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The Crystal and Molecular Structures of Lithium Hydrogen Oxydiacetate

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The structure of $LiC_4H_5O_5$ has been determined from X-ray data collected with an automatic diffractometer, and refined to $R=0{\cdot}034$. The crystals are monoclinic, space group $P2_1/n$, with $a=7{\cdot}259$ (2), $b=5{\cdot}468$ (1), $c=14{\cdot}256$ (2) Å, $\beta=91{\cdot}84$ (2)°, $Z=4$. The structure consists of layers of infinite chains of hydrogen-bonded $O(CH_2COO^-)_2$ ions held together by Li^+ ions. Between the layers there are only van der Waals forces. The oxydiacetate ion is twisted and the hydrogen bond is somewhat longer, 2·561 (2) Å, than in the other alkali hydrogen oxydiacetates. Li is coordinated by five O atoms which form a distorted trigonal bipyramid with Li–O distances from 2·031 (3) to 2·122 (3) Å. The bipyramids form pairs by sharing one edge. The shortest Li–Li distance is 3·156 (6) Å.

Introduction

With the determination of the structure of lithium hydrogen oxydiacetate, LiHOXY, the series of alkali hydrogen oxydiacetates is complete. Earlier publications describe the monoclinic structures of NaHOXY and KHOXY (Albertsson, Grenthe & Herbertsson, 1973*a*), and the tetragonal structures of RbHOXY, CsHOXY and TlHOXY (Albertsson, Grenthe & Herbertsson, 1973*b*). The monoclinic oxydiacetic acid has also been described (Herbertsson & Boman, 1973). In the alkali hydrogen oxydiacetates so far investigated the anion has been almost planar and the oxydiacetate ions are linked by short hydrogen bonds into infinite chains. The planar oxydiacetate ion is also found in the lanthanoid compounds (Albertsson, 1972), in Ca oxydiacetate (Uchtman & Oertel, 1973) and in two phases of Cd oxydiacetate (Boman, 1974). In a third phase of CdOXY, however, as well as in the monoclinic oxydiacetic acid, the oxydiacetate group is strongly twisted.

The purpose of this investigation is to find out how coordination to the small Li^+ ion affects the conformation of the hydrogen oxydiacetate ion and the topology of its hydrogen bonds.

Crystal data

Lithium hydrogen oxydiacetate, $LiC_4H_5O_5$; F.W. 140·0; monoclinic, space group $P2_1/n$; $a=7{\cdot}259$ (2), $b=5{\cdot}468$ (1), $c=14{\cdot}256$ (2) Å, $\beta=91{\cdot}84$ (2)°, $V=565{\cdot}6$ Å^3; $Z=4$; μ(Cu $K\alpha$) = 13·5 cm^{-1}; $D_m=1{\cdot}65$, $D_x=1{\cdot}644$ g cm^{-3}. Numbers within parentheses represent estimated standard deviations.

Experimental

Colourless, short prismatic crystals are formed when an aqueous solution containing equimolar amounts of LiOH and oxydiacetic acid is evaporated slowly at room temperature. Percentages of C and H in good agreement with the values calculated for $LiC_4H_5O_5$ were obtained from elemental analyses. The density was determined from the loss of weight in benzene. Weissenberg photographs showed monoclinic symmetry with systematic extinctions $0k0$ for $k\neq 2n$ and $h0l$ for $h+l\neq 2n$ characteristic of space group $P2_1/n$. The dimensions of the unit cell were determined from data collected with a Guinier–Hägg camera (Cu $K\alpha_1$ radiation, $\lambda=1{\cdot}54051$ Å, 22°C) with Al (cubic, $a=4{\cdot}04934$ Å) as internal standard. A single crystal, 0·15 × 0·15 × 0·25 mm, mounted along **b** was used for data collection on an automatic diffractometer of type CAD-4. Intensities were recorded with Cu $K\alpha$ radiation, monochromatized by reflexion from a graphite crystal, at a take-off angle of 5°. The ω–2θ technique was used with scan interval $\Delta\omega=0{\cdot}80+0{\cdot}50\tan\theta$. The background was measured before and after each reflexion. All 1154 independent reflexions in the interval $5° < \theta < 70°$ were measured with repeated scans, but 155 reflexions with $I < 3\sigma_c(I)$ were rejected in the subsequent calculations. The values of $\sigma_c(I)$ were based on counting statistics. The reflexions $\overline{1}\overline{1}7$, $\overline{3}\overline{1}5$ and $\overline{2}\overline{1}5$ were chosen as standards and the intensity of each was recorded every hour. The fluctuations were random and less than 5%. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects. The transmission factors varied from 0·726 to 0·851.

