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Hydrogen Bond Studies.

CXX.* An X-ray Determination of the Crystal Structure of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

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The crystal structure of lithium nitrate trihydrate, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, has been determined by X-ray diffraction at 295 K. The crystal is orthorhombic, space group *Cmcm*, $a = 6.8018$ (4), $b = 12.7132$ (9), $c = 5.9990$ (4) Å, $V = 518.75$ Å³, $Z = 4$. The nitrate ions, Li^+ ions and one of the two crystallographically non-equivalent water molecules lie in a mirror plane and are bonded to atoms in adjacent planes through the second water molecule. The Li^+ ion is octahedrally surrounded by six O atoms, four belonging to water molecules and two to nitrate ions. The two non-equivalent water molecules are present in the structure in distinctly different bonding situations. One is bonded to two Li^+ ions and is the donor of two hydrogen bonds. The other is involved in six hydrogen bonds: the O atom accepts two hydrogen bonds, and both protons are involved in bifurcated hydrogen bonds.

Introduction

This work is part of a project to determine the experimental electron density in simple solid hydrates containing only light atoms. By selecting compounds containing water molecules in a variety of different environments, it should be possible to observe, in a systematic way, the influence of the environment on the electron density of the water molecule. $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, having a high valence-electron/core-electron ratio, would seem a singularly suitable compound for this purpose. Since its crystal structure was unknown, however, an X-ray structure determination was an essential first step.

Experimental

Crystals of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ were grown by slow evaporation at room temperature from an aqueous solution of lithium nitrate. They were highly sensitive both to humidity (deliquescent and hygroscopic) and heat (m.p. 29.9°C) (see Donnan & Burt, 1903), and

had, therefore, to be handled with extreme caution. An approximately spherical crystal of mean radius 0.058 mm was selected for the subsequent data collection and sealed in a thin-walled glass capillary. Its general quality was checked with Laue and Weissenberg photographs. In agreement with the previous findings of Aravamudan & Ramaseshan (1961), the diffraction symmetry and systematic absences in the Weissenberg photographs indicated three space-group possibilities: (a) *Cmcm* (No. 63, centrosymmetric), (b) *Cmc*₂ (No. 36, noncentrosymmetric) and (c) *C2cm* (equivalent to *Ama*₂, No. 40, noncentrosymmetric). (Space-group numbering follows that given in *International Tables for X-ray Crystallography*, 1969.)

The unit-cell dimensions were determined by powder

Table 1. *Crystal data for* $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$

FW	123.00	$\rho_{\text{calc.}}$	1.575 g cm ⁻³
Space group	<i>Cmcm</i>	$\rho_{\text{obs.}}$ *	1.55
<i>a</i>	6.8018 (4) Å	<i>Z</i>	4
<i>b</i>	12.7132 (9)	m.p.	29.9°C
<i>c</i>	5.9990 (4)	$\mu_{\text{calc.}}$	1.60 cm ⁻¹
<i>V</i>	518.75 Å ³		

* Part CXIX: Berglund & Tegenfeldt (1977).

* Aravamudan & Ramaseshan (1961).

photographs taken with a Guinier-Hägg focusing camera at room temperature with monochromatized Cr $K\alpha_1$ radiation ($\lambda = 2.28975 \text{ \AA}$). CoP_3 ($a = 7.70778 \text{ \AA}$) was used as an internal standard. In a subsequent least-squares procedure, 16 reflexions were used to obtain the cell parameters. These are listed in Table 1 together with other crystal data.

Data collection and reduction

Data collection was carried out at 295 K on a Stoe-Philips four-circle X-ray diffractometer controlled by a PDP8/I computer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). An $\omega/2\theta$ scan mode was used.

Two symmetry-equivalent sets of reflexions were measured with $\sin \theta/\lambda < 0.81 \text{ \AA}^{-1}$. The data were corrected for background and assigned standard deviations, $\sigma_{\text{count}}(I)$, based on Poisson counting statistics. The internal consistency between the two reflexion sets was investigated by comparing symmetry-equivalent reflexions in a normal probability plot (Abrahams & Keve, 1971), which gave a straight line with a slope of 0.99 and an intercept of 0.07. An internal consistency index, defined as $\Sigma |I(hkl) - \bar{I}| / \Sigma I(hkl)$, where \bar{I} is the average of two symmetry-equivalent reflexions and the summations are taken over all the measured reflexions, was calculated as 0.013.

