(2·81 Å) than in the corresponding $NH_{sal}\cdots O(10)_{sal}$ (3·05 Å) hydrogen bond and the distance in $NH_{sal}\cdots O(4)_{barb}$ is longer (3·00 Å) than in the corresponding $NH_{barb}\cdots O(4)_{barb}$ hydrogen bonds (2·89, 2·91, 2·86 Å), in amobarbital I and II, and other hydrogen bonds of this type involving barbiturate as both donor and acceptor (Gartland & Craven, 1974). These distances are thus compatible with the conclusion that the barbiturates are more effective hydrogen-bonding donors than acceptors.

References

CRAVEN, B. M. & VIZZINI, E. A. (1969). *Acta Cryst.* B 25, 1993–2009.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104–109.

GARTLAND, G. L. & CRAVEN, B. M. (1974). *Acta Cryst.* B 30. in the press.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A 27, 368–376.

KUROYANAGI, S. (1956). Japanese Patent, 897.

SASADA, Y., TAKANO, T. & KAKUDO, M. (1964). *Bull. Chem. Soc. Japan*, 37, 940–946.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Acta Cryst.* 18, 1053–1058.

Lithium Nuclear-Magnetic-Resonance in Lithium Acetate Dihydrate, Li(CH3COO).2H2O

BY S. V. BHAT, A. C. PADMANABHAN AND R. SRINIVASAN

Department of Physics, Indian Institute of Science, Bangalore-12, India

^7Li n.m.r. in single crystals of lithium acetate dihydrate is used to determine the quadrupole coupling parameters: (e^2qQ/h) and η. The orientations of the principal z, y and x components of the electric field gradient tensor are determined to be along the crystallographic b, a and c axes respectively. The parameters experimentally determined are $(e^2qQ/h) = 154\cdot6$ kHz; and $\eta = 0\cdot9$. This study indicates a tetrahedral configuration around the Li ion, confirming the recent X-ray and p.m.r. results.

Introduction

The interaction between the quadrupole moment of a nucleus and the gradient of the electric field at the nuclear site perturbs the nuclear magnetic transitions between the Zeeman levels. The electric field gradient (e.f.g.) at a site thus reflects the local structural symmetry. It is possible, therefore, to obtain information regarding structural details around the resonating nucleus from a study of the quadrupole splitting of the nuclear-magnetic-resonance lines. With this objective a study of ^7Li n.m.r. in Li(CH3COO).2H2O is described.

Amirthalingam & Padmanabhan (1958) first studied the structure of Li(CH3COO).2H2O and fixed the space group as *Cmm2*. Clark (1964) however, after a calculation of the various bond lengths, drew attention to certain inconsistencies, and Galigné, Mouvet & Falgueirettes (1970), after a redetermination of the structure, concluded that the space group is *Cmmm* rather than *Cmm2* and further that the Li coordination is four-fold and not sixfold. The results of a proton-magnetic-resonance study in our laboratory by Padmanabhan & Srinivasan (1972) confirmed the results of Galigné *et al.* (1970) and indicated more probable locations for the water protons. It was therefore thought worth

while to look at the structure of this crystal from the point of view of the quadrupolar interaction at the Li sites.

According to Galigné *et al.* (1970), Li(CH3COO).2H2O crystals are orthorhombic with $Z = 4$. Two mirror symmetry elements, one in the *ac* plane and a second in the *bc* plane, pass through the Li sites, thus fixing the directions of the principal components of the e.f.g. tensor along the three crystallographic axes. The four Li ions in the unit cell are identical from the point of view of e.f.g. because of the mirror in the *ab* plane and the screw axis along **a**. So the structure predicts a spectrum characteristic of a single nucleus in each of the crystallographic planes: a central signal and a pair of satellites. Our n.m.r. study confirms this prediction.

Experimental

Single crystals of sufficient size (3 × 2 × 1·5 cm) were grown by slow evaporation of a saturated solution of AnalaR grade lithium acetate in distilled water, over calcium chloride in a desiccator. A Robinson oscillator working at 8·7 MHz was used with a 6 inch electromagnet. A magnetic field sweep calibrated by the ^7Li signal in

$Li_2SO_4.H_2O$ powder was used to record the signals at 10° intervals of rotation with respect to the static magnetic field. As the relaxation time of ^7Li nuclei in the sample was found to be long, the crystal was irradiated for 48 h with a 2000 Ci γ-ray source. This treatment improved the S/N ratio considerably.

