

The Crystal Structure of Anhydrous Lithium Glycolate, ${}^6\text{Li}(S)\text{-glycolate-2-}d^*$

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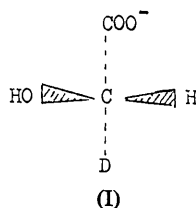
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The crystal structure of anhydrous lithium glycolate has been determined by the symbolic addition procedure from X-ray diffraction data measured on a General Electric XRD-5 diffractometer. Least-squares refinement with anisotropic thermal parameters on all atoms except hydrogen has yielded an $R=0.054$. The glycolate ion is not planar; both atoms of the hydroxyl group are significant distances from the plane defined by the carboxyl group and the α -carbon atom. The glycolate ions are chelated to lithium ions and are linked by chains of trigonal-bipyramidally coordinated lithium ions.

Introduction

The crystal structure of the anhydrous lithium salt of enzymatically formed α -monodeuteroglycolic acid has been determined as a preliminary to determining the absolute configuration (I) of the anion. The latter was



obtained by neutron diffraction using the anomalous scattering of neutrons by ${}^6\text{Li}$. The result with some of its biochemical implications has been published (Johnson, Gabe, Taylor & Rose, 1965). A detailed description of the crystal structure of ${}^6\text{Li}(S)\text{-glycolate-2-}d$ determined by X-ray diffraction methods is given here.

Experimental

The preparation of the compound is described in the earlier paper (Johnson *et al.*, 1965). The anhydrous salt crystallizes readily from aqueous solution as large colourless prisms.

$\text{C}_2\text{H}_2\text{DO}_3{}^6\text{Li}$ DCH . (OH)COO ${}^6\text{Li}$ F.W. 82.05

Monoclinic, $a=8.139 \pm 0.003$, $b=7.607 \pm 0.003$, $c=5.714 \pm 0.002$ Å. $\beta=93^\circ 23'$, $V=353.2$ Å 3 , $Z=4$, $D_x=1.543$ g.cm $^{-3}$, $\mu(\text{Cu } K\alpha)=14.0$ cm $^{-1}$. Space group $P2_1/n$ determined from the systematic absences in the X-ray diffraction pattern: the neutron diffraction pattern does not have the n -glide absences (Johnson *et al.*, 1965).

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The intensity data were measured on a General Electric XRD-5 diffractometer equipped with scintillation counter and pulse-height analyser. The $\theta/2\theta$ scan technique was used and the background was measured on the high θ side of the reflection with the instrument stationary. Scan times varied from one minute for low order reflections to two minutes for high order ones, and background counting times from one-sixth to one-third of the scan times. Cu $K\alpha$ nickel-filtered radiation was used to examine all reflections in a unique part of the reciprocal lattice and 743 of the 775 accessible with the instrument were found to be significantly above background. The stability of the system was checked by counting a standard reflection frequently during the course of the measurements. No significant variation in this count was observed. The usual corrections were applied to reduce the data to a set of observed structure factors. Absorption corrections were not applied because the regular shape of the crystal ($0.3 \times 0.3 \times 0.35$ mm) and the low value of μ made these unimportant.

Solution and refinement

The symbolic addition procedure of Karle & Karle (1963) was used to solve the structure. The IBM 1620 computer was programmed* to provide a listing of triples of reflections which obeyed the relationship $h_1k_1l_1 + h_2k_2l_2 = h_1 + h_2$, $k_1 + k_2$, $l_1 + l_2$. This listing was obtained for the 114 reflections with $E \geq 1.50$. Sign indications were quickly obtained for the 47 reflections with $E \geq 1.85$ by assigning origin determining signs to three reflections and letters a , b and c to three other reflections. Since there were several indications that $a=b=c=+$, signs were allotted to these 47 reflections on this basis and a three-dimensional E map computed. The positions of the one lithium, two carbon and three oxygen atoms in the asymmetric unit were immediately apparent.

* Computer programs used in this analysis were written by Drs D. van der Helm, J.P. Glusker, C.K. Johnson, E.J.G., M.R.T. and Mrs J. Minkin.

The atomic scattering factors used in the structure factor calculation were from *International Tables for X-ray Crystallography* (1962) for O, O⁻, C and Li⁺, and from Stewart, Davidson & Simpson (1965) for H. The scattering factors for O and O⁻ were averaged to give a composite O[±] curve which was used in the later stages of the refinement for the carboxyl oxygen atoms. The structure was refined in space group $P2_1/n$. Therefore both H(1) and H(2) represent the average of one deuterium and one hydrogen atom.

