

The Crystal Structure and Methyl Group Dynamics in the Room-Temperature and Low-Temperature Phases of Lithium Acetate Dihydrate

G. J. Kearley,* B. Nicolai,* P. G. Radaelli,* and F. Fillaux†

*Institut Laue-Langevin, B.P. 156X, 38042 Grenoble Cedex 09, France; and †LASIR, CNRS, Rue Henri Dunant, 94320 Thiais, France

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Neutron powder diffraction is used to determine the crystal structure of $\text{LiCD}_3\text{COO} \cdot 2\text{D}_2\text{O}$ at 293 and 1.5 K. Lithium acetate dihydrate crystallizes in the *Cmmm* space group in the room-temperature phase with $a = 6.82082(9)$ Å, $b = 10.88842(12)$ Å, $c = 6.59911(7)$ Å, and $Z = 4$. The CH_3 groups are dynamically disordered, and there are short H bonds between the water molecules and the acetate oxygen atoms. There is a phase transition to a low-temperature modification which has the space group *Pman* with $a = 6.70246(7)$ Å, $b = 10.87932(11)$ Å, $c = 6.56999(7)$ Å, and $Z = 4$. The CH_3 groups are ordered in this phase, but have large thermal ellipsoids even at 1.5 K. The H atoms of the water molecules also have large thermal ellipsoids even at 1.5 K, but the CH_3 group tunneling spectrum shows no evidence for coupling with the motions of the water molecules. © 1996 Academic Press, Inc.

INTRODUCTION

Rotational tunneling of small molecules or molecular groups such as CH_3 at low temperatures has been intensively studied for the past 20 years. Until recently these quantum motions were regarded as being entirely single particle in nature (1), but more recently unequivocal evidence of extensively correlated rotor–rotor coupling has accumulated (2–4). The first evidence for coupling of quantum rotors was obtained for lithium acetate dihydrate ($\text{LiAc} \cdot 2\text{H}_2\text{O}$, where $\text{Ac} = \text{CH}_3\text{COO}^-$ or CD_3COO^-), which showed extra splitting of the tunnel-split librational ground state (5–7). This was modeled in terms of isolated pairs of coupled tops. However, the coupled-pair model fails to account for the details of the librational spectrum of $\text{LiAc} \cdot 2\text{H}_2\text{O}$ (5), and recent experimental work with isotopically mixed $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}/\text{LiCH}_2\text{DCOO} \cdot 2\text{H}_2\text{O}$ (8) revealed that the energy-level scheme of LiAc is more complex than was originally thought. An alternative interpretation based on long-range rotor–rotor coupling of pairs has been suggested.

This work has been carried out on the assumption that

the room-temperature crystal structure of $\text{LiAc} \cdot 2\text{H}_2\text{O}$ persists down to liquid-helium temperatures. Even the crystal structure of this phase has been questioned, and the most recent study was made with X-rays more than 25 years ago (9). In the present paper we present the crystal structures of the room-temperature and low-temperature modifications of $\text{LiAc} \cdot 2\text{H}_2\text{O}$ as determined by neutron powder diffraction, and relate this to the low-temperature motions of the hydrogen atoms. The use of neutron diffraction allows us to locate the deuterium atoms.

EXPERIMENTAL

Samples of $\text{LiCD}_3\text{COO} \cdot 2\text{D}_2\text{O}$ were prepared via the reaction of lithium carbonate with deuterated acetic acid in D_2O . The sample was purified by recrystallization from D_2O . The polycrystalline sample was placed in a standard thin-walled vanadium container, and temperature control was achieved using a standard liquid-helium cryostat.

Diffraction patterns were measured at a fixed neutron wavelength of 1.5941 Å, using the D2B diffractometer (10) at the Institut Laue Langevin, France. Rietveld refinement of the patterns was achieved using the GSAS (11) suite of programs. Observed and calculated diffraction patterns are illustrated in Figs. 1a and 1b, and data collection and crystal structure parameters are given in Table 1. The tunneling spectra of $\text{LiCH}_3\text{COO} \cdot 2\text{D}_2\text{O}$ and $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$ were recorded with a resolution of 12 μeV using the IN5 spectrometer at the Institut Laue Langevin, France.

