The Crystal Structure of Lithium Oxalate Monoperhydrate,

$Li_2C_2O_4 \cdot H_2O_2$

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The crystal structure of lithium oxalate monoperhydrate has been determined from partial three-dimensional X-ray data. The compound is unstable and great difficulties have been experienced in the collection of intensity data. $Li_2C_2O_4 \cdot H_2O_2$ crystallizes in the triclinic system, space group $P\bar{1}$, with one formula unit in the cell.

The hydrogen peroxide molecule and the oxalate ion are both centrosymmetric and *planar*, and all interatomic distances and angles are of normal values. The crystal is built up of endless chains of alternating hydrogen peroxide molecules and oxalate ions linked together by hydrogen bonds of 2.687 ± 0.011 Å. The chains are interconnected by lithium ions with $(4+1)$ nearest oxygen neighbors in a somewhat distorted tetragonal pyramidal arrangement. The Li—O distances to the four nearest neighbors range from 1.90 to 2.14 ± 0.02 Å, and the distance to the apical oxygen is longer: 2.33 ± 0.02 Å.

The existence of lithium oxalate monoperhydrate has been reported in a previous publication.[1] The compound has also been studied by infrared spectroscopy,[2] and the comparison of the spectrum of lithium oxalate monoperhydrate with that of sodium oxalate monoperhydrate gives strong indications of the presence of the same conformation of the hydrogen peroxide molecule in the two compounds. The structure determination of sodium oxalate monoperhydrate [1] shows that the hydrogen peroxide molecule possesses the *trans* planar conformation in this compound, and this conformation is believed to be stabilized also in lithium oxalate monoperhydrate.

This study was started in the hope that the structure should give accurate dimensions of the *trans* planar hydrogen peroxide molecule in solids, as the lithium salt contains no heavy atoms that can reduce the accuracy in the positions of the lighter atoms.

The compound, however, is very unstable and great difficulties have been experienced in the collection of intensity data which therefore not are of the intended quality.

EXPERIMENTAL

Lithium oxalate (p.a. Merck) crystallizes from diluted perhydrol (p.a. Merck) as the monoperhydrate, $Li_2C_2O_4 \cdot H_2O_2$.* The crystals show dendritic growth, and are elongated along b which often acts as a twin axis. As the crystals were very unstable cooling was tried, but was not found to increase the lifetime of the crystals (only a few hours) markedly.

Oscillation- and Weissenberg diagrams were used to establish the symmetry and space group of the crystals. No symmetry was detected on the films, hence the crystals belong to the triclinic system. A N(Z) test performed [3] shows that the most probable space group is $P\bar{1}$. The NMR-spectrum of powdered lithium oxalate monoperhydrate has been recorded,[4] and comparison between the second moment of this spectrum and second moments calculated for the compound assuming the space group to be either $P1$ or $P\bar{1}$ gives best fit with $P\bar{1}$ as the space group choice. The expected *trans* planar conformation of the hydrogen peroxide molecule as deduced from the IR-spectrum also supports $P\bar{1}$ as the space group choice, as the unit cell dimensions determined give a cell content of only one unit of $Li_2C_2O_4 \cdot H_2O_2$.

The unit cell dimensions were determined from oscillation- and Weissenberg diagrams, and the constants arrived at were used as input parameters in a least squares refinement based on a powder diffraction pattern recorded with $CuK\alpha$ radiation ($\lambda = 1.5418$ Å) on a G.E. diffractometer, using slow scan. The instability of the compound prevented Guinier powder patterns to be taken.

The constants arrived at are:**

$$a = 5.663 \pm 0.005 \text{ Å}, \ b = 3.362 \pm 0.003 \text{ Å}, \ c = 5.968 \pm 0.004 \text{ Å}$$
$$\alpha = 98.43 \pm 0.06°, \ \beta = 97.92 \pm 0.07°, \ \gamma = 78.77 \pm 0.08°$$

The observed and calculated d-values are listed in Table 1. The density measured by the floatation method is 2.10 g/cm³, whereas the density determined with one $Li_2C_2O_4 \cdot H_2O_2$ in the unit cell is 2.06 g/cm³.