The model structure obtained from the E map was refined by a block-diagonal least-squares method, minimizing $\sum w(F_o - F_c)^2$, using isotropic temperature factors. All reflection data were included in the refinement, with weights estimated from counting statistics (Johnson, 1965). At $R=0.085$ a difference map showed the location of the three hydrogen atoms. These were included in the calculation and the refinement continued with anisotropic temperature factors for the heavier atoms and isotropic ones for the hydrogen atoms. All parameters were refined. The refinement was terminated when the maximum shift in a parameter had fallen to less than one-half the corresponding standard deviation. The final value of $R=0.054$. The observed and calculated structure factors are listed in Table 1 and the final atomic parameters with their standard deviations estimated from the least-squares analysis, in Table 2. The principal axes of the thermal ellipsoids were determined relative to the orthogonal E system (Patterson, 1952). The γ matrix defining this system is

$$\begin{array}{ccc} 8.1366 & 0 & -0.1982 \\ 0 & 7.6070 & 0 \\ -0.1982 & 0 & 5.7106 \end{array}$$

The magnitudes of the principal axes are included merely to give an indication of the anisotropy.

It was found that an empirical extinction correction of the form $F_o(1 - 0.000184 F^2)^{-1/2}$ improved the agreement of the large, low order terms to such an extent that R dropped to 0.039, e.g. $F_o(2.0.0)$ is 35.6 before correction and 50.6 after correction ($F_c=52.4$). The results reported here do not contain this correction since the least-squares weights of the affected terms were very small.

Description and discussion

The asymmetric units are denoted as follows:

Coordinates			Superscript none (Table 2)
x	y	z	
$\frac{1}{2}-x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$	'
$1-x$	$1-y$	$1-z$	''
$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	'''
$1-x$	$1-y$	$-z$	iv

The coordination requirements of the lithium ion, and the hydrogen bonding potential of the hydroxyl group, dominate the packing of the glycolate ions in this structure (Fig. 1). The lithium ion coordination

polyhedron consists of five oxygen atoms at the corners of an irregular trigonal-bipyramid. These polyhedra share two different edges across centres of symmetry to form infinite chains parallel to the c axis. The chains are cross-linked by glycolate ions, each one of which is part of, or is bonded to, two different chains of polyhedra. It is attached to one chain through O(1) which is bonded to Li and Li^{iv}, and also by the hydrogen bond O(3)-H(3)---O(2'); and to the other by chelation of O(2) and O(3) to Li.

Both carboxyl oxygen atoms have similar trigonal, nearly planar, environments: O(1) is part of a shared edge of the lithium polyhedra and is therefore bonded to two lithium ions; and O(2) is bonded to Li and the hydrogen atom of the hydrogen bond. This similarity in their environments is reflected in the lengths of their bonds with C(1). The C(1)-O(1) and C(1)-O(2) bond lengths corrected for thermal motion, assuming that O(1) and O(2) 'ride' on C(1) (Busing & Levy, 1964), are 1.257 and 1.260 Å respectively. Neither this difference (0.003 Å) nor the difference between the uncorrected distances (0.001 Å) is significant. The thermal motion of O(2) is more anisotropic than that of O(1) (Table 2), and the major principal axes of the thermal ellipsoids of both these atoms are, within experimental error, normal to the C(1)C(2)O(1)O(2) plane.

The hydroxyl oxygen atom O(3) has a tetrahedral environment [H(3), C(2), Li and Li^{iv}] and is part of the second shared edge of the lithium polyhedra. C(1), C(2), O(1) and O(2) are coplanar but O(3) is not in this plane. This displacement of 0.17 Å ($\sigma=0.01$ Å) is

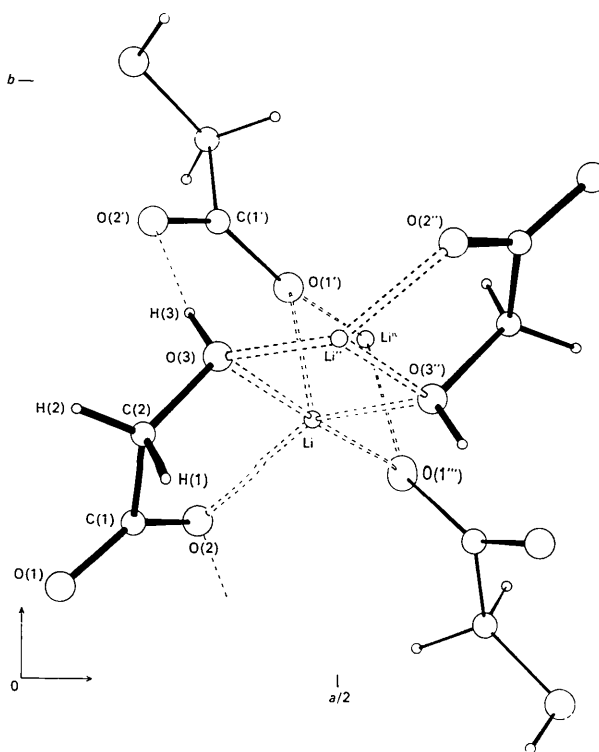


Fig. 1. The structure viewed normal to (001).

