The Crystal Structure Determination of Lithium 2-Hydroxy-3,4-dioxocyclobut-1-en-1-olate Monohydrate, LiHC$_4$O$_4$.H$_2$O

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Single crystals of lithium squarate monohydrate have been prepared and studied by X-ray diffraction. The crystals are monoclinic, space group $C2/c$ with unit-cell dimensions: $a = 13.627(2)$, $b = 7.782(1)$, $c = 10.843(1)$ Å, $\beta = 120.31(1)°$. The structure was determined by direct methods from 1580 observed intensities measured with counter methods. The structure consists of infinite chains of hydrogen squarate ions joined by strong asymmetric hydrogen bonds [2.431(1) Å]. These chains are tied into a three-dimensional network by weaker hydrogen bonds [2.720(1) and 2.737(1) Å] via the water molecules and Li$^+$⋯O(squaric acid) electrostatic forces. The refinement terminated with a conventional R-value of 0.041. Standard deviations in bond lengths between carbon and oxygen atoms are 0.001 Å.

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) (H$_2$SQ) was first prepared by Cohen, Lacher and Park[1] and is a member of a series of oxocarbon ring systems with strong acidic properties.[2] The crystal structure of the free acid is now well established by X-ray diffraction methods.[3,4] In the crystal structure the molecules are linked together into infinite planar sheets by short asymmetric hydrogen bonds. The high acidity of H$_2$SQ[5] and extensive delocalization of the SQ^{2-} ion as suggested by IR and Raman spectroscopy of K$_2$SQ and X-ray structural investigation of K$_2$SQ.H$_2$O implicate that acid salts of squaric acid may form very short hydrogen bonds similar to those found in acid salts of carboxylic acids.[6] The main purpose of the present investigation has been to examine the hydrogen bonding properties of the HSQ$^-$ residue. The acid salt of lithium was chosen in order to minimize the scattering contribution from the cation. While the present

investigation was in progress, the crystal structure determinations of KHSQ.H$_2$O[9] and [H$_2$NMe$_2$]$^+$[H$_3$SO$_2$]$^{-10}$ came to the author's knowledge.

EXPERIMENTAL

Crystals of LiHSQ.H$_2$O were prepared by dissolving lithium carbonate and squaric acid in a molar ratio 1:2 in water. Colourless, approximately bipyramidal crystals bound by eight faces were formed by slow evaporation. A crystal of dimensions $0.4 \times 0.5 \times 0.35$ mm was selected for the data collection. The systematic absences ($h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$) correspond to those of the space groups Cc and $C2/c$. Unit-cell parameters were determined from the diffractometer setting angles of 15 reflexions (MoKα radiation, $\lambda = 0.71069$ Å). Intensity data were collected on a SYNTEX P1 computer-controlled diffractometer with the crystal arbitrarily mounted. The diffractometer was operated in the $\omega - 2\theta$ scanning mode and one quadrant of the reciprocal lattice was examined out to a 2θ limit of 70° with graphite monochromatized MoKα radiation. A variable scan speed (2−8°/min) dependent on intensity and a 2° symmetrical scan range, corrected for wavelength dispersion, was used. Background counts were taken at the beginning and end of each scan. The ratio of total background to scan time was 0.7.

As a control of crystal and diffractometer stability three reference reflections were measured at regular intervals. A total of 1961 independent reflexions were recorded, of which 1580 had intensities greater than twice their standard deviations estimated from counting statistics. The intensities and their standard deviations were corrected for Lorentz and polarization effects, and a 2 % uncertainty in diffractometer stability was included in e.s.d.'s.

The structure was determined by application of direct methods[11] assuming the space-

group $C2/c$. Full-matrix least-squares refinements with anisotropic thermal parameters for the heavy atoms including Li$^+$, and isotropic ones for the hydrogen atoms terminated with $R = 0.041$, and $R_w = 0.050$. The function minimized was $M = \sum w (F_o - F_c)^2$, $w = [\sigma(F_o)]^{-2}$. The positions of the hydrogens for the outset of the final refinements were calculated from the short oxygen-oxygen approach distances. Weight analysis showed that weighting based on standard deviations from counting statistics was satisfactory. Atomic form factors for the heavy atoms were taken from Doyle and Turner,[12] while for the hydrogens those of Stewart, Davidson and Simpson[13] were used. All programs used are written or revised for CD 6600 as described in Ref. 14. No corrections for absorption, extinctions or multiple scattering have been carried out. Tables of observed and calculated structure factors are available from the author on request.