The intensity data consisted of multiple film Weissenberg diagrams of zeroth- and first-layer along the b-axis, taken with Ni-filtered Cu-radiation. The zeroth-layer diagrams were of good quality, but to get a complete set of intensities from the first layer, crystals

Table 1. Observed and calculated d-values for $Li_2C_2O_4 \cdot H_2O_2$ (Å).

h	k	l	d_{obs}	d_{calc}	h	k	l	d_{obs}	d_{calc}
0	0	1	5.91	5.87	2	0	−2	2.132	2.133
1	0	0	5.54	5.52	0	1	2	2.060	2.061
1	0	−1	4.27	4.27	2	1	1	2.036	2.037
1	0	1	3.818	3.812	0	0	3	1.953	1.955
0	1	0	3.269	3.272	1	0	−3	1.909	1.912
1	1	0	3.058	3.064	3	0	0	1.838	1.840
0	0	2	2.940	2.939	1	1	−3	1.799	1.800
1	1	−1		2.933	0	1	−3	1.781	1.778
2	0	0	2.755	2.759	3	1	0	1.743	1.742
0	1	1	2.718	2.719	2	1	2	1.678	1.678
1	1	1	2.535	2.537	0	2	−1	1.626	1.629
1	0	2	2.481	2.477	−1	1	−3	1.600	1.602
−1	1	−1	2.432	2.432	1	1	3	1.528	1.530
2	0	1	2.398	2.395	−3	1	1		1.460
1	1	−2		2.337	1	0	−4	1.461	1.459
0	1	−2	2.333	2.332					

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* The analysis was kindly carried out by cand. real. C.U. Wetlesen.

** If transformed to the conventional reduced cell [5] the constants are: $a = 3.362$ Å, $b = 5.968$ Å, $c = 5.996$ Å, $\alpha = 92.75°$, $\beta = 112.13°$, $\gamma = 98.43°$.

of different quality had to be used. With three film sets covering different parts of the first layer, a data set was obtained which was used in the subsequent structure determination. The intensities were visually estimated and corrected in the usual way for Lorentz- and polarization effects. No absorption correction was considered necessary because of the low absorption coefficient, $\mu = 18.9$ cm^{-1}, for Cu-radiation. The total number of reflexions recorded was 197 out of which 35 had unobservable intensities. The scattering factors used throughout the calculation were taken from *International Tables for X-ray crystallography.*[8]

STRUCTURE DETERMINATION

From the Weissenberg data of the $(h0l)$ zone a Patterson map was calculated. Peaks observed in this map enabled the orientation of the oxalate ion to be roughly determined, and hydrogen bonding considerations led to the determination of the hydrogen peroxide oxygen parameters, as both molecules had to be placed around symmetry centres. In a Fourier map calculated based on the above assumptions, the Li$^+$ ion site was recognized. Successive Fourier refinements were performed, preceded by least squares refinement,[7] introducing isotropic thermal parameters for the five atoms included in the calculation: C, O$_1$, O$_2$, O$_p$, and Li$^+$, thus reaching a reliability index of $R = 0.09$. The final Fourier map projected along b is shown in Fig. 1. Careful inspection of this map also gives indication on the hydrogen atom position at a site suitable for hydrogen bond formation.
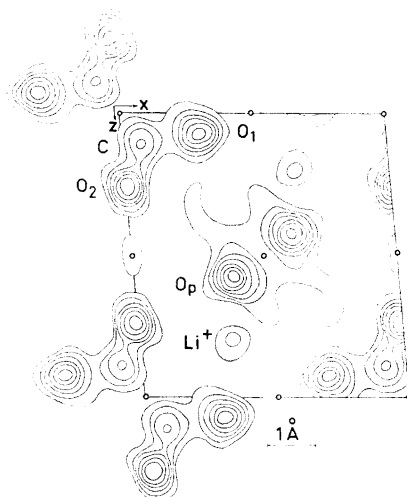

Fig. 1. Orthogonal Fourier projection of Li$_2$C$_2$O$_4$·H$_2$O$_2$ as projected along the b-axis.