On these grounds, the 1238 measured reflexions were reduced by averaging to give 661 independent reflexions. The intensities were corrected for Lorentz, polarization and absorption effects (the crystal was taken to be spherical); the calculated transmission factor for all reflexions was 0.986.

Structure determination and refinement

All calculations were performed on IBM 370/155 and IBM 1800 computers with programs described by Lundgren (1974).

An attempt to solve the crystal structure by Patterson methods was unsuccessful. The structure was solved by direct methods. The normalized structure factor amplitudes $|E|$ were calculated with the program *EFAK* (see also Kvick & Backéus, 1974).

The statistical distribution of the $|E|$ values is shown in Table 2, together with the theoretical distributions expected for centrosymmetric and non-centrosymmetric structures. The theoretical values are those given by Karle, Dragonette & Brenner (1965). Inspection of the distributions indicated a centrosymmetric space group. The space group *Cmcm* was thus used in the structure refinements. As an additional check, the two noncentrosymmetric space groups (*Cmc2₁* and *C2cm*) were tested, but no satisfactory convergence could be achieved.

Table 2. Statistical distribution of the normalized structure amplitudes ($|E|$) compared with theoretical values

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle E \rangle$	1.000	1.000	1.000
$\langle E ^2 - 1 \rangle$	1.080	0.968	0.736
$\langle E \rangle$	0.894	0.798	0.886
$ E > 3$	0.3%	0.3%	0.01%
$ E > 2$	5.6	5.0	1.8
$ E > 1$	35.5	32.0	37.0

The 105 reflexions with $|E| > 1.5$ were used as input to the program *REL* (a program for sign determination by reiterative application of Sayre's equation). Of the sixteen possible solutions, the one with the highest consistency index (99%) gave uninterpretable *E* maps. The solution with the next highest consistency index (95%) and an equally fast convergence resulted in *E* maps in which all except the H atoms could be located. All predicted phases were later found to agree with the phases obtained from the final least-squares refinement.

The atomic positions for the non-hydrogen atoms obtained from the *E* maps were used as input to the full-matrix least-squares refinement program *UPALS*. The quantity minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w^{-1} = \sigma^2(|F_o|^2) = \sigma_{\text{count}}^2(|F_o|^2) + (k|F_o|^2)^2$. Of the original 661 reflexions, 286 with $|F_o|^2 < 2\sigma_{\text{count}}(|F_o|^2)$ were given zero weight in the refinements. (The inclusion of *all* reflexions did not change the parameters obtained in the final refinement, but gave about 8% lower standard deviations.)

After the first cycles of refinement, in which one scale factor and positional and anisotropic thermal parameters for the non-hydrogen atoms were refined, a Fourier difference synthesis was calculated which revealed the H atom positions. The spurious peaks in the maps were all less than 0.1 e \AA^{-3} .

The following parameters were refined in the final refinements: one scale factor, one isotropic extinction parameter, positional parameters (13) for the nine atoms in the asymmetric unit, anisotropic thermal parameters (21) for the non-hydrogen atoms, and isotropic thermal parameters (3) for the H atoms. The atomic scattering factors used for H, Li^+ , N and O, and the anomalous-dispersion corrections included for N and O were taken from *International Tables for X-ray Crystallography* (1974, pp. 72–73, 149). Six weak reflexions, for which the disagreement between the symmetry-equivalent reflexions was large, and two of the strongest extinction-affected reflexions (extinction reduced these intensities by 12% and 8%) were removed in the final refinement. The effect of using different *k* values in the weighting scheme was tested empirically. A *k* value of 0.02 was chosen after inspection of the weight analyses and standard

deviations of the final parameters resulting from the various refinements.

The final shifts of the refined parameters were all smaller than 0.07σ . The agreement indices for the 367 reflexions were

$$R(|F|^2) = \frac{\sum ||F_o|^2 - |F_c|^2|}{\sum |F_o|^2} = 0.038,$$

$$R_w(|F|^2) = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w(|F_o|^2)^2} \right]^{1/2} = 0.058,$$

and

$$R(|F|) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.040.$$

Very few reflexions were affected by extinction. The refined value of the isotropic extinction parameter g was 1200 (1000) (Coppens & Hamilton, 1970). The atomic coordinates after the last refinement are given in Table 3.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32595 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Atomic coordinates for non-hydrogen atoms ($\times 10^3$) and hydrogen atoms ($\times 10^3$)

	x	y	z
Li	0	0	0
N	0	21745 (15)	25000
O(1)	0	17032 (10)	7000 (21)
O(2)	0	31663 (12)	25000
O(3)	29154 (18)	47831 (10)	25000
O(4)	0	63756 (16)	25000
H ₂ O(3) {			
H(1)	233 (3)	427 (2)	250
H(2)	220 (3)	524 (2)	250
H ₂ O(4) {			
H(3)	0	673 (2)	144 (4)