CRYSTAL DATA

LiHSQ monoclinic; $C2/c$

$a = 13.627(2)$, $b = 7.782(1)$, $c = 10.834(1)$ Å,

$\beta = 120.31(1)°$, $\varrho_{obs} = 1.84$ g cm^{-3}, $\varrho_{calc} = 1.85$ g cm^{-3},

$Z = 8$, $V = 991.4(7)$ Å^3, F.W. $= 138.00$, $F(000) = 560$ $\mu(\text{Mo}K\alpha) = 1.85$ cm^{-1}.

DISCUSSION

Final coordinates and thermal parameters are given in Table 1, while interatomic distances and angles are given in Table 2. A stereo view of the structure is presented in Fig. 1. The atomic numbering scheme and the structure of the HSQ-ion is shown in Fig. 2. The structure is seen to consist of layers extending parallel to the (001) planes, which are related alternately by twofold axes and twofold screw

axes. The nearly planar HSQ$^-$ ions form strongly bonded chains along the c glide planes by means of short asymmetric hydrogen bonds. These chains are transversely linked along [010] *via* the water molecules through weaker hydrogen bonds and Li$^+$---O interactions. The interactions between layers are in the region of the twofold screw axes ($x = \pm\frac{1}{4}$), mainly due to van der Waals forces and dipolar interactions between C $-$ O bonds stacked antiparallel to each other.[16] The shortest distances are O1---C4' (3.21 Å) and C1---O4' (3.14 Å), related by screw axes and O2---C2' (3.22 Å) across centers of inversion.

In the vicinity of the twofold axes ($x = 0, \frac{1}{2}$) there are alternately interactions between water molecules and Li$^+$ ions, and closely stacked pairs of HSQ$^-$ ions. The average distance between the planes of the latter is 3.16 Å and short interatomic contacts occur for C3---C3' (3.22 Å) and C2---C2' (3.22 Å). If the thickness of a π conjugated planar system is taken to be 3.4 Å, the layer separation of 3.16 Å may indicate additional attraction possibly of the charge transfer type. Interactions of this kind have been invoked to explain similar short contacts in K$_2$SO.H$_2$O.[7]

The arrangement close to the water molecules and Li$^+$ ions around the twofold axes is shown in Fig. 3. There is an almost equidistant distorted tetrahedral environment of oxygen atoms around the Li$^+$ ions, the Li$^+$---O distances being only slightly longer than the sum of ionic radii (2.00 Å). An additional, rather long contact from O3 to Li$^+$ of 2.535(2) Å (not shown in Fig. 3) may, however, also be of some importance. The water molecules and Li$^+$ ions form a regular, nearly planar ar-

Table 1. Fractional coordinates and thermal parameters with estimated standard deviations. Expression for anisotropic vibration is $\exp[-2\pi^2(U11h^2a^{*2} + \cdots + 2U23klb^*c^*)]$.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1	.13275(8)	.14538(10)	.10172(9)	.0394(5)	.0159(4)	.0179(4)	-.0001(3)	.0175(4)	-.0023(3)
O2	.12829(8)	.13583(10)	.40291(9)	.0371(5)	.0188(4)	.0175(4)	-.0031(3)	.0154(4)	.0030(3)
O3	.13549(8)	.55581(10)	.40653(8)	.0519(6)	.0168(4)	.0186(4)	.0004(4)	.0249(4)	-.0009(3)
O4	.13527(8)	.55980(10)	.11480(8)	.0489(6)	.0144(4)	.0188(4)	.0005(3)	.0238(4)	.0012(3)
C1	.13492(9)	.25226(13)	.18753(10)	.0236(5)	.0146(4)	.0122(4)	-.0008(4)	.0094(4)	.0004(4)
C3	.13666(10)	.43572(14)	.32593(11)	.0279(6)	.0158(4)	.0128(4)	-.0006(4)	.0123(4)	.0001(4)
C2	.13358(9)	.24666(13)	.32588(11)	.0235(6)	.0161(4)	.0128(4)	-.0009(4)	.0095(4)	.0005(4)
C4	.13658(10)	.43887(13)	.19513(10)	.0274(6)	.0138(4)	.0131(4)	-.0002(4)	.0125(4)	-.0001(3)
OW	.42423(8)	.35541(12)	.30553(10)	.0392(6)	.0152(4)	.0250(4)	-.0011(4)	.0208(4)	-.0003(3)
LI	.40262(22)	.37603(32)	.10605(24)	.0380(12)	.0367(13)	.0201(10)	.0025(10)	.0158(9)	-.0024(9)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
HO	.1342(16)	.4973(27)	.5007(20)	5.9(5)	HW1	.4070(20)	.4421(31)	.3347(25)	6.6(6)
HW2	.4065(20)	.2646(28)	.3287(26)	5.6(5)					

Table 2. Interatomic distances and angles.