The projections of interatomic distances were calculated, whereby the deviation from this plane for the different atoms was roughly determined. A model of the compound was built and possible three-dimensional arrangements considered. Several arrangements were tried in least squares calculations where only the y-parameters were allowed to vary. In most cases R-values

in the vicinity of 0.60 were reached, but in one case a markedly lower value of 0.28 was attained. A three-dimensional Fourier synthesis was calculated on the basis of phases determined from the atomic parameters from this least squares refinement.

All atoms were found in the vicinity of the anticipated positions and with relative electron densities of the peaks as expected. The positional parameters calculated from this map were used as input variables in a three-dimensional least squares refinement allowing all positional and thermal parameters to vary simultaneously. This refinement led to small variations in all the atomic positions and reduced the reliability index, R, to 0.17, all unobserved reflexions included.

The hydrogen atom could be located in the three-dimensional Fourier map, and this atom was accordingly included in the three-dimensional least squares refinement and reached plausible positional parameter values during the refinement cycles. Only isotropic thermal parameters for all the atoms were used throughout the calculations. The final reliability index calculated was 0.15, excluding unobserved reflexions calculated less than the minimum observable value and including the others with the difference between the calculated and half the minimum observable value.

The variation of spot sizes of the first-layer reflexions has not been accounted for, but is recognized in the differences between observed and calculated structure factor values. The symmetry of the unit cell makes it necessary to include both elongated- and point-reflexions, and obviously leads to errors in the measured intensities which are difficult to account for.

According to this inaccuracy inherent in the starting material, and to the fact the intensities of only one layer along the b-axis is measured, an accurate three-dimensional structure determination, as the original intension was, is prevented, and hence this structure determination does not give more accurate dimensions of the H_2O_2-molecule than previously determined.[1]

The final positional and thermal parameters with standard deviations are given in Table 2, and the interatomic distances and angles calculated based on these parameter values are given in Table 3. Table 4 is a listing of observed and calculated structure factors.

Table 2. Final positional and thermal parameters with estimated standard deviation in parentheses.

	x	y	z	B
C	0.0962 (20)	−0.1004 (66)	0.0918 (18)	1.17 (25)
O_1	0.3117 (15)	−0.1238 (43)	0.0638 (14)	1.90 (23)
O_2	0.0158 (14)	−0.2304 (42)	0.2472 (13)	1.62 (22)
O_p	0.3932 (15)	0.5584 (45)	0.5583 (15)	1.67 (23)
Li^+	0.3661 (46)	0.1655 (128)	0.7903 (43)	2.67 (55)
H	0.2814 (170)	0.5952 (480)	0.4549 (160)	−2.12 (1.95)

Table 3. Interatomic distances and angles with estimated standard deviations.

In the oxalate ion:

$C-C = 1.564 \pm 0.020$ Å $\qquad \angle O-C-O = 127.2 \pm 0.9°$
$C-O_1 = 1.240 \pm 0.014$ Å $\qquad \angle C-C-O_1 = 116.3 \pm 1.0°$
$C-O_2 = 1.254 \pm 0.014$ Å $\qquad \angle C-C-O_2 = 116.5 \pm 1.0°$

Hydrogen bond distance:

$O_p \cdots O_2 = 2.687 \pm 0.011$ Å
$\angle O_p - O_p \cdots O_2 = 107.6 \pm 0.8°$

In the hydrogen peroxide molecule:

$O_p - O_p = 1.439 \pm 0.015$ Å $\qquad \angle H - O_p - O_p = 103.9 \pm 5°$
$O_p - H = 0.83 \pm 0.10$ Å

Interionic distances and valence angles:

