Ce résultat permet de conclure que l'énantiomère dextrogyre de la forme $F = 70°C$ de l'o-méthoxy (hydroxy-1' éthyl) benzène chrome tricarbonyle a pour configuration absolue:

(1R) méthoxy-2[(S) hydroxy-1' éthyl]benchrotrène. On peut enfin en déduire immédiatement la configuration absolue de tous les composés qui ont pu être reliés par filiation chimique à cet énantiomère.

En particulier les configurations absolues suivantes correspondent respectivement aux formes dextrogyres (+) ou lévogyres (−) indiquées:
acide (1R) méthoxy-2 benzoïque chrome tricarbonyle: (−),

(1R) méthoxy-2 acétyl benchrotrène: (−),

(1R) hydroxy-2 acétyl benchrotrène: (+),

(1R) hydroxy-2 [(R) hydroxy-1' éthyl] benchrotrène $(F = 184°)$: (+).

Références

BESANCON, J. & TIROUFLET, J. (1969). Bull. Soc. Chim. Fr. p. 861.

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). Nature, Lond. 168, 271.

CAHN, R. S., INGOLD, C. & PRELOG, V. (1966). Angew. Chem. Int. Ed. 5, n° 4, 385.

DABARD, R. & MEYER, A. (1967). C.R. Acad. Sci. Paris, Série C, 264, 903.

DUSAUSOY, Y., PROTAS, J., BESANCON, J. & TIROUFLET, J. (1970). C.R. Acad. Sci. Paris, Série C, 271, 1070.

HOREAU, A. (1961). Tetrahedron Letters, n° 15, 506.

PAULING, L. (1960). The Nature of Chemical Bond. Ithaca: Cornell Univ. Press.

SCHÖGL, K. (1966). Fortschr. Chem. Forsch. 6, 479.

A Proton Magnetic Resonance Study of Lithium Acetate Dihydrate, Li(CH3COO).2H2O

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A proton magnetic resonance study of single crystals of Li(CH3COO).2H2O is reported. It confirms the earlier X-ray studies on the crystal by Galigné, Mouvet & Falgueirettes [Acta Cryst. (1970). B26, 368] and suggests a more probable location for the protons of the water molecules.

Introduction

The structure of Li(CH3COO).2H2O was first studied by Amirthalingam & Padmanabhan (1958). The space group was fixed as $Cmm2$, purely on the packing considerations of the four acetate ions. Clark (1964) pointed out that this structure was not satisfactory and needed refinement on the grounds that (i) the lithium coordination is sixfold and (ii) the bond-lengths are not consistent. Galigné, Mouvet & Falgueirettes (1970) have since carried out a refinement and conclude that the crystals are orthorhombic, space group $Cmmm$ (not $Cmm2$), with $Z = 4$, and cell dimensions $a = 6.820 \pm 0.007$, $b = 10.88 \pm 0.01$, $c = 6.620 \pm 0.007$ Å. The coordination number of the lithium ion is 4 (not 6). They proposed two different types of water molecules, confirming the observation of Cadene (1969), who noted a splitting of certain absorption bands in IR spectra at low temperatures.

Galigné et al. (1970) have also tried to fix the positions of the protons. The O–H distances in the water molecules, so obtained, are very short. The inaccuracy in the proton positions is to be expected in their sort of study, the electronic cloud being strongly asymmetric in an O–H bond. However, the positions found require too short a distance between the protons of the water molecule. Hence the present p.m.r. study was carried out to locate the water protons more precisely, using the magnitudes of the p–p vectors obtained from the p.m.r. data, in conjunction with the X-ray results.

Experimental

Crystals of Li(CH3COO).2H2O were grown by slow evaporation of an aqueous solution of the salt at room temperature. Most of the crystals tended to twin on [110]. Rejecting these, and selecting the proper seeds, 'single crystals' were finally obtained. These had a tendency to grow in one of two habits: (a) in the form of thin plates with six sides, the ab face being well developed, the c axis being dwarfed; (b) in the form of bigger crystals with a well-developed bc face and a retardation in the direction of the a axis. The crystals were verified to be 'single', by using a polarizing microscope. Crystals of dimensions $1.5 \times 1.5 \times 0.5$ cm were used in the experiment.

The n.m.r. spectrometer used was a modified Pound–Knight–Watkins or a Robinson Oscillator in conjunction with a 12″ magnet. Suitable crystals were mounted with (i) a axis vertical, H_0 being horizontal, the reference axis being the b axis; (ii) b axis vertical, H_0 being horizontal, the reference axis being the c axis. Signals were recorded for every 10° rotation in the ac and bc planes.