RESULTS AND DISCUSSION

The first X-ray diffraction study of $\text{LiAc} \cdot 2\text{H}_2\text{O}$ proposed the *Cmm2* space group (12) but this was subject to some question regarding the interatomic distances (13). Infrared and Raman studies also militated against this structure (14–16). In 1970 Galigne *et al.* (9) proposed the *Cmmm* space group with somewhat different cell parameters, but this is only plausible if the methyl groups are

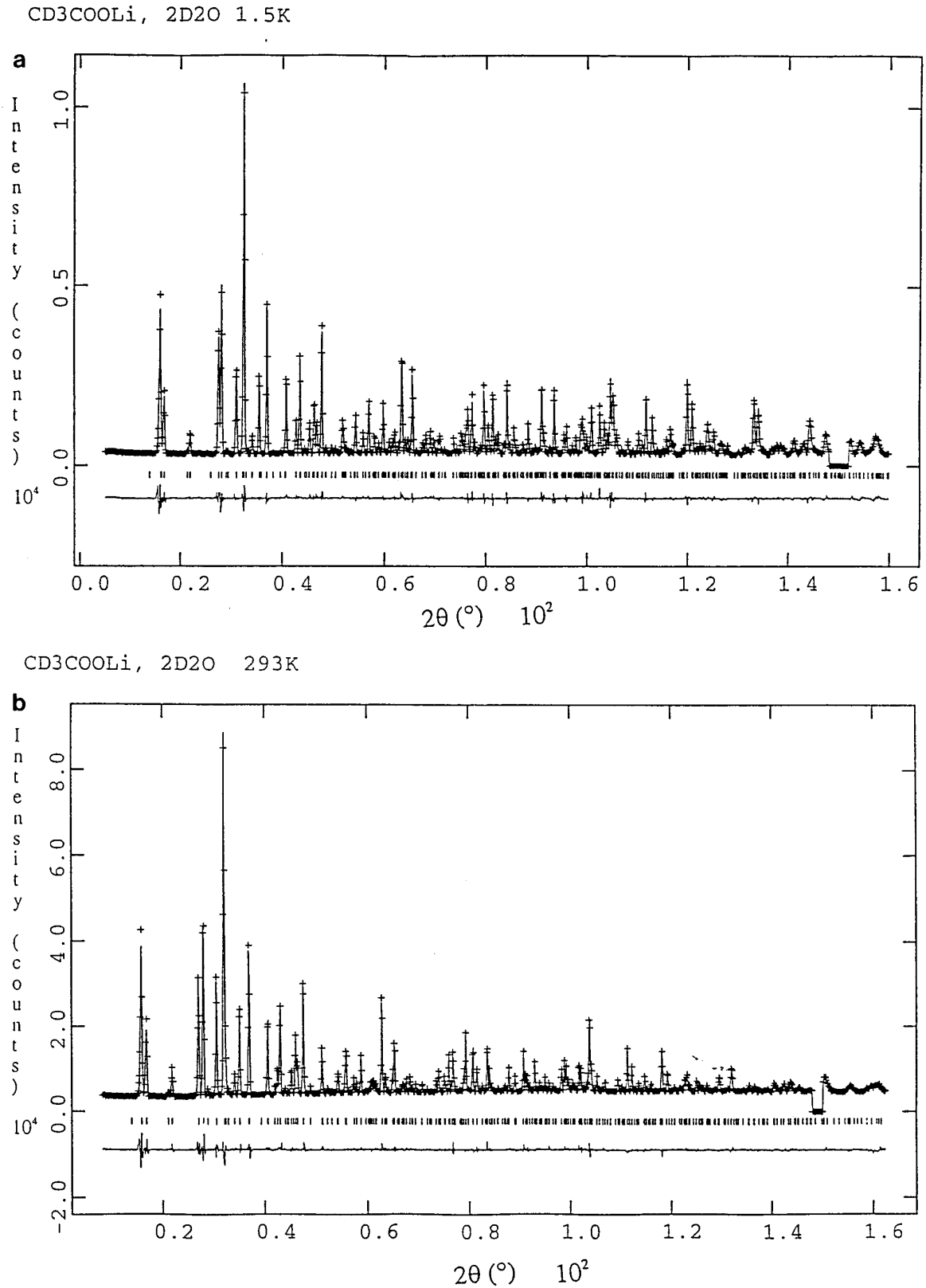


FIG. 1. Observed (crosses), calculated (line), and difference (lower line) diffraction patterns for $\text{LiCD}_3\text{COO} \cdot 2\text{D}_2\text{O}$ at room temperature (b) and at 1.5 K (a). The vertical lines mark the positions of the Bragg reflections.