$Li^+ - O_1' = 2.11 \pm 0.02$ Å $\qquad \angle O_2' - Li^+ - O_p = 89.2 \pm 1.2°$
$Li^+ - O_1'' = 1.90 \pm 0.02$ Å $\qquad \angle O_1' - Li^+ - O_1'' = 83.2 \pm 1.2°$
$Li^+ - O_2' = 2.11 \pm 0.02$ Å $\qquad \angle O_1'' - Li^+ - O_p = 95.8 \pm 1.2°$
$Li^+ - O_p = 2.14 \pm 0.02$ Å $\qquad \angle O_p - Li^+ - O_p' = 97.6 \pm 1.2°$
$Li^+ - O_p' = 2.33 \pm 0.02$ Å $\qquad \angle O_p - Li^+ - O_2' = 96.3 \pm 1.2°$
$\qquad\qquad\qquad\qquad\qquad\qquad \angle O_2' - Li^+ - O_1' = 78.6 \pm 1.2°$
$\qquad\qquad\qquad\qquad\qquad\qquad \angle O_1'' - Li^+ - O_p' = 99.1 \pm 1.2°$
$\qquad\qquad\qquad\qquad\qquad\qquad \angle O_1' - Li^+ - O_p = 89.1 \pm 1.2°$

Table 4. Observed and calculated structure factors. The columns given are h, k, l, F_{obs} and F_{calc}.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
0	0	1	8.19	8.12	4	0	1	3.63	-4.08	-3	1	1	12.98	17.00	2	1	2	15.27	-16.06
0	0	2	5.41	6.25	4	0	2	9.06	-9.56	-3	1	-1	3.20	-3.50	2	1	3	4.70	-4.73
0	0	3	3.15	-4.55	4	0	5	4.12	-3.55	-3	1	-2	3.43	-2.38	2	1	4	5.22	-3.61
0	0	4	4.33	5.05	5	0	1	9.45	-10.52	-3	1	-4	2.60	1.84	2	1	5	5.02	3.89
0	0	6	7.05	-9.17	5	0	4	4.45	5.23	-3	1	-5	5.56	-4.65	2	1	6	3.24	-1.38
1	0	-4	12.12	13.86	0	1	4	2.47	3.31	-3	1	-6	2.92	2.16	3	1	-6	8.17	-8.04
1	0	-3	8.13	8.62	0	1	2	7.67	8.08	-4	1	5	5.33	6.22	3	1	-5	5.25	-3.84
1	0	-2	1.26	-2.29	0	1	1	38.67	41.57	-4	1	2	4.25	3.79	3	1	-4	4.37	-4.16
1	0	-1	15.39	15.59	0	1	0	4.25	5.86	-4	1	1	3.70	2.87	3	1	-3	11.99	11.39
1	0	0	4.17	3.23	0	1	-1	4.81	5.41	-4	1	0	4.45	-5.08	3	1	-2	8.85	-7.77
1	0	1	8.28	7.49	0	1	-2	15.82	-15.63	-4	1	-1	4.44	-3.66	3	1	-1	1.90	-1.47
1	0	2	26.59	-28.43	0	1	-3	10.40	7.38	-4	1	-2	13.23	-12.22	3	1	0	7.43	6.41
1	0	3	3.77	-4.15	0	1	-4	9.19	-7.02	-4	1	-4	2.26	-1.59	3	1	1	10.18	10.82
1	0	4	7.02	-8.19	0	1	-5	12.40	-9.66	-5	1	4	1.13	-1.86	3	1	2	4.03	4.57
1	0	5	4.47	-4.61	0	1	-6	6.14	-4.66	-5	1	3	6.07	-6.33	3	1	3	6.79	-7.49