Structure determination and refinement

The positions of the non-hydrogen atoms were determined by symbolic addition (Karle & Karle, 1963, 1966). Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ was performed with $w = 1/(\sigma_c^2 + a|F_o|^2 + b)$, a and b being chosen to make the average values of $w(|F_o| - |F_c|)^2$ as equal as possible in the different $|F_o|$ and $\sin\theta$ intervals. The values $a = 0{\cdot}00001$ and $b = 0{\cdot}0$ were used in the last cycles of refinement. The convergence was checked by R and R_w defined by $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Refinement of the scale factor, the positional parameters and the isotropic thermal parameters resulted in $R = 0{\cdot}119$ and $R_w = 0{\cdot}172$. The positions of the H atoms were found in a difference map calculated from data with $\sin\theta/\lambda \le 0{\cdot}5$ Å^{-1}. Anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for the H atoms gave $R = 0{\cdot}043$ and $R_w = 0{\cdot}062$. After introduction of an isotropic extinction parameter (Zachariasen, 1967) the final values were $R = 0{\cdot}034$ and $R_w = 0{\cdot}044$. The value of $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m is the number of observations and n the number of parameters varied, was 1·03. A final difference map showed no peaks higher than 0·3 e Å^{-3}. In the last cycle of refinement the shifts in the parameters were less than 5% of the estimated standard deviations. The refined value of the extinction parameter $g = 0{\cdot}036\,(10) \times 10^4$ corresponds to a mosaic spread of 160″ if the crystal is of type I and a domain size of $5{\cdot}59 \times 10^{-6}$ cm if it is of type II. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968) for the non-hydrogen atoms and from Hanson, Herman, Lea & Skillman (1964) for H. The positional and thermal parameters, and the r.m.s. components along the principal axes of the thermal-motion ellipsoids, are given in Tables 1 and 2.*

Table 1. *Atomic coordinates with standard deviations* ($\times 10^5$ *for* Li, O *and* C *and* $\times 10^4$ *for* H) *and isotropic temperature factors*

	x	y	z	B (Å^2)
Li	62245 (39)	67234 (49)	6527 (19)	
O(1)	64497 (17)	99418 (20)	37204 (8)	
O(2)	57204 (18)	84468 (24)	18859 (8)	
O(3)	34714 (20)	112136 (25)	17405 (8)	
O(4)	86295 (16)	84767 (20)	50632 (8)	
O(5)	76534 (16)	46286 (19)	50081 (8)	
C(1)	49466 (27)	109424 (33)	31998 (12)	
C(2)	47712 (23)	100317 (28)	22010 (11)	
C(3)	61597 (25)	75025 (32)	40150 (12)	
C(4)	76132 (21)	68325 (27)	47500 (10)	
H(1)	3687 (33)	10534 (41)	3502 (16)	4·0 (5)
H(2)	5112 (29)	12636 (43)	3147 (14)	3·2 (4)
H(3)	6256 (30)	6330 (38)	3482 (15)	3·3 (4)
H(4)	4941 (33)	7324 (40)	4314 (15)	3·6 (5)
H(5)	3317 (46)	10764 (57)	1087 (23)	7·5 (8)

All computations were carried out on the Univac 1108 computer in Lund, Sweden and a list of the programs is given by Oskarsson (1973).

Description of the structure

The structure (Fig. 1) is composed of layers parallel to [101]. In each layer oxydiacetate residues are linked end-to-end by short hydrogen bonds to form infinite chains which are held together by Li$^+$ ions. The forces between the layers are of van der Waals type. It is noteworthy that the Li compound crystallizes from aqueous solution without water of crystallization.

The coordination about Li is fivefold; the polyhedron formed by the O atoms, Fig. 2, can be described either as a distorted trigonal bipyramid or a distorted

Table 2. *Anisotropic thermal parameters with standard deviations* ($\times 10^4$)

The form of the temperature factor is $\exp(-\beta_{11}h^2 - \ldots - 2\beta_{12}hk - \ldots)$. The r.m.s. components R_i ($\times 10^3$) in Å of thermal displacement along the ellipsoid axes are also listed.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Li	123 (5)	176 (9)	29 (1)	−25 (6)	−9 (2)	8 (3)	141 (2)	148 (2)	229 (2)
O(1)	140 (2)	154 (4)	32 (1)	−31 (2)	−26 (1)	11 (1)	161 (2)	174 (2)	254 (2)
O(2)	167 (3)	318 (5)	27 (1)	83 (3)	−5 (1)	−15 (1)	149 (2)	175 (2)	285 (2)
O(3)	206 (3)	327 (5)	28 (1)	115 (3)	−26 (1)	−20 (1)	137 (2)	162 (2)	240 (2)
O(4)	122 (2)	185 (4)	40 (1)	−49 (3)	−27 (1)	17 (1)	145 (2)	159 (2)	202 (2)
O(5)	143 (2)	151 (4)	25 (1)	−21 (2)	−6 (1)	7 (1)	152 (3)	156 (3)	229 (2)
C(1)	163 (4)	173 (6)	29 (1)	31 (4)	−20 (1)	−10 (2)	153 (2)	164 (2)	174 (2)
C(2)	106 (3)	176 (5)	25 (1)	0 (3)	−3 (1)	4 (2)	137 (3)	158 (3)	224 (2)
C(3)	134 (3)	169 (5)	31 (1)	−51 (4)	−19 (1)	12 (2)	139 (2)	147 (3)	167 (2)
C(4)	90 (3)	160 (5)	20 (1)	−18 (3)	5 (1)	−1 (1)	154 (4)	161 (4)	200 (4)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31667 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