The crystallographic axes were checked by X-ray measurements of cell dimensions, and the spectra were recorded first for rotation about **b** with **a** as the reference axis. When the orientation of the principal axes is known, rotation about a single axis is sufficient to determine the remaining relevant parameters: the magnitudes of the principal components, the quadrupole coupling constant (e^2qQ/h) and the asymmetry
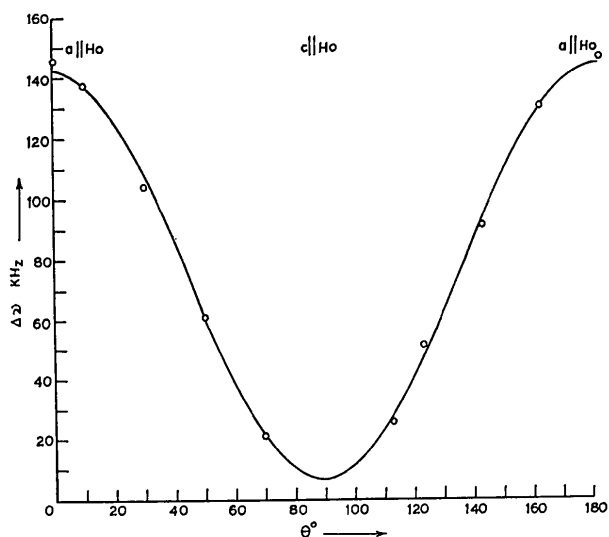

● O (3)   ⊗ H_2O (2)   ◉ H_2O (1)   ● Li

Fig. 3. Projection of the structure of $Li(CH_3COO).2H_2O$ down a (Galigné et al., 1970).

Fig. 1. Theoretical curve and experimental points of the satellite separation Δv versus the angle of rotation θ for b-axis rotation.
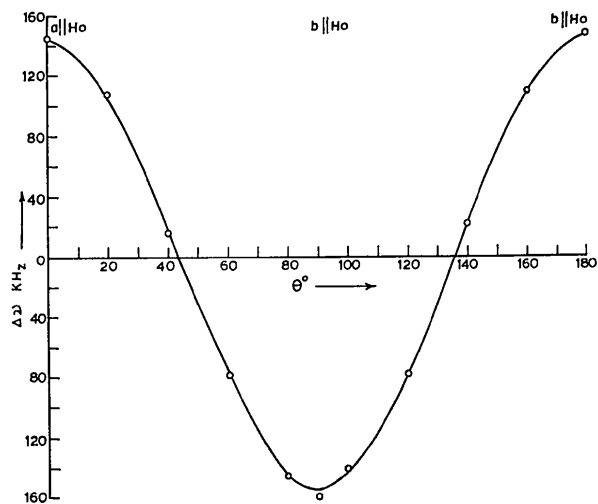

⊘ WATER OXYGENS

O ACETATE OXYGENS

● LITHIUM

Fig. 4. Oxygen tetrahedron surrounding the Li ion, together with the orientation of the principal components of the e.f.g.
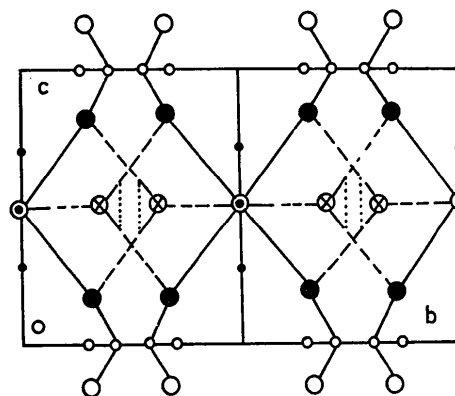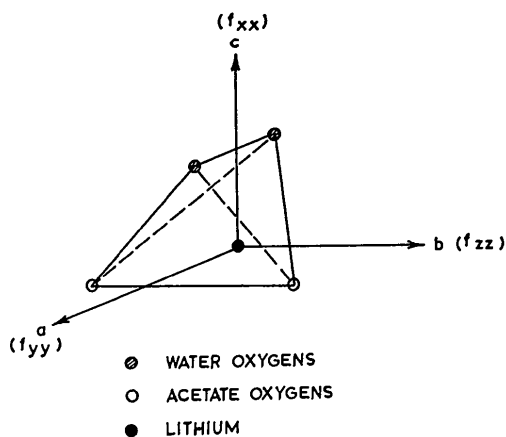

Fig. 2. Theoretical curve and experimental points of satellite separation Δv versus the angle of rotation θ for c-axis rotation.

parameter η. However, spectra were recorded also for rotation about **c** to obtain additional confirmation of the results.

Results

In each orientation a central signal and a pair of satellites symmetrically placed on either side of the central signal were observed indicating that there is only one e.f.g. tensor and confirming that all the four Li ions in the unit cell are identical as predicted by the crystal structure. Since the satellites were symmetrically placed about the central signal, second-order effects were assumed to be of the order of the experimental errors.