1	0	6	4.08	-4.30	0	1	-7	2.58	-1.47	-5	1	2	2.48	-3.11	3	1	4	3.68	3.65
2	0	-6	4.17	-5.65	-1	1	6	2.25	-1.92	-5	1	1	6.07	-7.39	3	1	6	2.18	1.98
2	0	-5	3.15	3.59	-1	1	5	10.48	8.76	-5	1	-1	2.50	-1.99	4	1	-5	4.34	-2.70
2	0	-4	2.04	-3.37	-1	1	3	3.03	1.82	-5	1	-3	8.24	7.83	4	1	-4	8.72	8.66
2	0	-2	14.91	-15.47	-1	1	2	1.75	-1.07	-5	1	-4	2.36	1.80	4	1	-3	8.04	6.18
2	0	-1	3.43	3.34	-1	1	1	4.25	3.94	-6	1	1	3.30	2.08	4	1	-2	13.23	11.93
2	0	0	7.85	6.79	-1	1	0	2.14	-1.56	-6	1	0	2.69	1.66	4	1	-1	3.31	-2.18
2	0	1	17.10	-14.88	-1	1	-1	22.11	-27.18	1	1	-6	6.22	-4.30	4	1	0	8.20	7.94
2	0	2	7.55	-6.83	-1	1	-2	6.04	-4.43	1	1	-5	6.91	7.57	4	1	2	4.50	-4.70
2	0	3	4.25	4.48	-1	1	-3	12.63	-10.33	1	1	-4	3.21	1.88	4	1	3	4.52	-4.24
2	0	4	9.68	10.10	-1	1	-4	2.43	-1.42	1	1	-3	15.05	14.50	4	1	4	4.66	-3.81
3	0	-6	2.73	-3.88	-1	1	-5	8.31	-6.49	1	1	-2	22.79	18.48	4	1	5	1.65	1.45
3	0	-4	8.96	11.06	-1	1	-6	4.11	2.42	1	1	-1	7.83	-8.11	5	1	-5	2.12	2.09
3	0	-3	4.41	-4.81	-1	1	-7	4.82	4.45	1	1	1	24.85	23.51	5	1	-4	6.06	5.25
3	0	-2	4.36	3.92	-2	1	4	2.58	1.39	1	1	3	3.92	3.82	5	1	-3	5.22	5.86
3	0	-1	3.31	2.24	-2	1	3	10.67	-11.54	1	1	4	12.74	-13.58	5	1	-2	6.44	-6.26
3	0	0	21.82	19.41	-2	1	2	7.03	7.19	1	1	5	5.04	-4.25	5	1	-1	2.62	-2.36
3	0	1	3.49	2.78	-2	1	1	2.55	1.92	1	1	6	4.51	-3.43	5	1	0	5.25	-5.14
3	0	2	6.96	-6.93	-2	1	0	3.44	-3.02	2	1	-5	6.08	-5.50	5	1	2	6.68	-9.18
3	0	6	3.41	-3.67	-2	1	-1	8.87	-9.43	2	1	-4	9.42	-6.27	5	1	3	5.00	-5.07
4	0	-5	3.58	5.57	-2	1	-2	2.04	-1.36	2	1	-3	6.67	5.09	5	1	4	1.64	.79
4	0	-4	5.47	6.83	-2	1	-3	14.59	12.86	2	1	-2	5.53	-4.45	6	1	-3	2.20	1.47
4	0	-3	7.59	9.06	-2	1	-4	2.59	-1.69	2	1	-1	8.33	-7.64	6	1	-2	4.08	-3.34
4	0	-2	2.96	-3.34	-2	1	-5	2.57	1.71	2	1	0	4.34	-3.78	6	1	-1	5.88	-7.20
4	0	-1	7.57	7.62	-3	1	5	6.38	7.10	2	1	1	6.64	8.48	6	1	2	1.89	1.62
4	0	0	4.53	-3.99	-3	1	3	4.41	3.76						6	1	3	1.73	-1.74