Description of the structure

General

The structure has the form of a three-dimensional network. The atomic arrangement is illustrated in Fig. 1. Selected interatomic distances and angles are given in Table 4.

The nitrate ion, Li⁺ ion and one of the two independent water molecules, H₂O(4), lie in mirror planes $a/2$ apart. Atoms in adjacent planes are linked transversely by water molecules of the second type, H₂O(3). These surround the Li⁺ ions in one plane and are hydrogen bonded to O atoms in an adjacent plane. Within the mirror planes, Li⁺ ions are bonded to nitrate ions which, in turn, form infinite chains by means of hydrogen-bond linkage *via* the H₂O(4) water molecules.

The Li⁺ ion

As illustrated in Fig. 2, the Li⁺ ion is surrounded by six O atoms, forming an approximately regular octahedron, at an average distance of 2.124 Å. The four H₂O(3) water molecules form a rectangle about the Li⁺ ion. The nitrate O(1) atoms are situated approximately at right angles to the plane of the rectangle.

A limited literature survey of structures containing O coordinated Li⁺ ions reveals that of nineteen cases considered, twelve involve a nearly regular tetrahedral coordination. The average Li—O distances within the LiO₄ groups are in the range 1.94–1.99 Å, with an overall mean of 1.960 Å. The corresponding range in four cases where the Li⁺ ions are surrounded by five O atoms is 2.04–2.12 Å, with an overall mean of 2.077 Å. In three compounds containing octahedrally coordinated Li⁺ ions, the range is 2.13–2.17 Å with an

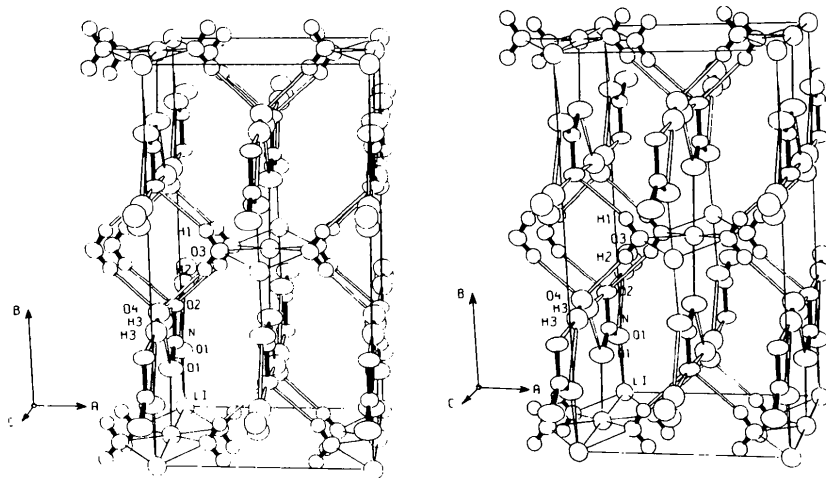


Fig. 1. A stereoscopic illustration of the structure. Here, and in the figures which follow, thermal ellipsoids for non-hydrogen atoms are drawn to include 50% probability. Covalent bonds are filled, H...O bonds are open and ionic bonds are drawn as single lines.

Table 4. *Interatomic distances (Å) and angles (°)*

The interatomic distances have not been corrected for thermal motion.