Distance (Å)		Angle (°)			
a. Within the squarate residue					
C1 − O1	1.237(1)	C2 − C1 − O1	136.0(1)	C4 − C1 − O1	135.1(1)
C2 − O2	1.227(1)	C1 − C2 − O2	136.9(1)	C3 − C2 − O2	135.5(1)
C3 − O3	1.285(1)	C2 − C3 − O3	135.8(1)	C4 − C3 − O3	132.3(1)
C4 − O4	1.276(1)	C1 − C4 − O4	134.7(1)	C3 − C4 − O4	133.4(1)
C1 − C2	1.509(1)	C1 − C2 − C3	87.5(1)	C2 − C3 − C4	91.8(1)
C1 − C4	1.454(1)	C3 − C4 − C1	91.8(1)	C4 − C1 − C2	88.9(1)
C2 − C3	1.472(2)				
C3 − C4	1.417(1)				
b. Around the Li⁺ ion					
Li − OW	2.035(2)	OW − Li − O1	169.8(1)	OW − Li − O2	92.5(1)
Li − O1	2.057(2)	OW − Li − OW	89.0(1)	O1 − Li − OW	94.8(1)
Li − O2	2.057(3)	O2 − Li − OW	105.0(1)	O2 − Li − O1	95.7(1)
Li − OW	2.057(3)				
c. For the hydrogen bonds					
O3 − O4	2.431(1)	C3 − O3 − O4	111.6(1)	C3 − O3 − HO	109.5(11)
OW − O1	2.737(1)	C4 − O4 − O3	110.7(1)	C4 − O4 − HO	112.6(9)
OW − O4	2.720(1)	O3 − HO − O4	175.8(19)	HW1 − OW − HW2	113.5(24)
O3 − HO	1.125(20)	O1 − OW − O4	113.3(1)	O1 − HW1 − OW	178.5(24)
O4 − HO	1.307(20)	O4 − HW2 − OW	178.4(24)		
OW − HW1	0.827(25)				
OW − HW2	0.825(23)				
HW2 − O4	1.895(24)				
HW1 − O1	1.910(25)				
HW2 − HW1	1.382(28)				

rangement, the $Li^+ \cdots O_w$ distances are 2.035(2) and 2.057(3) Å while the angles $O_w \cdots Li^+ \cdots O$ and $Li^+ \cdots O_w \cdots Li^+$ are 89.0(1) and 90.31(2)°, respectively. Apparently this cluster is held together relatively strongly since there are open regions in the structure between the water molecules and the next layer of HSQ⁻ ions. The coordination around the water mole-

cules is nearly tetrahedral. The two weak hydrogen bonds formed by the water molecule [2.737(1), 2.720(1) Å] (see Table 2) are linear with $O - H \cdots O$ angles insignificantly different from 180°.

Evidence from the bond lengths within the HSQ⁻ ion as well as the H_O peak in a difference Fourier synthesis, confirm the presence of a
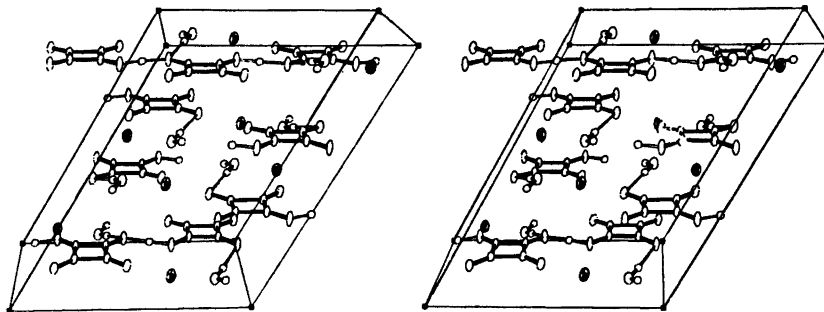

Fig. 1. Stereoscopic illustration [15] of the crystal structure of LiHSQ.H₂O, as viewed along the *b* axis. Thermal ellipsoids are scaled to include 50 % probability.
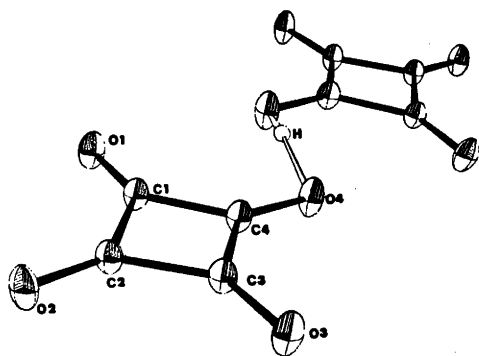
Fig. 2. Perspective drawing of hydrogen-bonded HSQ chain with atom numbering as indicated (50 % probability).

