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The Structure of Lithium Perchlorate Trihydrate $Li(H_2O)_3ClO_4$ – an X-ray and Neutron Diffraction Study

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The crystal structure of $Li(H_2O)_3ClO_4$ has been refined from X-ray (R = 0·034) and neutron diffraction (R = 0·087) measurements. The compound, which crystallizes in the space group $P6_3mc$ with a = 7·719 and c = 5·455 Å, consists of columns of alternating $-Li-(H_2O)_3-Li-$, hydrogen bonded to regular tetrahedral ClO_4^- ions with Cl–O = 1·440 (2) (1·458 Å corrected for riding motion). The Li atoms are coordinated by an almost regular octahedron of water molecules [average Li–O = 2·133 (4) Å]. Each hydrogen atom forms a weak bond [H–O = 2·044 (7) Å] with one perchlorate O atom and a very weak but structurally significant bond [H–O = 2·617 (8) Å] with a second perchlorate O atom. The thermal motions of the atoms can be accounted for by a combination of librational and translational motions with a particularly large translational component in the **c** direction. The occurrence of weak hydrogen bonding is shown to be the consequence of the low valence of the ClO_4^- ion and not the result of crystal packing.

Introduction

Studies of the physical properties [*e.g.*, viscosity, n.m.r., infrared and Raman spectra, *etc.*; see for example Conway & Barradas (1966)] of ionic solutions have resulted in a set of empirical rules which characterize the behaviour of electrolytes with respect to their effect on the properties of the pure solvent. Specifically, the ability of an ion to form stronger hydrogen bonds with water than water molecules can form amongst themselves is measured by a parameter called 'the structure-forming character' of that ion. From this standpoint, the combination of the Li^+ and ClO_4^- ions in $Li(H_2O)_3ClO_4$ is interesting since they are, respectively, strong 'structure-forming' and 'structure-breaking' ions. As a result, it seemed worthwhile to establish accurately the structure and hydrogen-bonding scheme in this particular salt. In addition, the Raman spectroscopic study (Couture-Mathieu & Mathieu, 1952) and the n.m.r. investigations (Aleksandrov & Ptrzhak, 1965; Scheller & Lippold, 1973) of single crystals of $Li(H_2O)_3ClO_4$ emphasize the necessity of having an accurate description of the length and direction of the hydrogen bonds and hydrogen–hydrogen vectors in these crystals.

The structure of $Li(H_2O)_3ClO_4$ was first determined by West (1934) with X-rays. Subsequently, a neutron diffraction study was published by Datt, Rannev & Ozerov (1968) and an X-ray structure refinement was performed but apparently never fully published by Prosen (1955). The present X-ray and neutron-diffraction refinements are considerably more accurate than the previous work and permit a more detailed discussion of the bonding.

X-ray diffraction measurements and refinement

The crystal data are summarized in Table 1. A good quality single crystal of commercially available $LiClO_4.3H_2O$ (G. Fredrick Smith Chemical Co.) was ground to a sphere with a radius of approximately 0·12 mm and mounted on a goniometer. Intensities were measured by a θ–2θ scan on a Syntex $P\bar{1}$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 1483 reflections in one quarter of the reciprocal lattice with $\sin\theta/\lambda < 0·756$ were measured and of these 1048 had $I > 3\sigma$, where σ was determined from counting statistics. They were corrected for Lorentz, polarization and absorption but crystal-

Table 1. *Crystal data*

$Li(H_2O)_3ClO_4$
Space group $P6_3mc$

	Swanson *et al.* (1959)	Prosen (1955)
a	= 7·719 (2) Å	7·712 (2) Å
c	= 5·455 (2)	5·445 (14)
d_m	= 1·89 g cm^{-3}	
d_x	= 1·88	

Neutron scattering lengths, b, ($\times 10^{-14}$ m)