square pyramid. The Li^+–O distances, listed in Table 3, range between 2·031 (3) and 2·122 (3) Å, in good agreement with the values found by Thomas (1972) for five-fold coordination. The shortest Li–Li distance is 3·156 (6) Å; and the polyhedra surrounding two adjacent Li^+ ions have one edge in common. The aggregates thus formed are linked by carboxylate groups to form infinite chains parallel to **b**.

One ligand chelates Li^+ through coordination by O(1) and O(4). The other atoms coordinated are the carboxylate O(2), O(4) and O(5) of adjacent ligands. The protonated O(3) is not coordinated.

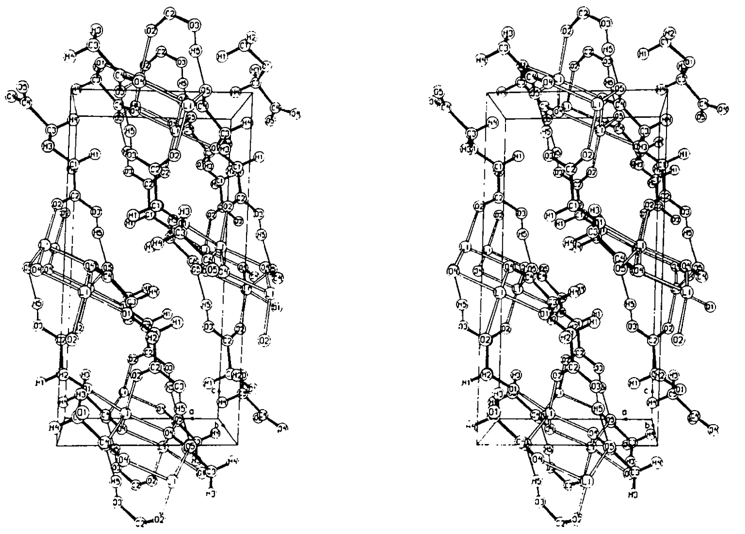

Fig. 1. A stereoscopic view of the structure of LiHOXY with the hydrogen bond marked by a thin line. Figs. 1–3 were drawn by the program *ORTEP*.

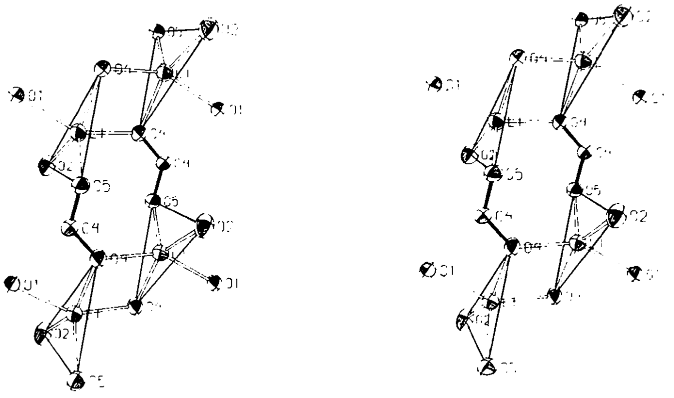

Fig. 2. The coordination around Li^+. The figure shows how the layers are held together along the *b* axis, pointing upwards.

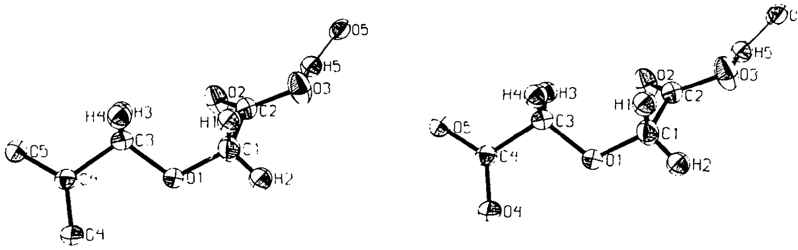

Fig. 3. The oxydiacetate ion and the hydrogen bond. In Figs. 2 and 3 thermal ellipsoids were used for the non-hydrogen atoms.