TABLE 1
Experimental and Statistical Results of the Data Collection
and Crystal Structure Solution

Data collection parameters of D2B		
Incident wavelength: 1.6 Å		
64 Detectors of ^3He		
2θ range: 5° to 165°		
Crystal structure		
Temperature (K)	293	1.5
Space group	<i>Cmmm</i>	<i>Pman</i>
<i>a</i> (Å)	6.82082 (9)	6.70246 (7)
<i>b</i> (Å)	10.88842 (12)	10.87932 (11)
<i>c</i> (Å)	6.59911 (7)	6.56998 (7)
Volume (Å ³)	490.10	479.07
Calculated density (g/cm ³)	1.477	1.511
<i>R</i> values	0.0404	0.0521
Goodness of fit	5.086	8.414

disordered. Our work confirms this space group, *Cmmm*, with 1 formula unit in the unit cell, and locates the hydrogen atoms of the water molecules. Atomic positions are collected in Table 2 and structural parameters are reported in Table 3.

The structure consists of layers of water and acetate ions in the *xy* plane which are separated by layers of Li ions (see Fig. 2). There are two crystallographically distinct water molecules, which are H bonded to each other (1.85 Å). In addition, one of the water molecules also forms H bonds (1.79 Å) which link the acetate and water planes.

The methyl groups of neighboring acetate ions are separated by 3.24 Å (C–C), a relatively short distance being at the origin of the models involving coupled pairs of rotors. Symmetry constrains each CH₃ group to be disordered between two orientations related by a $\pi/3$ rotation (Fig. 2). Given the known rotational tunneling of the CH₃ groups in the low-temperature phase, this disorder is certain to be dynamic in nature.

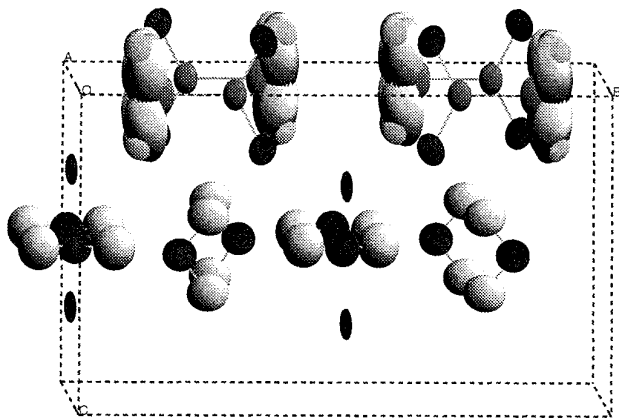


FIG. 2. Illustration of the crystal structure of $\text{LiCD}_3\text{COO} \cdot 2\text{D}_2\text{O}$ at room temperature showing the disorder of the CD_3 groups.

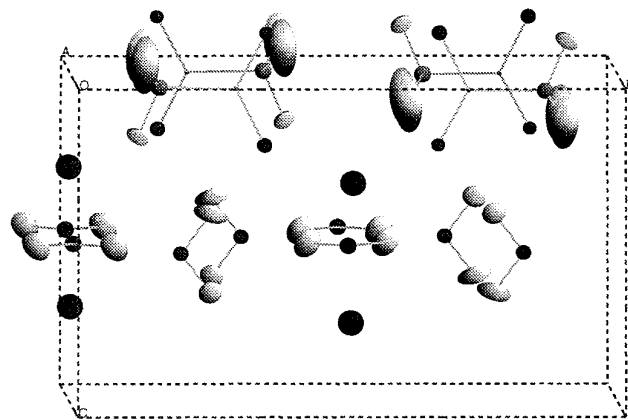


FIG. 3. Illustration of the crystal structure of $\text{LiCD}_3\text{COO} \cdot 2\text{D}_2\text{O}$ at 1.5 K showing the thermal ellipsoids of the CD_3 groups and the D_2O molecules.