H	−0·378
Li	−0·180
Cl	0·980
O	0·580

Absorption coefficients μ

Mo $K\alpha$ X-rays	0·65 mm^{-1}
Neutrons	0·225 mm^{-1}

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lographically equivalent reflections were not averaged. The atomic scattering factors of Cromer & Waber (1965) were used; that for Cl^- was corrected for anomalous dispersion. In the final round of full-matrix least-squares refinement all the coordinates whose standard errors are given in Tables 2 and 3 were refined and these showed shifts of less than half the indicated standard error. The structure factors were corrected for extinction by the expression $F_c^* = F_c(1+5{\cdot}8\times10^{-5}\times\beta(2\theta)F_c^2)^{-1/2}$ (Larson, 1967) and were weighted by $\omega=0{\cdot}15+0{\cdot}0015|F_o|+0{\cdot}00054|F_o|^2$, except that ω was set equal to zero for F_o and $F_c<3\sigma$. The final agreement index, $R_2=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega F_o^2]^{1/2}$, was 0·034 for the 1075 reflections that did not have zero weight. Computer programs of the X-RAY 71 system were used.

Neutron diffraction measurements and refinement

Large hexagonal columnar crystals were obtained from an acidified solution of the salt in water. The sample used in the neutron diffraction study was a cylinder ground from a very large, transparent, crystal of hexagonal cross-section. Gently rolling the crystal on a wet cloth eventually yielded a cylindrical crystal of 3·0 mm in diameter, whose axis corresponded to the *c* axis of the hexagonal cell. Since the crystal was too long, it was cleaved to a length of 4·0 mm. The crystal was mounted on a Cd-plated brass pin and aligned on a four-circle diffractometer. The details of intensity measurement, programs for processing the neutron data and for the absorption and extinction corrections are the same as those used by Sequeira & Hamilton (1967).

The mean neutron diffraction wavelength was 1·076 Å and two forms of the asymmetric intensity data set were measured for $2\theta\le90°$, smoothed and integrated, and corrected for absorption and for extinction using program *GONO*9. The intensities of symmetry-related reflections were averaged and the total number of independent reflections thus obtained was 247. The agreement between symmetry-related pairs was always better than 8% for the entire set.

Starting with the positional parameters of West (1934) we refined the scale factor, the positional parameters of the heavy atoms and their isotropic thermal parameters. A difference Fourier map computed at this stage revealed the position of the independent hydrogen atom. Refinement of the positional and anisotropic thermal parameters of all the atoms eventually yielded agreement indices of $R_1(F)=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}066$, $R_2(F)=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega F_o^2]^{1/2}=0{\cdot}087$, error of fit$=[\sum\omega(|F_o|-|F_c|)^2/(\mathrm{NO}-\mathrm{NV})]^{1/2}=1{\cdot}08$, where ω are the weights used; F_o and F_c are the observed and calculated structure amplitudes, NO is the number of observations (247) and NV the number of variables (30). The weighting scheme used was such that the weights are inversely proportional to the estimated variance $\sigma(F^2)$, with $\sigma(F^2)$ defined as follows:

$$\text{for } F\ge24{\cdot}0;\ \sigma(F^2)=[\sigma^2_{\text{Poisson}}+(0{\cdot}25F^2)^2]^{1/2}$$
$$\text{and } 1{\cdot}0<F<24{\cdot}0;\ \sigma(F^2)=[\sigma^2_{\text{Poisson}}+(0{\cdot}15F^2)^2]^{1/2}$$
$$\text{and } \sigma(F)=\sigma(F^2)/2F.$$

Structure factors for which $F_o^2\le3\sigma(F^2)$ were given zero weight. The final positional and thermal parameters are given in Tables 2 and 3.*

Discussion

Apart from the coordinates of the hydrogen atom the X-ray results are more accurate than the neutron results. The two determinations agree in all essentials except that in the X-ray study larger thermal parameters result from the use of free-atom form factors and the position of the hydrogen atom, corresponding to the center of the electron density, is displaced from the

Table 2. *Atomic positional coordinates* ($\times10^4$)