Figs. 1 and 2 show the plots of satellite separations against the orientations of the crystal for **b** and **c** rotations respectively. The experimental points were fitted by the method of least squares to the theoretical curve

$$\Delta v_m^* = (m - \tfrac{1}{2})\,(a_x + b_x \cos 2\theta_x)$$

Cohen & Reif (1957).

From the graphs, it is seen that the splitting is maximum when the crystallographic b axis is parallel to H_0, minimum when c is parallel to H_0, and intermediate when a is parallel to H_0.

This result is characteristic of a tetrahedrally coordinated lithium nucleus with z, y and x principal axes along the b, a and c directions respectively, confirming the results of Galigné et al. (1970) according to which two water oxygens in the ac plane at a distance of 2·045 Å from the lithium ion and two acetate oxygens in the bc plane at a distance of 1·895 Å from the lithium ion form a slightly distorted tetrahedron around the lithium ion [Figs. 3 and 4]. Consequently the component of the e.f.g. tensor along c should be very small and the components along a and b should be nearly equal. This is in agreement with our results.

The values of (e^2qQ/h), η, and the orientation and magnitudes of the principal components of the e.f.g. tensor obtained for the two rotations are given in

Table 1. ^7Li quadrupole coupling constant (e^2qQ/h) and asymmetry parameter η of $Li(CH_3COO).2H_2O$

Axis of rotation	(e^2qQ/h)	η
b	154·6 kHz	0·86
c	154·6	0·90

Tables 1 and 2. The value of (e^2qQ/h) for ^7Li has been found to vary from 15 to 200 kHz. Our value of 154·6 kHz is on the high side, indicating considerable covalency.

Table 2. Direction cosines of the principal axes of the ^7Li quadrupole coupling tensor in $Li(CH_3COO).2H_2O$

Axis of rotation	Principal components	a	b	c
b	f_{zz}	0	1	0
	f_{yy}	1	0	0
	f_{xx}	0	0	1
c	f_{zz}	0	1	0
	f_{yy}	1	0	0
	f_{xx}	0	0	1

References

AMIRTHALINGAM, V. & PADMANABHAN, V. M. (1958). Acta Cryst. 11, 896.

CLARK, J. R. (1964). Acta Cryst. 17, 459–461.

COHEN, M. H. & REIF, F. (1957). Solid State Phys. 5, 321–438.

GALIGNÉ, J. L., MOUVET, M. & FALGUEIRETTES, J. (1970). Acta Cryst. B26, 368–372.

PADMANABHAN, A. C. & SRINIVASAN, R. (1972). Acta Cryst. B28, 3188–3190.

The Crystal Structure of $Bi_2Cu_3S_4Cl$

BY J. LEWIS JR AND V. KUPČÍK

Mineralogisch-Kristallographisches Institut der Universität Göttingen, Germany (BRD)

Crystals of $Bi_2Cu_3S_4Cl$ were prepared and the structure was determined from three-dimensional diffractometer data. The substance is orthorhombic, with $a_0=20·719$, $b_0=10·308$, and $c_0=4·00$ Å. The space group is $P2_12_12_1$ with $Z=4$. The reliability index is 6·6 % for 937 reflexions. The bismuth coordination polyhedra are connected by common edges and form chains of the type $(Bi_2S_4)^{2-}_\infty$ and $(BiS_2Cl)^{2-}_\infty$ which lie parallel to the c axis. These chains are linked over a 2_1 axis by chlorine atoms so that channels are formed. Splitting of the Cu(1) atom site into two nearly equivalent sites statistically occupied by copper atoms of unusual coordination is considered.

Experimental

The crystals were synthesized in a closed Pyrex glass ampoule with a volume of 20 ml; 2·2 ml of HCl (conc.) and 0·01 mol each of PbS, Cu_2S and Bi_2S_3 were used for synthesis. The temperature maintained over a period of 60h was 240°C and the calculated pressure was 270 bar. Other by-products were CuCl, $PbCl_2$ and H_2S. The composition was determined from electron-microprobe analysis as well as from crystal-structure analysis. The size of the crystal used for the investigation was $400 \times 25 \times 13·5 \ \mu m$. The Weissenberg equi-inclination technique with Cu $K\alpha$ radiation was used for the determination of lattice parameters and space group. The only observed systematic absences were $h00$ with $h=2n+1$; $0k0$ with $k=2n+1$ and $00l$ with $l=2n+1$, thus uniquely establishing the space group as $P2_12_12_1$. For the structure determination, the intensities of 937 reflexions with $\sin \theta$ up to 0·42 were collected on a Weissenberg diffractometer (STADI-2 system from