Table 3. *Coordination distances* (Å) *in* LiHOXY

The superscripts indicate transformations applied to the coordinates given in Table 1: (i) $1+(\frac{1}{2}-x), -1+(\frac{1}{2}+y), \frac{1}{2}-z$; (ii) $-1+(\frac{1}{2}+x), 1+(\frac{1}{2}-y), -1+(\frac{1}{2}+z)$; (iii) $1+(\frac{1}{2}-x), \frac{1}{2}+y, \frac{1}{2}-z$.

Li–O(2)	2·038 (3)
Li–O(4^{i})	2·052 (3)
Li–O(5^{iii})	2·031 (3)
Li–O(1^{i})	2·122 (3)
Li–O(4^{ii})	2·040 (3)

The oxydiacetate ion is shown in Fig. 3 and its interatomic distances, angles, and dihedral angles are given in Table 4. In contrast to the other alkali hydrogen oxydiacetates, the oxydiacetate ion in LiHOXY is nonplanar. The non-hydrogen atoms in each half of the ligand are almost coplanar, however, and the deviations from the least-squares planes through the ligand-halves are given in Table 5. The angle between these planes is 60°.

Table 4. *Selected interatomic distances* (Å) *and angles* (°), *with estimated standard deviations, in* LiHOXY

(*a*) The ligand

O(1)–C(1)	1·410 (2)	C(1)–O(1)–C(3)	113·7 (1)
O(1)–C(3)	1·417 (2)	O(1)–C(1)–C(2)	114·1 (2)
C(1)–C(2)	1·510 (2)	O(1)–C(3)–C(4)	109·1 (1)
C(3)–C(4)	1·508 (2)	C(1)–C(2)–O(2)	123·9 (2)
C(2)–O(2)	1·203 (2)	C(1)–C(2)–O(3)	110·5 (1)
C(2)–O(3)	1·304 (2)	O(2)–C(2)–O(3)	125·6 (2)
C(4)–O(4)	1·237 (2)	C(3)–C(4)–O(4)	118·1 (2)
C(4)–O(5)	1·260 (2)	C(3)–C(4)–O(5)	116·4 (1)
O(2)–O(3)	2·231 (2)	O(4)–C(4)–O(5)	125·6 (2)
O(4)–O(5)	2·221 (2)	H(1)–C(1)–H(2)	111 (2)
O(1)–O(2)	2·774 (2)	H(3)–C(3)–H(4)	110 (2)
O(1)–O(4)	2·572 (2)		
O(1)–O(3)	3·569 (2)		
O(1)–O(5)	3·531 (2)		
C(1)–H(1)	1·05 (2)		
C(1)–H(2)	0·94 (2)		
C(3)–H(3)	1·00 (2)		
C(3)–H(4)	1·00 (2)		

(*b*) Dihedral angles

O(1)–C(1)–C(2)–O(2)	−5·8
O(1)–C(1)–C(2)–O(3)	173·7
O(1)–C(3)–C(4)–O(4)	8·9
O(1)–C(3)–C(4)–O(5)	−172·7

(*c*) The hydrogen bond

O(3)···O(5)	2·563 (2)	O(3)–H(5)···O(5)	167 (3)
O(3)—H(5)	0·97 (3)	C(2)–O(3)—H(5)	115 (2)
O(5)···H(5)	1·61 (3)	C(4)–O(5)···H(5)	114 (1)

Table 5. *Deviations* (Å) *from the least-squares planes through the independent halves in the oxydiacetate ion*

Atoms defining plane: (I) O(1), C(1), C(2), O(2), O(3); (II) O(1), C(3), C(4), O(4), O(5). The angle between the planes is 60°.

Atom	(I)	Atom	(II)
O(1)	0·041	O(1)	−0·057
C(1)	−0·052	C(3)	0·069
C(2)	−0·011	C(4)	0·003
O(2)	−0·012	O(4)	0·026
O(3)	0·034	O(5)	−0·042

The hydrogen-bond system in LiHOXY is analogous to those in NaHOXY and KHOXY, (Albertsson, Grenthe & Herbertsson, 1973*a*). The hydrogen bond is asymmetric with O···O = 2·563 (2) Å. This is slightly longer than the corresponding distances in the K [2·480 (2) Å] and Na [2·462 (3) Å] compounds.

The small size of the Li^+ ion prevents the formation of a tridentate chelate. The fact that only a bidentate chelate is formed while the remaining half of the ligand is coordinated to an adjacent Li^+ ion results in a fairly large conformational change of the ligand and a changed topology of the hydrogen bonds. The distances O(1)–O(2) 2·774 (2) and O(1)–O(4) 2·572 (2) Å differ significantly from the corresponding distances [2·643 (3)–2·660 (2) Å] in the other alkali hydrogen oxydiacetates. The decrease in the bite O(1)–O(4) is due to the small Li^+ ion.

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