		X-ray			Neutron		
		West (1934)	Prosen (1955)	Present work	Datt *et al.* (1968)	Present work	Best† values
Li in (2(*a*)	*z*	2500	2213 (20)	2217 (9)	2174	2254 (24)	2222 (9)
Cl *in (2(b)*	*z*	*0*	*0 (4)*	*0 (2)*	*0*	*0 (*)*	*0*
O(1) in 2(*b*)	*z*	2800	2656 (13)	2641 (4)	2631	2640 (14)	2642 (4)
O(2) in 6(*c*)	*x*	4390	4363 (12)	4348 (2)	4346	4346 (3)	4347 (2)
	z	−900	−954 (16)	−885 (3)	−787	−914 (13)	−892 (3)
O(3) in 6(*c*)	*x*	1250	1228 (10)	1221 (2)	1220	1233 (3)	1227 (2)
	z	5000	4722 (12)	4730 (*)	4810	4765 (10)	4733 (3)
H in 12 (*d*)	*x*		2640	2347 (26)	2600	2671 (10)	2671 (10)
	y		3670	3138 (27)	3317	3306 (10)	3306 (10)
	z		4850	4919 (44)	4841	4636 (18)	4636 (18)
Number of reflections			143	1075	260	247	
R			0·098	0·034	0·149	0·087	

* Fixed to define origin.

† Best values are, for the heavy atoms, a weighted average of the two present determinations and that of Prosen and, for the H atoms, the values obtained in the neutron diffraction experiment.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication SUP 30942 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Atomic thermal parameters* ($\times 10^4$)

$T=\exp\,[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*$
$+2u_{13}hla^*c^*+2u_{23}klb^*c^*)]$.

		X-ray	Neutron
Li	u_{11}	299 (13)	145 (48)
	u_{33}	304 (18)	234 (62)
Cl	u_{11}	170 (1)	100 (11)
	u_{33}	314 (2)	213 (17)
O(1)	u_{11}	442 (10)	376 (30)
	u_{33}	302 (9)	285 (36)
O(2)	u_{11}	309 (7)	267 (16)
	u_{33}	558 (6)	487 (24)
	u_{12}	210 (4)	186 (16)
	u_{13}	45 (4)	20 (7)
O(3)	u_{11}	257 (4)	190 (16)
	u_{33}	327 (4)	264 (15)
	u_{12}	156 (3)	138 (16)
	u_{13}	4 (3)	−30 (9)
H	u, u_{11}	338 (50)	283 (36)
	u_{22}		364 (36)
	u_{33}		633 (36)
	u_{12}		14 (30)
	u_{13}		−92 (29)
	u_{23}		17 (35)

Table 4. *Interatomic distances* (Å) *and angles* (°)
(calculated from averaged coordinates)

Cl—O(1)	1·441 (2)		1·460*		
Cl—O(2) ×3	1·440 (2)		1·456*		
O(1)–Cl—O(2)		109·8 (2)			
O(2)–Cl—O(2)		109·2 (2)			
Li—O(3) ×3	2·129 (4)		2·130*		
Li—O(3′) ×3	2·137 (4)		2·140*		
O(3)–Li—O(3)	83·7 (2)				
O(3)–Li—O(3′)	96·5 (2)				
O(3′)–Li—O(3′)	83·3 (2)				
O(3)–H	0·972 (7)		1·014*		
H—O(3)–H	107·9 (3)				
Li—O(3)–H	114·5 (5)				
Li—O(3′)–H	119·4 (4)				
Li—O(3)–Li	79·5 (2)				
H—O(2)	2·044 (7)			O(3)–O(2)	2·989 (2)
H—O(1)	2·617 (8)			O(3)–O(1)	3·038 (2)
O(3)–H—O(2)	163·6 (8)				
O(3)–H—O(1)	106·4 (6)				
H—H	1·572 (9)				

*Corrected for riding thermal motion.

nucleus towards the donor oxygen atom. The atomic coordinates are summarized in Tables 2 and 3. Since the neutron and X-ray positional coordinates of the heavy atoms are not significantly different and agree with those of Prosen (1955), a weighted average of all three determinations has been used in calculating the molecular geometry (Table 4). The hydrogen-atom position, which is taken from the neutron experiment, agrees with that proposed from Raman spectroscopy (Couture-Mathieu & Mathieu, 1955), n.m.r. (Aleksandrov & Ptrzhak, 1965) and earlier neutron diffraction work (Datt, Rannev & Ozerov, 1968).

