(41)	0.960 (16)	H(41)- $W(4)$ -H(42)	102 (2)
$W(4)$ -H(42)	0.952 (15)		

* Related by C_3 .† Related by C_{3i} .

whether or not bonding does exist. Application of Hamilton & Ibers's (1968) criterion for weak hydrogen bonds in crystalline hydrates, in this instance that the $(\text{H}\cdots\text{A})$ distance be considerably less than the sum of the van der Waals radii of O and H (2.6 \AA), includes all the bonds. Their more restrictive criterion that the $(\text{D}\cdots\text{A})$ distance be less than the sum of their van der Waals radii (2.8 \AA) would include only two bonds, H(11) (2.801 \AA) and H(21) (2.767 \AA). Clearly in this case, the latter criterion is much too restrictive. The bifurcated bond, H(42), is similar to that found in CMN although the $(\text{H}\cdots\text{A})$ distances are shortened owing to the systematically longer $(\text{D}-\text{H})$ distances found by neutron diffraction, these distances being 0.90 (2) to 1.01 (1) \AA with an average value of 0.95 \AA . The spread in the X-ray determination of CMN was 0.5 (2) to

