

The Crystal Structure of Sodium Oxalate Perhydrate, $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$

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The positions of all the atoms, including hydrogen, in sodium oxalate perhydrate have been determined from threedimensional X-ray data. The observed hydrogen configuration has been verified by proton magnetic resonance studies, and the structure is found to be static and ordered. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with two $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ groups in a unit cell of dimensions:

$$a = 3.548 \text{ \AA}, b = 8.23 \text{ \AA}, c = 9.01 \text{ \AA} \text{ and } \beta = 96.0^\circ$$

The oxalate ion and the hydrogen peroxide molecule are found to be centrosymmetric. The structure is built up of endless chains of alternating hydrogen peroxide molecules and oxalate ions linked together by hydrogen bonds. These chains are interconnected by sodium ions which are surrounded by a distorted octahedral coordination of oxygen atoms.

The dimensions of the found extended *trans* conformation of the hydrogen peroxide molecule are: $\text{O}-\text{O} = 1.466 \pm 0.009 \text{ \AA}$, $\text{O}-\text{H} = 0.89 \pm 0.05$ and the $\text{H}-\text{O}-\text{O}$ angle $97^\circ \pm 3^\circ$. The hydrogen bond distance is $2.588 \pm 0.006 \text{ \AA}$. The oxalate ion is planar. The $\text{C}-\text{O}$ distances are 1.270 \AA and 1.259 \AA , both $\pm 0.007 \text{ \AA}$. The $\text{C}-\text{C}$ distance is $1.570 \text{ \AA} \pm 0.011 \text{ \AA}$.

As is well known, both lithium and sodium oxalate crystallize from a water solution with no water of crystallization contrary to the remaining alkali oxalates which crystallize as monohydrates. In the two isomorphous salts, K- and Rb-oxalate, the water molecules have been found to act as bridges between neighboring oxalate ions, demonstrating the excellent hydrogen bond acceptor properties of the oxalate ions.¹ In the Li- and Na-oxalate this tendency of the oxalate ions to form hydrogen bonds must be counterbalanced by an energetically unfavourable packing of the constituents making the monohydrate unstable relative to the anhydrous salt. The idea occurred to try whether Li- and Na-oxalate would form stable *perhydrates* by crystallization from perhydrol, as in such a salt the packing was expected to be different, while the possibilities of hydrogen bond formation were conserved. This was found to be the case, both Li- and Na-oxalate crystallize as monoper-

hydrates from perhydrol at room temperature. The two salts are not isomorphous, and, to the best of the authors' knowledge, these salts have not been described earlier in the literature.

In this paper we report on the structure of sodium oxalate perhydrate. The space group symmetry found, requires, if the structure is static and ordered, that the H_2O_2 -molecule possess a centre of symmetry. This is surprising as hydrogen peroxide in earlier investigations is found to have a skew configuration where the two oxygen-hydrogen bonds are nearly orthogonal.²

To investigate the conformation of the H_2O_2 -molecule more closely, a complete determination of the structure by X-ray methods was undertaken. To get additional information on the proton configuration and to ascertain that the structure is static and ordered, the compound was also studied by proton magnetic resonance methods.

EXPERIMENTAL

Sodium oxalate (*p.a.* Merck) crystallizes from perhydrol (*p.a.* Merck) as the monoperhydrate $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ in the form of thin needles. The composition was determined by KMnO_4 titration.* The needles very often consisted of twin crystals with the (001) plane as twin plane. The crystals were unstable and had to be kept in sealed capillary-tubes during the exposure, but even then they decomposed over a period of a few days. The intensity data consisted of multiple film zero-, first- and second-layer equi-inclination Weissenberg-diagrams taken rotating about the *a*-axis (needle-axis) and using Ni-filtered $\text{CuK}\alpha$ -radiation. The diameter of the crystal was approximately 0.1 mm. The intensities were estimated visually and corrected in the usual way for Lorentz and polarization effects but not for absorption. The appearance of the spots on the higher level Weissenberg-diagrams were allowed for using a method described by Philips.³ The unit cell dimensions were determined from oscillation and Weissenberg-diagrams, and refined by Guinier powder patterns, using $\text{CuK}\alpha$ radiation.