short asymmetric O−H···O hydrogen bond. The length of this bond [2.431(1) Å] compares well with the crystallographically symmetrical hydrogen bond recently determined in $(H_2NMe_2)^+[H_3SQ_2]^-$ (2.435(2) Å).[10] The hydrogen bond in the present study may therefore probably be classified as pseudo type A_2 in the convention adopted by Speakman.[8] This bond is also nearly linear ($\angle$O−H···O = 176°), and with C−O···O angles [111.6(1), 110.7(1)°] close to values found in type A hydrogen bonds in acid salts of carboxylic acids [112(2)°].[8] The assymmetry of the hydrogen bond is certainly due to asymmetries in the environments. O4, in particular, participates in one of the
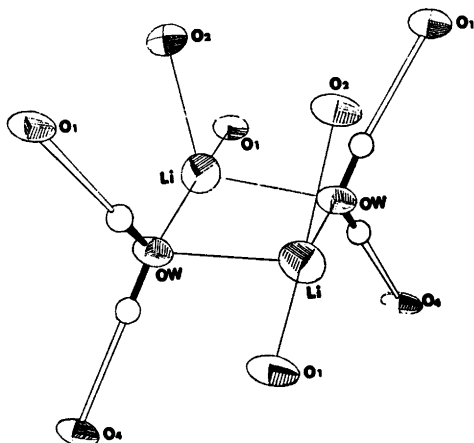

Fig. 3. Perspective drawing of the environment around Li+ ions and water molecules (50 % probability).

weaker hydrogen bonds, whereas O3 is presumably only weakly attracted by the Li+ ions. However, differences in the more distant surroundings, namely at O1 and O2, may be transmitted through the π conjugated double bond system of the HSQ− ion and therefore also influence the potential experienced by the proton H_O.

Despite the differences in the environments of the oxygen atoms of the HSQ− ion there is, in agreement with previous studies of acid salts,[9,10] and the parent molecule,[3] approximate C_{2v} symmetry in the bond lengths of the SQ unit. This may indicate a preference for a localized double bond in the cyclobutene ring in such systems and may be contrasted to the reported fourfold symmetry of the SQ²⁻ ion in the $K_2SQ.H_2O$ structure.[7]

The bond lengths within the HSQ− ion do not deviate greatly from those found previously in H_2SQ.[3] The average C−O hydroxylic bond of 1.280 Å in $LiHSQ.H_2O$ is similar to, though shorter than that [1.291(1) Å] observed in H_2SQ[3] and the averaged C−O bond in the diketonic group (1.232 Å) is also in agreement with that [1.229(1) Å] found in H_2SQ.[3] Similarly only small though significant deviations are found for the C−C bonds. Thus, although single and double bonds are recognizable, there is in agreement with the H_2SQ investigation appreciable conjugation within the HSQ− entity.

It appears, however, as if the degree of conjugation along the O1−C1−C4−C3−O3 diagonal is somewhat higher than that along the other (O2−C2−C3−C4−O4). This may be due to the fact that O1 is more engaged in external interactions than O2, resulting in a lengthening of the C1−O1 bond which is transmitted through conjugated system of π electrons. The bond lengths of the present study also agree (within the experimental error for most bonds) to those obtained in the recent study of $KHSQ.H_2O$,[9] while they deviate somewhat from those obtained in the structure determination of the slightly different system of $(H_2NMe)^+[H_3SQ_2]^-$.[10]

There is one significant feature displayed by all the structures involving squaric acid[3] and its acid salts so far investigated.[9,10] That is that the exocyclic angles *cis* to the hydrogen atoms are significantly enlarged irrespective

of the kind of hydrogen bonding scheme adopted. (The hydrogen atoms in these systems are found to be situated close to the mean square plane of the squarate residue). Thus in the present structure these distortions conform to the approximate C_{2v} symmetry of HSQ^- ion, whereas in the squaric acid structure they follow the pseudo fourfold axis of the molecule. The angles within the fourmembered ring system agree well with those previously found in H_2SQ.

Deviations from a least-squares plane through the heavy atoms in the HSQ^- ion have been calculated. The ion is significantly non-planar, since O2 and O4 are displaced about 0.026 Å from the mean plane, while the carbon atoms are displaced approximately 0.017 Å to the opposite side (the mean square displacement is about 0.018 Å). The thermal motions of the atoms in the HSQ^- ion have their largest amplitudes almost perpendicular to the plane through these atoms. The value of the maximum root-mean-squares amplitudes range between 0.23 and 0.20 Å for the oxygen atoms and 0.17 to 0.16 Å for the carbon atoms. A riding-body analysis of the translational, librational and screw motion failed, probably because the atoms of HSQ^- ion lie close to a quadratic curve.[17]

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