The structure consists of columnar $Li(H_2O)_3^+$ ions, each pair of Li atoms separated by a layer of three water molecules (Fig. 1). The ClO_4^- ions lie between the columns and are hydrogen bonded to them as shown in Figs. 2 and 3.

The thermal parameters in $Li(H_2O)_3ClO_4$ can be explained by a model in which a number of independent motions are superimposed. All atoms have an isotropic component of motion of r.m.s. vibration amplitude = 0·113 Å (a larger value of 0·130 Å is obtained in the X-ray experiment for the reasons given above). In addition, all atoms have a vibration of r.m.s. amplitude 0·115 Å along the *z* axis that results from the lack of strong bonding in this direction between the $Li(H_2O)_3^+$ and ClO_4^- ions. The ClO_4^- ion librates around the *z* axis with an r.m.s. amplitude of 5·3° and around axes perpendicular to *z* with an r.m.s. amplitude of 6·4°. The librations of the $Li(H_2O)_3^+$ columns around the *z* axis have an r.m.s. amplitude of 3·5° and of the water molecules around all axes have r.m.s. amplitudes of around 12°. The values of the amplitudes of thermal motion predicted by this model are compared with the observed values in Table 5.

The most striking feature of the structure is the complete regularity of the ClO_4^- ion which deviates by less than 0·002 Å and 0·3° from a regular tetrahedral

Table 5. *The r.m.s. components of thermal motion in* Å *along the major* (1), *intermediate* (2) *and minor* (3) *axes are given for each atom for the X-ray and the neutron experiment*

The predicted values are derived from the model of thermal motion described in the test.

		X-ray		Neutron		Direction
		Predicted	Observed	Predicted	Observed	
Cl	u_1	0·173	0·177	0·161	0·146	along *z*
	$u_2=u_3$	0·130	0·130	0·113	0·100	
O(1)	$u_1=u_2$	0·206	0·210	0·196	0·196	
	u_3	0·173	0·174	0·161	0·169	along *z* (Cl–O bond)
O(2)	u_1	0·236	0·241	0·227	0·222	close to *z*
	u_2	0·185	0·186	0·172	0·174	
	u_3	0·130	0·132	0·113	0·126	close to Cl–O bond
O(3)	u_1	0·173	0·181	0·161	0·168	along *z*
	u_2	0·164	0·166	0·151	0·148	
	u_3	0·130	0·142	0·113	0·092	close to bisector of Li–O–Li
Li	u_1	0·173	0·174	0·161	0·153	along *z*
	$u_2=u_3$	0·130	0·173	0·113	0·120	
H	u_1			0·230	0·271	
	u_2			0·230	0·230	
	u_3			0·113	0·145	close to O(3)–H bond

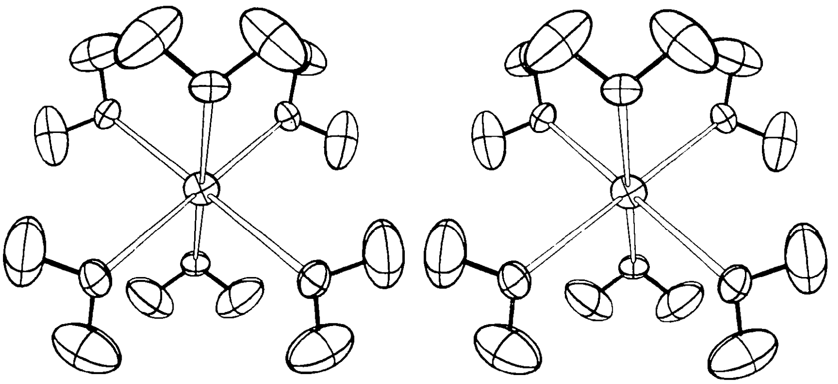

Fig. 1. Stereoscopic view of the arrangement of water molecules around Li viewed down the *c* axis. Each water bonds to a second Li atom directly above or below the one shown.