A study of the space-group symmetry indicates that there are two non-equivalent p–p vectors of the water molecules, in each of the two planes. The recorded signals therefore contain (i) a central peak from the protons of the rotating methyl group and (ii) two Pake doublets from the water molecules of the hydrates. Subtracting out the methyl group peak, and choosing a standard component curve for the Pake doublet from a well-resolved spectrum, the signals were resolved, in the usual way, and the peak separations (ΔH oersteds) of the doublets obtained for various values of φ.

These ΔH values were then fitted by the method of least squares to the Pake (1948) equation:

$$\Delta H = 2\alpha[3\cos^2\delta\cos^2(\varphi-\varphi_0)-1]; \quad 2\alpha = 3\mu r^{-3}.$$

The parameters γ, φ_0, δ obtained therefrom give the length and orientation of the inter-proton vectors with respect to the crystallographic axes. The parameters of the vectors are given in Table 1. In the bc plane the p–p vectors have their positive maxima at approximately $\varphi_0 = 0$ and 90°. The maximum value of positive $\Delta H = 4\alpha$. In the ac plane the I p–p vector is a straight line parallel to the φ axis at $\Delta H = -2\alpha$, the II vector has a positive maximum $= 4\alpha$, approximately at $\varphi_0 = 0°$. The mean values of the inter-proton distances are 1·581 and 1·583 Å respectively for the two vectors.

Fig. 1. Projections of the structure of Li(CH₃COO).2H₂O looking down (a) the a axis and (b) the c axis. The dotted lines indicate the p–p vectors as obtained from the p.m.r. data.

● O(3)   ⊗ H₂O(2)   ◉ H₂O(1)   • Li

Table 1. *Parameters of the p–p vectors*

	I Vector		II Vector	
	bc plane	ac plane	bc plane	ac plane
φ_0	0° 10′	–	89° 50′	0° 23′
δ	0°	90°	0°	$0° \pm (1\cdot5)°$
r	1·581 Å	1·582 Å	1·581 Å	1·586 Å

Discussion

The projections of the atomic positions down the a axis and c axis are given in Fig. 1. The water molecules H₂O(1) are in contact with two lithiums. These water molecules make H-bonds with oxygens of the water molecules of type H₂O(2) situated at $x = \frac{1}{2}$. The H₂O(1)–H₂O(2) distance is 2·812 Å and the angle H₂O(2,I)–H₂O(1)–H₂O(2,II) is 92°9′, using the notation of Galigné *et al.* (1970). The line joining the two H₂O(2) is parallel to the b axis, with direction cosines $l=0$, $m=1$, $n=0$. If we assume the p–p vector of H₂O(1) to be parallel to this 'acceptors line', we get $\delta_a=0$, $\varphi_{0a}=0$ in the bc plane; and $\delta_b=90°$ in the ac plane. This agrees with our p.m.r. data for vector I, within limits of experimental error.

The H₂O(2) are, in turn, H-bonded to the oxygens O(3) of the acetate groups. The H₂O(2)–O(3) distances are each = 2·771 Å, and the angle O(3)–H₂O(2)–O(3,III) = 105°15′. Here again, the line joining the O(3) is in the bc plane, parallel to the c axis with direction cosines $l=0$, $m=0$, $n=1$, leading to $\delta_a=0$, $\varphi_{0a}=90°$ in the bc plane and $\delta_b=0$, $\varphi_{0b}=0$ in the ac plane. Again, if we assume the p–p vector of H₂O(2) to be parallel to the 'acceptors line', there is agreement with our p.m.r. data for vector II within limits of experimental error.
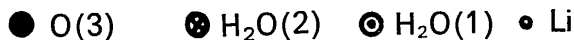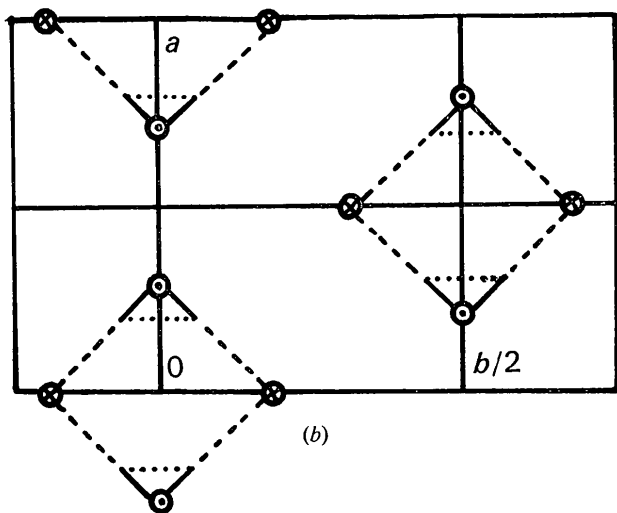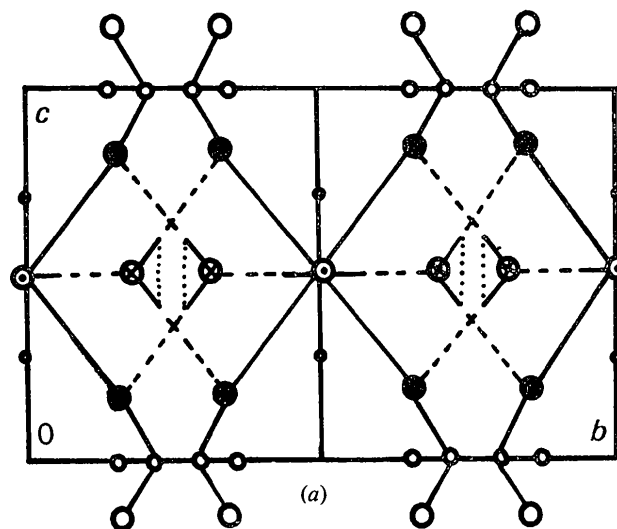
Table 2. *Coordinates of water protons* (Å)