DISCUSSION OF THE STRUCTURE

Fig. 2 displays the packing relations in $Li_2C_2O_4 \cdot H_2O_2$ viewed along the *b*-axis. The oxalate ions and the hydrogen peroxide molecules are tied together in chains by hydrogen bonds of 2.687 ± 0.011 Å in fair agreement with the
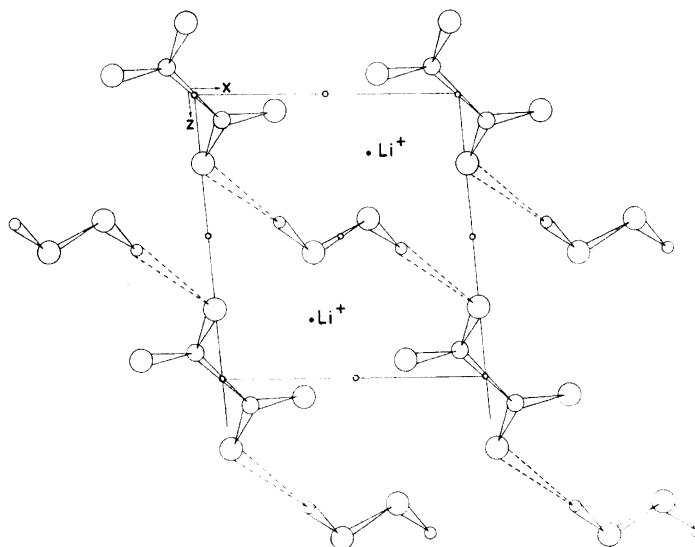
Fig. 2. Packing relations in $Li_2C_2O_4 \cdot H_2O_2$ viewed along the b-axis.

value predicted from the IR-spectrum of the compound, 2.63 Å². The chains are held together by lithium ions situated between them. Each Li^+ ion is surrounded by $(4+1)$ nearest neighbors in a somewhat distorted tetragonal pyramidal arrangement. A similar lithium coordination is also observed in anhydrous Liα-monodeuteroglycolate.[8] The four nearest oxygen neighbors are almost coplanar with the Li^+ ion and the Li^+-O distances range from 1.90 to 2.14 ± 0.02 Å, in agreement with earlier observations,[6] whereas the distance to the apical oxygen is 2.33 ± 0.02 Å.

The calculated $O-Li-O$ angles are relatively close to 90°, from 79 to 99°. Of the nearest oxygen neighbors three originate from oxalate ions and the other two are hydrogen peroxide oxygens from two different molecules. The Li^+ ion thus is bound to three oxalate hydrogen peroxide chains building an intricate three-dimensional network.

The space group symmetry requires the hydrogen peroxide molecule to possess a centre of symmetry which leads to a *trans* planar hydrogen peroxide molecule. This conformation, which is not the stable conformation for the isolated molecule, has been observed earlier in $Na_2C_2O_4 \cdot H_2O_2$.[1] Both theoretical and experimental investigations of H_2O_2 have given as result that the *trans* barrier, hindering internal rotation is low,[9-11] and the crystal structures of $Li_2C_2O_4 \cdot H_2O_2$ and $Na_2C_2O_4 \cdot H_2O_2$ show that intercrystalline forces are strong enough to overcome this barrier and thus stabilize the *trans* planar conformation of hydrogen peroxide.

The hydrogen bond distance in the present structure is fairly short, 2.687 ± 0.011 Å, indicating a relatively strong hydrogen bond. However, the distance is long compared to the hydrogen bonds in the previously inves-

tigated perhydrates [1,12] and may be connected to the lower stability of the present compound. The *trans* conformation is further stabilized in the lattice by two Li^+ contacts for each hydrogen peroxide oxygen, 2.14 and 2.33 ± 0.02 Å away with Li^+-O-Li^+ angle of $97.6°$.

The bond lengths in the *trans* conformation, shown in Table 3, are not significantly different from the corresponding bond lengths found in the usually observed skew conformation, but rather large standard deviations in the present structure prevent minor details between the two conformations to be detected.

The commonly observed conformation of the oxalate ion is centrosymmetric and planar, and this conformation for the oxalate ion is, within the experimental uncertainty, also found in the present compound.

The interatomic distances determined for the oxalate ion are of normal values, the $C-O$ distances are 1.240 and 1.254 ± 0.014 Å, and the $C-C$ distance is 1.564 ± 0.017 Å. The $O-C-O$ angle is $127.2°$ and hence conforms to the usual deviation from $120°$ as observed earlier in several oxalates.[13-16] The $C-C-O_1$ angle is $116.3°$ and the $C-C-O_2$ angle is $116.5°$.

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