Symmetry code

(i)	$x - \frac{1}{2}, y - \frac{1}{2}, z$	(vi)	$x + \frac{1}{2}, y + \frac{1}{2}, z$
(ii)	$x - \frac{1}{2}, -y + \frac{1}{2}, -z$	(vii)	$x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$
(iii)	$-x + \frac{1}{2}, y - \frac{1}{2}, z$	(viii)	$x, -y + 1, -z$
(iv)	$x, -y, -z$	(ix)	$-x, y, z$
(v)	$x, y, -z + \frac{1}{2}$		

(a) Li⁺ ion

Li—O(3) ⁱ	2.082 (1)	O(3) ^j —Li—O(3) ⁱⁱ	94.16 (5)
Li—O(1)	2.206 (1)	O(3) ^j —Li—O(3) ⁱⁱⁱ	85.84 (5)
Mean Li—O	2.124	O(3) ^j —Li—O(1) ^{ix}	90.41 (4)
		O(3) ^j —Li—O(1)	89.59 (4)

(b) NO₃⁻ ion

N—O(1)	1.235 (2)	O(1)—N—O(1) ^v	121.96 (19)
N—O(2)	1.261 (2)	O(1)—N—O(2)	119.02 (9)
Mean N—O	1.244		

(c) H₂O molecules and hydrogen bondsH₂O(3) molecule

O—H...O	O—H	O...O	H...O
O(3)—H(1)...O(2)	0.76 (2)	2.856 (2)	2.12 (2)
O(3)—H(2)...O(4)	0.76 (2)	2.834 (2)	2.08 (2)

H(1)—O(3)—H(2)	108 (2)
O(3)—H(1)...O(2)	163 (2)
O(3)—H(2)...O(4)	174 (2)
Li ^{vi} —O(3)—Li ^{vii}	92.15 (5)
Li ^{vi} —O(3)...O(2)	124.62 (4)
Li ^{vi} —O(3)...O(4)	112.45 (5)
O(2)...O(3)...O(4)	91.62 (5)

H₂O(4) molecule

O—H...O	O—H	O...O	H...O
O(4)—H(3)...O(1) ^{viii}	0.78 (2)	3.107 (2)	2.37 (2)
O(4)—H(3)...O(2) ^{viii}		3.056 (1)	2.37 (2)

H(3)—O(4)—H(3) ^v	109 (4)
O(4)—H(3)...O(1) ^{viii}	158 (2)
O(4)—H(3)...O(2) ^{viii}	148 (2)
O(3)...O(4)...O(3) ^{ix}	88.81 (8)

overall mean of 2.154 Å. These numbers are in good agreement with the values of 1.98 and 2.16 Å given in *International Tables for X-ray Crystallography* (1968, p. 258) for mean Li⁺ ion coordination distances to four and six O atoms respectively.

The nitrate ion

The nitrate ion has *mm* symmetry with two significantly different N—O distances [two N—O(1) distances of 1.235 (2) Å and one N—O(2) distance of 1.261 (2) Å] and a mean N—O bond length of 1.244 Å. In twenty-eight solid hydrates containing nitrate groups, the average over 109 N—O distances, ranging from 1.20 to 1.32 Å, was found to be 1.251 Å. The

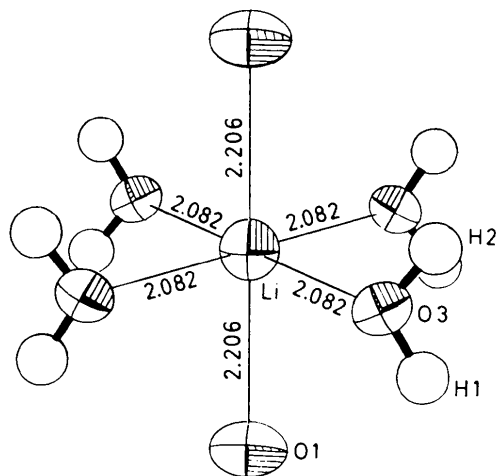


Fig. 2. The environment of the Li⁺ ion. Here, and in the figures which follow, *B*(H) values are fixed at 2.0 Å². The Li⁺ ion occupies a *2/m* symmetry site.

mean N—O distance given by *International Tables for X-ray Crystallography* (1968, p. 270) for NO₃⁻ and NO₂⁻ ions in crystals is 1.24 Å.

The difference in the N—O distances found in the present structure suggests that O(2) is more strongly bonded than O(1) to atoms outside the nitrate group. In Fig. 1 we see that O(1) is only bonded within the nitrate plane [to a Li⁺ ion and possibly also through a weak hydrogen bond to H₂O(4)]. On the other hand, O(2) participates in four hydrogen bonds: two weak interactions within the nitrate plane [to H₂O(4) molecules] and two stronger interactions with H₂O(3) molecules lying outside the plane. The difference in bonding out of the nitrate plane for O(1) and O(2) is reflected by the elongation of the thermal ellipsoid of O(1) in the direction of the *a* axis. The r.m.s. thermal displacements perpendicular to the nitrate plane are 0.265 (2) Å for O(1) and 0.215 (2) Å for O(2). Another feature of the nitrate O thermal ellipsoids is the pronounced elongation of O(2) in the direction of the *c* axis. Whether this is an effect of thermal vibration, disorder or an inappropriate choice of space group has not been possible to ascertain in the present study. It is hoped that this question can be resolved in a current low-temperature neutron diffraction study.