The transition to the low-temperature phase leads to the appearances of a set of new reflections. With the exception of two very weak peaks around $2\theta \approx 25^\circ$ (for which we have not found any satisfactory indexing), all extra reflections can still be indexed on the original unit cell. Analysis of the systematic absences indicates that two of the glide planes of the room-temperature structure ($a \perp y$ and $u \perp z$) are still present at 1.5 K, but that the C-centering translation is absent, consistent with the loss of two mirror planes ($\perp y$ and $\perp z$) and a number of centers of inversion. Based on the aforementioned extinction rules, two space groups are possible for the low-temperature structure: *Pman* (centrosymmetric) and *P2an* (noncentrosymmetric). The non-standard space groups *Pman* and *P2an* are used instead of the standard ones, *Pmna* and *Pnc2*, for consistency with the lattice constants of the previously published room-temperature structure (9). Preliminary refinements carried out using the *Pman* space group indicated that all the “heavy” atoms (C and O) have small Debye–Waller factors. Furthermore, any attempt to remove the mirror plane $\perp x$ resulted in divergences of the positional parameters. We therefore concluded that the low-temperature structure is centrosymmetric and carried out all subsequent refinements in the *Pman* space group. Atomic positions are collected in Table 2 and structural parameters are reported in Table 3. The change from *Cmmm* to *Pman* entails an ordering of the CH₃ groups (Fig. 3). There is a shortening of the hydrogen bonds, and a small reduction of the separation between the methyl groups which, taken alongside the ordering of these groups, tends to lend support to the proposed rotor/rotor coupling (5–7). Overall, the structural changes in going from the room-temperature to the low-temperature phase are rather slight, as would be expected for transitions in which molecular groups move from a regime of classical rotational diffusion to one of quantum rotational tunneling.

TABLE 2
Atomic Positions and Thermal Parameters of Lithium Acetate Dihydrate at 293 and 1.5 K

Name	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Occupancies	$U_i/U_e * 100$	
at 293 K						
Li	0.0000	0.5000	0.2850(1)	1	2.94	
C1	0.0000	0.2880(2)	0.0000	1	1.65	
C2	0.0000	0.1486(2)	0.0000	1	2.82	
O1	0.2153(5)	0.50000	0.5000	1	2.33	
O2	0.0000	0.1863(3)	0.5000	1	2.54	
O3	0.0000	0.3413(2)	0.1687(3)	1	2.70	
D1	0.3011(3)	0.4292(2)	0.5000	1	3.20	
D2	0.0000	0.2396(2)	0.3815(3)	1	3.41	
D3	0.1195(1)	0.1172(4)	0.0835(9)	0.5	6.30	
D4	0.0000	0.1103(8)	0.1449(1)	0.5	10.53	
at 1.5 K						
Li	0.0000	0.5018(2)	0.2868(1)	1	1.1(1)	
C1	0.0000	0.2864(2)	-0.002(1)	1	-0.03(4)	
C2	0.0000	0.1465(2)	-0.0051(7)	1	0.43(5)	
O1	0.2169(4)	0.5000	0.5000	1	0.44(5)	
O2	0.0000	0.1866(2)	0.5013(9)	1	0.36(5)	
O3	0.0000	0.3395(4)	0.1711(5)	1	0.36(9)	
O3bis	0.0000	0.3419(4)	-0.1698(5)	1	0.29(8)	
D1	0.3063(2)	0.4284(1)	0.5016(5)	1	1.41	
D2	0.00000	0.2407(4)	0.3808(6)	1	1.36	
D2bis	0.00000	0.2404(3)	-0.3791(6)	1	1.26	
D3	0.1296(3)	0.1157(2)	-0.0871(4)	1	2.80	
D4	0.00000	0.1073(3)	0.1452(5)	1	3.44	
Name	U11 * 100	U22 * 100	U33 * 100	U12 * 100	U13 * 100	U23 * 100
at 293 K						
Li	6.9(7)	0.3(4)	1.6(4)	0.00	0.00	0.00
C1	2.4(2)	0.9(1)	1.7(1)	0.00	0.00	0.00
C2	4.6(3)	1.2(1)	2.7(2)	0.00	0.00	0.00
O1	2.5(2)	1.9(2)	2.4(2)	0.00	0.00	0.00
O2	3.8(2)	1.9(2)	1.9(2)	0.00	0.00	0.00
O3	5.1(2)	1.2(1)	1.8(1)	0.00	0.00	-0.3(1)
D1	3.3(1)	2.8(1)	3.5(1)	0.16(9)	0.00	0.00
D2	5.0(1)	2.9(1)	2.3(1)	0.00	0.00	0.1(1)
D3	6.6(4)	2.8(2)	9.5(5)	1.4(2)	-2.1(3)	0.9(2)
D4	27.4(23)	1.8(3)	2.3(3)	0.00	0.00	0.1(3)
at 1.5 K						
Li	1.06(14)	1.06	1.06	0.00	0.00	0.00
C1	-0.03(4)	-0.03	-0.03	0.00	0.00	0.00
C2	0.43(5)	0.43	0.43	0.00	0.00	0.00
O1	0.44(5)	0.44	0.44	0.00	0.00	0.00
O2	0.36(5)	0.36	0.36	0.00	0.00	0.00
O3	0.36(9)	0.36	0.36	0.00	0.00	0.00
O3bis	0.29(8)	0.29	0.29	0.00	0.00	0.00
D1	1.85(9)	1.14(9)	1.24(8)	0.29(8)	-0.1(1)	-0.3(1)
D2	1.74(20)	1.78(21)	0.6(2)	0.00	0.00	0.4(2)
D2bis	2.23(20)	0.83(21)	0.7(2)	0.00	0.00	-0.08(15)
D3	2.12(11)	1.25(12)	5.0(2)	-0.1(1)	1.5(1)	-0.26(9)
D4	9.21(33)	0.69(17)	0.4(1)	0.00	0.00	0.23(13)