The values are:

$$a = 3.548 \text{ \AA}, b = 8.23 \text{ \AA}, c = 9.01 \text{ \AA}, \beta = 96.0^\circ$$

Systematic absences unambiguously determine the space group to be $P2_1/c$. With two $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ in the unit cell a density of 2.10 g/cm^3 is derived, whereas the density determined by the floatation method is 2.09 g/cm^3 .

STRUCTURE DETERMINATION

From the Weissenberg-data the [100]-Patterson projection was worked out. The peaks in the Patterson map gave a first rough indication on the positions of the sodium atom, the oxalate ion and the peroxide molecule. Structure factors were calculated and a Fourier synthesis based on the strongest reflections was evaluated. Refinement was carried out and resulted in a reasonable Fourier map. It was, however, impossible to refine the structure thoroughly, and consequently a new starting point had to be sought.

The projection is well suited for direct methods as very little overlap of the atoms is expected, and the structure is built up of atoms with approximately the same scattering power. The intensity data were brought on absolute scale and the *U*-values evaluated.⁴

* The analysis was kindly carried out by Cand.real. Carl U. Wetlesen.

On the basis of these values, the phases of the strongest reflections were determined from direct methods.⁵ A new Fourier synthesis was calculated, and was rather similar in appearance to the first one. There were, however, shifts in the parameters for all the atoms. A new set of structure factors was calculated, showing significantly better agreement with the observed ones, hence, some of the weaker reflections could be included in the next Fourier map. The coordinates of the atoms were refined in this way until all the observed reflections were included. The final Fourier map in the [100] projection is shown in Fig. 1.

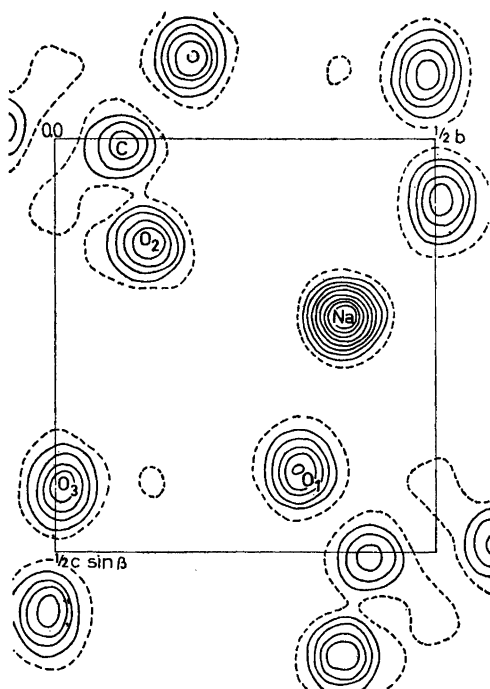


Fig. 1. Final Fourier map in the [100] projection. Contour lines at intervals of $2.5 \text{ e} \cdot \text{\AA}^{-2}$. Zero lines is broken.

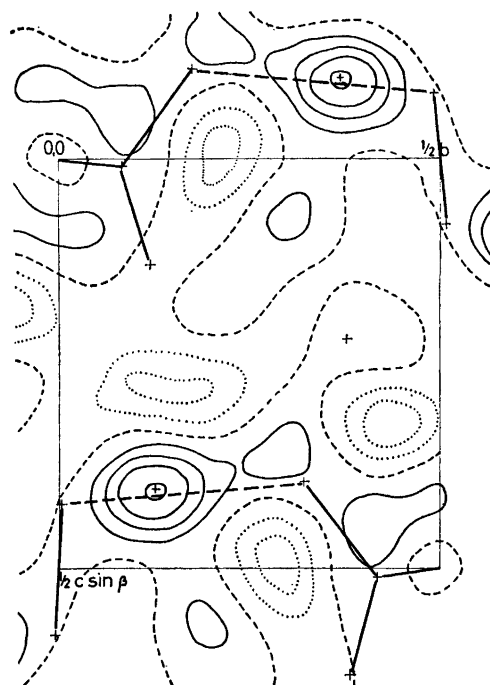


Fig. 2. Difference synthesis in the [100] projection. Contour lines at 0.28, 0.42, 0.56, 0.70 $\text{e} \cdot \text{\AA}^{-2}$. Zero line broken, negative contour lines dotted.