arrangement even though possessing a lower crystallographic site symmetry. Even with the correction of the bond lengths for thermal motion the two crystallographically distinct Cl–O distances are equal. This result is most surprising considering the very different chemical environments of the two oxygen atoms. Baur (1973) has shown that regular tetrahedra are the exception rather than the rule among the isoelectronic PO_4^{3-} groups and similar, if somewhat smaller, distortions are expected among ClO_4^- groups.

The bonding in $Li(H_2O)_3ClO_4$ can be analysed using bond valences or bond strengths (Brown & Shannon, 1973). The regularity of the ClO_4^- ion indicates that each Cl–O bond must have a strength of 1·75 valence units (v.u.) using the constraints that the sum of bond valences around each atom is equal to its atomic valence and that shorter bonds have larger valences. This leaves each O atom to form bonds with a total of 0·25 v.u. Since O(2) forms two bonds with H, each of them must have a strength of 0·125 v.u. and since O(1) forms six bonds to H each of these must have a strength of 0·042 v.u. Thus the regularity of the ClO_4^- ion indicates that the bonding from O(1) to H (see Fig. 4) is structurally significant even though the H–O distance of 2·617 Å exceeds the often quoted but somewhat arbitrary Hamilton & Ibers (1968) limit of 2·6 Å. Application of the above constraint to the remainder of the structure indicates that the Li–O bonds should have an average valence of 0·167 v.u. corresponding, according to Brown & Shannon (1973), to a length of 2·14 Å, identical with the observed values of 2·13 and 2·14 Å.

The environment of the Li atom is an octahedron elongated along one threefold axis (*c* crystal axis). The small difference in the two crystallographically distinct Li–O distances may not be significant but it is observed in the same sense in both the X-ray and neutron studies, the shorter bond being the one lying closer to the bisector of the H–O(3)–H angle.

Hydrogen bonding

The occurrence of weak hydrogen bonds in $Li(H_2O)_3ClO_4$ is in accord with the observation of relatively high frequency O–H stretch vibrations [3520–3590 cm^{-1} compared to more usual values around 3400 cm^{-1} (Couture-Mathieu & Mathieu, 1952; Brink & Falk, 1970*a*)]. Such high frequencies are found in other perchlorates and perchlorate solutions (Brink & Falk, 1970*b*) suggesting that weak hydrogen bonding is a characteristic of all hydrated perchlorate groups. In a discussion of the hydration and dissociation constants in aqueous solution of various acid species Brown (1975) has concluded that each oxygen atom of the ClO_4^- ion in neutral water will normally act as an acceptor to three hydrogen bonds leading to the formation by the whole ion of 12 hydrogen bonds of average valence of $\frac{1}{12} = 0{\cdot}083$ v.u. Such bonds are considerably weaker than normal hydrogen bonds [H–O(acceptor) = 0·20 v.u.; see Brown (1975)] of the kind found in ice or in hydrates of higher valence anions such as sulfates [*e.g.* $Mg(H_2O)_6SO_4.H_2O$; Ferraris, Jones & Yerkess