TABLE 3
Structural Data of Lithium Acetate Dihydrate
at 293 and 1.5 K, Bond Lengths (Å) and
Angles (°)

	293 K	1.5 K
Coordination of lithium		
Li-Li	2.84(1)	2.801(13)
Li-O1	2.042(6)	2.019(5)
Li-O3	1.89(4)	1.92(1)
Li-O3bis		1.87(1)
O1-Li-O1	91.9(3)	92.2(3)
O3-Li-O3	132.1(4)	
O3-Li-O3bis		132.4(4)
O1-Li-O3	106.4(1)	105.4(6)
O1-Li-O3bis		107.2(6)
Li-Li-O1	45.9(2)	46.07(14)
Li-Li-O3	113.9(2)	112.5(9)
Li-Li-O3bis		115.2(9)
Acetic groups		
C1-C2	1.518(3)	1.522(3)
C1-O3	1.255(2)	1.277(5)
C1-O3bis		1.256(5)
C2-D3	1.042(8)	1.08(3)
C2-D4	1.042(10)	1.076(4)
C2-C1-O3	117.5(1)	117.6(35)
O3-C1-O3	124.9(3)	
C2-C1-O3bis		118.0(4)
O3-C1-O3bis		124.4(23)
C1-C2-D3	109.2(3)	108.55(22)
C1-C2-D4	113.5(5)	112.7(4)
D3-C2-D3	102.9(5)	107.7(4)
D3-C2-D4	110.6(3)	109.6(2)
D4-C2-D4	133.0(10)	
Water molecules		
O1-D1	0.968(2)	0.982(2)
O2-D2	0.973(2)	0.986(5)
O2-D2bis		0.979(5)
D1-O1-D1	105.6(4)	104.9(3)
D2-O2-D2	106.9(4)	
D2-O2-D2bis		109.7(3)
Hydrogen bonds		
O2-D1	1.8502(3)	1.803(2)
O3-D2	1.788(3)	1.748(5)
O3bis-D2bis		1.748(5)

The thermal ellipsoids of the methyl hydrogens have their major axes in the plane of the triangle of hydrogens (Fig. 3). Such large displacements at 1.5 K are a direct consequence of the low rotational barrier, and therefore tunneling, of these groups. It is interesting to note that the thermal ellipsoids of the H atoms on the water molecules are almost as large as those of the methyl hydrogens (Fig. 3). However, while methyl tunneling results from the con-

siderable overlap of the wavefunctions, the geometry of the water molecule would require much greater delocalization for tunneling to occur. Nevertheless, the large amplitude of the water molecules suggests that the water molecules may play a role in the rotational tunneling of the methyl groups. In order to test this suggestion we recorded the methyl group tunneling spectrum of $\text{LiCH}_3\text{COO} \cdot 2\text{D}_2\text{O}$ and compared this with that of $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$. There were no perceivable differences between these spectra from which we conclude that the water motion is independent from that of the methyl groups, although the relaxation pathway for methyl tunneling could involve the water molecules.

CONCLUSIONS

There is a low-temperature phase transition in $\text{LiAc} \cdot 2\text{H}_2\text{O}$ which involves an ordering of the methyl group orientations, along with a small reduction of intermolecular separations. The juxtaposition of nearest neighbor methyl groups is consistent with coupled pairs of rotors, but the disordering of these pairs (on heating) cannot be distinguished from long-range disorder. Large thermal displacements of the water molecules at 1.5 K seem to be independent of the methyl group tunneling.

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