The parameters were further refined by the method of least squares. The thermal parameter B was given a value of 0.95 \AA^2 . The reliability index R at this stage is equal to 0.086. From comparison of the observed and calculated structure factors it was obvious that the strongest reflections for low 2θ -values were influenced by extinction. This was accounted for by the method described by Pinnock, Taylor and Lipson.⁶ The R -value dropped to 0.081. From the change in the reliability index the extinction effect might seem to

be of minor importance. But in trying to locate the hydrogen atom in a difference map it is of great importance to have the extinction effect ruled out.

A possible hydrogen position can be seen from the Fourier map. To get more accurate coordinates for the hydrogen atom, a difference synthesis was calculated, where the contributions to the structure factors from all the atoms except hydrogen were subtracted. Only reflections where $\sin \theta \leq 0.55$ were included in the difference synthesis. The atomic form factor of hydrogen has dropped to 0.15 at this point and hence makes a very small contribution to the structure factors further out.

In the difference map, Fig. 2, the hydrogen atom is clearly seen. It is situated close to the line connecting each peroxide oxygen to its closest oxygen neighbor.

To determine the x -coordinates of the atoms, the first- and second-layer equi-inclination Weissenberg-diagrams were used. From the expected interatomic distances and the distances calculated from the [100] projection, a first set of x -coordinates was evaluated.

A set of structure factors was calculated on this basis giving R -values of 0.25 and 0.32 in the first- and second-layer respectively (all reflections included). From this calculation the observed reflections could all be brought on an approximate absolute scale. The x -parameters were then refined by the use of a three-dimensional least square program (6023 FACIT LS). In the first four cycles of refinement all parameters except the x -values, the thermal parameters and the scale factors were kept constant. The R -value dropped to 0.13, all reflections included. In the next cycles the parameters of all atoms except hydrogen were refined, and the value of the reliability index dropped to 0.074, with all reflections included. In the last cycles also the hydrogen parameters were refined. The effect on the R -value was small, but the standard deviation of the H-atom parameters decreased during the refinement.

After the refinement with individual isotropic temperature factors was terminated, a new three-dimensional least squares program where individual anisotropic temperature factors could be introduced, became available.⁷ Consequently, 3 cycles of refinement with anisotropic temperature factors for all atoms except hydrogen were carried out. The reliability index decreased slightly to 0.066, all reflections included, but the changes in the parameters were less than the standard deviation for all atoms. The final parameter values and their standard deviations are given in Table 1. The observed and calculated structure factors are listed in Table 6. In Table 2 the anisotropic thermal parameters are listed with their standard deviations. The interatomic distances and angles calculated from the final parameters are given in Table 4.

The expression used for the anisotropic temperature factor is

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$$

From the anisotropic thermal parameter values in Table 2, the mean square atomic displacements of the different atoms along their principal axes were calculated, using the formulae developed by Busing and Levy.⁸ Also the directions of the principal axes relative to the crystallographic axes were calculated, and the result of these calculations is given in Table 3.

Table 1. Final positional parameters and their standard deviations in fractions of corresponding cell edges.

	<i>x</i>	<i>y</i>	<i>z</i>
Na ⁺	0.5040 (0.0008)	0.3756 (0.00025)	0.2188 (0.00023)
O ₁	0.0297 (0.0014)	0.3210 (0.00045)	0.3963 (0.00040)
O ₂	0.2979 (0.0016)	0.1177 (0.00048)	0.1282 (0.00041)
O ₃	0.0307 (0.0016)	0.0077 (0.00048)	0.4211 (0.00041)
C	0.0951 (0.0020)	0.4139 (0.00058)	0.5086 (0.00056)
H	0.038 (0.016)	0.1162 (0.0051)	0.4179 (0.0064)

Inspection of the data presented in Table 3 reveals some anisotropy of the motion of the different atoms. However, great care should be exercised in the interpretation of these data, as the original intensity data are not particularly accurate, being determined by visual estimation from non-integrated films. It is difficult to analyze the anisotropic motion of the atoms in terms of the different degrees of freedom the atoms or molecules possess in the lattice: intramolecular vibrations, rigid body translational and oscilla-