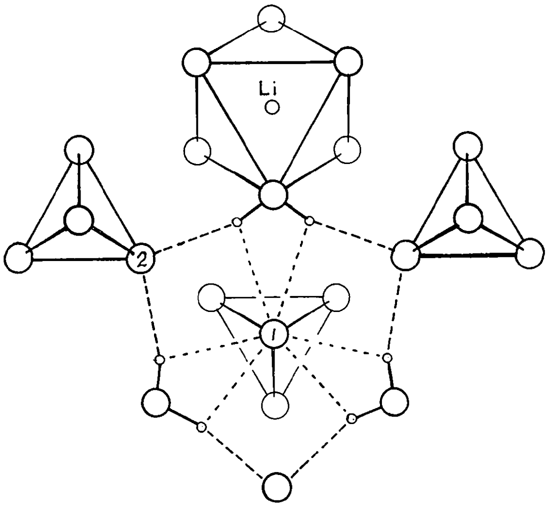

Fig. 2. Hydrogen bonding in $Li(H_2O)_3ClO_4$. The octahedron represents the $Li^+(H_2O)_6$ group, the tetrahedron the ClO_4^- ion. The acceptor H···O bonds are shown as broken lines.

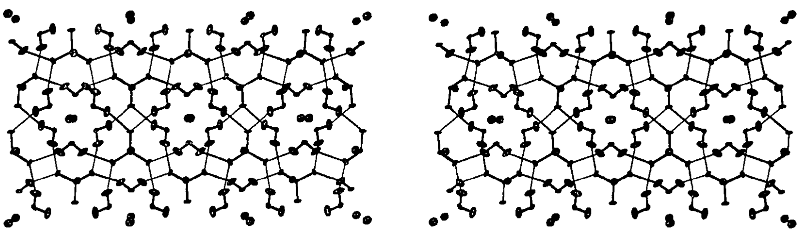

Fig. 3. A stereoscopic view of the basal planes containing the stronger O(3)–H···O(2) hydrogen bonds.

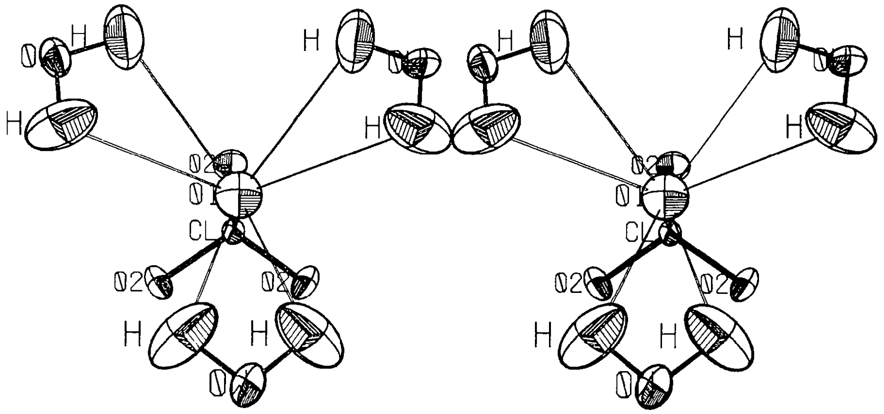

Fig. 4. A stereoscopic view of the weaker O(3)–H···O(1) hydrogen bonds.

(1973)]. The structure of $Li(H_2O)_3ClO_4$ is a good model for aqueous $LiClO_4$ solution since the ions bond to each other only through the water molecules. As expected in the solution, the ClO_4^- ion in the solid forms 12 hydrogen bonds, six of strength 0·125 and six of strength 0·042 v.u. Furthermore, the O–H infrared stretching frequency is virtually identical in the solid [O–D stretch 2619 cm^{-1}; Brink & Falk (1970*a*)], and in liquid solutions [O–D stretch 2620 cm^{-1}; Brink & Falk (1970*b*)], although the half width in the latter case is much larger indicating a larger variety of local environments.

Brown (1975) has also discussed the relationship between the O–H···O angle of a hydrogen bond and the H···O length and has suggested that in many cases the formation of weak hydrogen bonds is a direct result of a crystal packing requirement for a bent bond. Such is not the case here. The O–H···O angle of the stronger bond is only 164° instead of the value of around 140° that would normally be expected of a bond with H···O equal to 2·04 Å. The weaker bond is, however, bent by the expected amount (O–H···O = 106°). One can conclude that the weak hydrogen bonding observed in $Li(H_2O)_3ClO_4$ is directly related to the low valence of the perchlorate ion and is not the result of crystal packing forces.

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