A careful study of the nitrate ions occurring in the same twenty-eight structures referred to above reveals no clear relationship between N—O distance and number of hydrogen bonds, number and type of cation neighbours, etc. On the other hand, for a given type of environment, a certain correlation can be found between N—O distance and the distance from the nitrate O to its coordinated neighbour(s). This is in good agreement with earlier findings (e.g. Britton & Dunitz, 1965; Morosin, 1970).

It should be remembered that any discussion of this

type involving the effect of the environment on bond length strictly requires that thermal effects are adequately taken into account.

The water molecules

The roles of the two non-equivalent water molecules in the structure are very different. The $\text{H}_2\text{O}(3)$ water molecules act as ligands for the Li^+ ions, while the

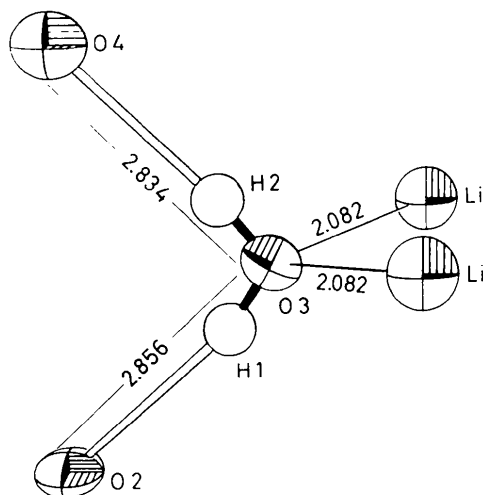


Fig. 3. The bonding situation around the $\text{H}_2\text{O}(3)$ water molecule. The molecule occupies an m symmetry site, the mirror plane lying roughly in the plane of the paper.

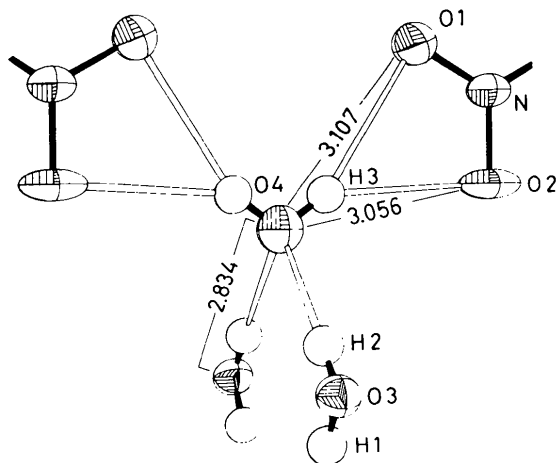


Fig. 4. The bonding situation around the $\text{H}_2\text{O}(4)$ water molecule. The molecule occupies an mm symmetry site.

$\text{H}_2\text{O}(4)$ water molecules bind the nitrate ions together by means of hydrogen bonding.

The $\text{H}_2\text{O}(3)$ molecule (Figs. 1 and 3) has an approximately regular tetrahedral coordination with electrostatic contacts to two Li^+ ions and interactions *via* two hydrogen bonds of intermediate lengths to an O(2) nitrate O atom [$\text{O}(3)\cdots\text{O}(2)$ 2.856 (2) Å] and to an O(4) water O atom [$\text{O}(3)\cdots\text{O}(4)$ 2.834 Å].

The $\text{H}_2\text{O}(4)$ molecule (Fig. 4) has mm symmetry and is involved in six hydrogen bonds. Two $\text{H}_2\text{O}(3)$ molecules donate one proton each to $\text{H}_2\text{O}(4)$ in forming two medium-strength hydrogen bonds [$\text{O}(4)\cdots\text{O}(3)$ 2.834 (2) Å]. Each of the H atoms in $\text{H}_2\text{O}(4)$ also appears to participate in bifurcated hydrogen bonding to O(1) and O(2) of the same nitrate ion.

Preliminary low-temperature neutron diffraction data support the hydrogen-bond scheme indicated by the present study.

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