Values in parentheses are taken from Galigné *et al.* (1970).

		x	y	z	Distance O_w–proton (Å)
I Vector	Proton 1	2·221	4·650	3·31	1·097
		(2·0324)	(4·7763)	(3·31)	(0·87)
p–p vector of $H_2O(1)$	Proton 2	2·221	6·230	3·31	1·097
		(2·0324)	(6·1037)	(3·31)	(0·87)
II Vector	Proton 1	0	2·629	4·101	0·996
		(0)	(2·5459)	(4·0117)	(0·9)
p–p vector of $H_2O(2)$	Proton 2	0	2·629	2·519	0·996
		(0)	(2·5459)	(2·6083)	(0·9)

Location of protons of water molecules

Assuming a linear H-bond in each case and putting in the value $r = 1·581$ and $1·583$ Å (as determined by this investigation) in the two cases, the coordinates of the water protons were calculated. The results are given in Table 2.

The assumption of a linear H-bond appears to be more valid for $H_2O(2)$ than for $H_2O(1)$. The latter might be involved in slightly non-linear H-bonds. This point must be borne in mind when one considers the co-ordinates of the protons of $H_2O(1)$. The distances between the protons and their parent oxygen atoms are 1·097 and 0·996 Å respectively. These values appear to be 'normal', contributing to fairly strong H-bonds. An IR spectrum was obtained for the salt and this also suggests such normal H-bonds. On the other hand, using the values of the coordinates of the protons given by Galigné *et al.* (1970), if 2α is calculated from the inter-proton distances, improbable values of the order of 18 and 15 Oersteds are obtained. Thus, our p.m.r. data lead to a more probable location for the protons.

Conclusion

The p.m.r. data on single crystals of lithium acetate dihydrate confirm the space group *Cmmm* and the presence of the two types of water molecules. The water oxygen atoms are tetra-coordinated, in $H_2O(2)$ by four H, and $H_2O(1)$ by two Li and two H. More probable locations for the water protons have been obtained.

References

AMIRTHALINGAM, V. & PADMANABHAN, V. M. (1958). *Acta Cryst.* **11**, 896.
CADENE, M. (1969). *C.R. Acad. Sci. Paris*, **268 B**, 1079.
CLARK, J. R. (1964). *Acta Cryst.* **17**, 459.
GALIGNÉ, J. L., MOUVET, M. & FALGUEIRETTES, J. (1970). *Acta Cryst.* **B 26**, 368.
PAKE, G. E. (1948). *J. Chem. Phys.* **16**, 327.

The Crystal and Molecular Structure of a Lactone Oxime

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The base-catalyzed condensation of dimedone with β-nitrostyrene gives an unusual lactone oxime, $C_{16}H_{17}NO_3$, which crystallizes in the monoclinic space group, $P2_1/n$. The unit-cell parameters are $a = 13·158$, $b = 8·657$, $c = 12·205$ Å, and $\beta = 98·84°$. Data were collected on an automated diffractometer; the structure was solved by direct methods and refined to an R value of 0·044 by the least-squares method. The oxime is exclusively *anti* with respect to the oxygen of the lactone ring and, in the crystalline state, is hydrogen-bonded to the carbonyl oxygen of an adjacent molecule.

Introduction

Several plausible structures (IIIa–IIIc) can be written for the product $C_{16}H_{17}NO_3$ of the base-catalyzed con-densation of dimedone (I) and β-nitrostyrene (II). Be-restovitskaya, Sopova & Perekalin (1967) apparently were the first to synthesize this compound, to which they assigned the structure (IIIa).