Table 3. *Interatomic distances and angles*
Standard deviations in parentheses are for the last place listed

Atoms	<i>d</i>	Atoms	<i>d</i>
C(1)–C(2)	1.525 (2) Å	Li—O(2)	1.952 (3) Å
C(1)–O(1)	1.254 (2)	Li—O(3)	2.357 (3)
C(1)–O(2)	1.255 (2)	Li—O(1')	1.988 (3)
C(2)–O(3)	1.415 (2)	Li—O(3'')	1.998 (3)
C(2)–H(1)	0.98 (2)	Li—O(1''')	2.020 (3)
C(2)–H(2)	0.93 (3)	Li—Li''	3.269 (5)
O(3)–H(3)	0.87 (3)	Li—Li ^{iv}	2.903 (5)
H(3)–O(2')	1.79 (3)	O(3)–O(3'')	2.900 (2)
O(3)–O(2')	2.649 (2)	O(1')–O(1''')	2.765 (2)
	Angle		Angle
O(1)–C(1)–O(2)	125.0 (1)°	C(1)–O(2)–Li	124.4 (1)°
O(1)–C(1)–C(2)	116.9 (1)	C(1')–O(2)–H(3)	110 (1.3)
O(2)–C(1)–C(2)	118.1 (1)	H(3)–O(2)–Li'	126 (1.3)
C(1)–C(2)–O(3)	112.8 (1)	Li—O(1')–C(1')	129.4 (1)
C(1)–C(2)–H(1)	103 (1.3)	C(1')–O(1')–Li ^{iv}	131.7 (1)
C(1)–C(2)–H(2)	105 (1.3)	Li—O(1')–Li ^{iv}	92.8 (1)
O(3)–C(2)–H(1)	111 (1.3)	O(3)–Li—O(2)	76.2 (1)
O(3)–C(2)–H(2)	116 (1.3)	O(3)–Li—O(1')	91.7 (1)
H(1)–C(2)–H(2)	109 (2)	O(3)–Li—O(3'')	83.1 (1)
C(2)–O(3)–O(2')	113.1 (1)	O(2)–Li—O(1''')	103.3 (1)
C(2)–O(3)–H(3)	107 (1.3)	O(1')–Li—O(1''')	87.2 (1)
C(2)–O(3)–Li	107.2 (1)	O(3'')–Li—O(1''')	98.4 (1)
C(2)–O(3)–Li''	119.1 (1)	O(2)–Li—O(1')	117.6 (1)
Li—O(3)–Li''	97.0 (1)	O(2)–Li—O(3'')	129.1 (1)
Li—O(3)–H(3)	87 (1.3)	O(1')–Li—O(3'')	108.9 (1)
H(3)–O(3)–Li''	129 (1.3)	O(3)–Li—O(1''')	178.4 (1)
O(3)–H(3)–O(2')	170 (2)		

significant and is a result of the strong hydrogen bond between O(3) and O(2').

The hydrogen atom H(3) of the hydrogen bond lies a significant distance (0.11 Å, $\sigma = 0.025$ Å) from the line of centres of O(3) and O(2'). This non-linearity could be the result of repulsive forces between H(3) and Li, which cause the Li–O(3)–H(3) angle to be increased to 87.0° from the 81.8° that it would be if H(3) were on the O(3)–O(2') line. The difference between the angles C(2)–O(3)–H(3) and C(2)–O(3)–O(2') of 5.7° (Table 3), which arises from packing requirements, also contributes to the non-linearity of the hydrogen bond.

Pooley & Whiffen (1961) have shown from electron-spin resonance studies on the HC(OH)CO₂⁻ radical ion, trapped in γ -irradiated crystals of anhydrous lithium glycolate, that the hydroxyl hydrogen atom is not in the plane of the carbon and oxygen atoms of the radical. This structure determination confirms their prediction that this conformation is also present in the parent anhydrous lithium glycolate crystal.

In lithium glycolate monohydrate (Colton & Henn, 1965) the hydroxyl group is in the same plane as the other carbon and oxygen atoms. This is the only significant difference between the glycolate ions in the two structures, though the larger standard deviations

(≈ 0.01 Å in interatomic distances) in Colton & Henn's determination preclude the possibility of making detailed comparisons.

We are grateful to Dr I. A. Rose for preparing this substance; Drs I. L. and J. Karle for some helpful discussions about the application of the symbolic addition procedure during the early stages of this work; and Dr A. L. Patterson for his continued interest in and co-ordination of this project. Fig. 1 is a reproduction of a Glusker original.

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