Table 2. Anisotropic temperature parameters β_{ij} and their standard deviations in parentheses. The expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na ⁺	0.0393 (0.0039)	0.0070 (0.0003)	0.0060 (0.0002)	-0.0031 (0.0014)	0.0099 (0.0013)	-0.0004 (0.0004)
O ₁	0.0286 (0.0063)	0.0051 (0.0005)	0.0061 (0.0005)	0.0021 (0.0024)	0.0111 (0.0025)	-0.0008 (0.0007)
O ₂	0.0371 (0.0063)	0.0071 (0.0006)	0.0058 (0.0005)	-0.0033 (0.0025)	0.0085 (0.0025)	-0.0018 (0.0008)
O ₃	0.0502 (0.0063)	0.0066 (0.0005)	0.0057 (0.0004)	0.0012 (0.0025)	0.0187 (0.0023)	0.0001 (0.0007)
C	0.0138 (0.0082)	0.0047 (0.0006)	0.0054 (0.0006)	-0.0039 (0.0031)	0.0126 (0.0030)	-0.0002 (0.0009)

Final isotropic temperature factor $\exp-(B \sin^2\theta/\lambda^2)$ for the hydrogen atom is 0.5 Å².

Table 3. Mean square vibrational displacements along the principal axes and the components in Å of unit principal axes vectors (1 Å) along the direct cell edges.

	principal axes	m.s.d. $\langle \mu^2 \rangle$	principal axis components		
			<i>x</i>	<i>y</i>	<i>z</i>
Na ⁺	1	0.0299	0.7588	-0.2152	0.6991
	2	0.0240	0.0020	0.9200	0.3922
	3	0.0181	0.6601	0.3258	-0.6114
O ₁	1	0.0282	0.5743	0	0.8808
	2	0.0175	0	1.000	0
	3	0.0131	0.8252	0	-0.4851
O ₂	1	0.0303	0.5918	-0.5621	0.6429
	2	0.0217	0.5414	0.8103	0.2380
	3	0.0184	0.6171	-0.1493	-0.7108
O ₃	1	0.0391	0.8489	0	0.6247
	2	0.0226	0	1.000	0
	3	0.0132	0.5390	0	-0.7879
C	1	0.0254	0.5006	-0.1270	0.9102
	2	0.0166	0.1179	-0.9723	-0.1898
	3	0.0032	0.8727	0.2013	-0.3630

tional vibrations. For the oxalate ion, the data in Table 3 seem to indicate that the most pronounced rigid body oscillation is about the C—C bond, in accordance with the findings of Beagley and Small⁹ for the oxamate ion. This is also to be expected from arguments based on the relative order of magnitude of the three principal moments of inertia of the oxalate ion, the moment of inertia about the C—C bond is by far the smallest. This shows that the unexpectedly long C—C distance can not be explained as being due to anisotropic motion of the kind discussed by Cruickshank.¹⁰ Also for the peroxide group it is difficult to separate the motion into the part due to translation and the part due to oscillation to perform a correction in the O—O distance.

PROTON MAGNETIC RESONANCE STUDIES

The X-ray data led to a rather surprising and unexpected conformation of the H₂O₂-molecule. To get additional evidence for the proposed proton configuration, the compound has been investigated with proton magnetic resonance methods.

The atomic structure obtained from diffraction data will in general be an average of the scattering density of the whole crystal expressed as the scattering density distribution in one unit cell. This averaged structure will be a measure of the long range order in the crystal, and even if it is expressed as a local picture might not show the local order in the crystal.

The second moment of the nuclear magnetic resonance spectrum on the other hand, is directly related to the local order and is rather insensitive to the long range order in the structure. This is seen from the formula for the second moment of the proton magnetic resonance spectrum of a powder given by Van Vleck:¹¹

$$M_2 = \frac{4}{5} \left[\left(\frac{3\mu}{2} \right)^2 \sum_j \frac{1}{r_{oj}^6} + \frac{1}{3} \sum_i \mu_i^2 \frac{(I_i + 1)}{I_i} \frac{1}{r_{oi}^6} \right] \quad (1)$$

μ is the proton magnetic moment, r_{oj} is the distance from the proton at o to the proton at j , and r_{oi} is the distance from the proton at o to the nucleus at i carrying the magnetic moment μ_i , and spin I_i . Because the contribution from a neighbor nucleus decreases as the 6th power of the distance, only neighbors within about 5–10 Å will give a significant contribution to the theoretical second moment. Hence, eqn. (1) is applicable to a powder where all the protons are surrounded by the same configuration of nuclei within a sphere of radius 5–10 Å.

For the compound under study, the X-ray data have given a centrosymmetrical conformation for the H_2O_2 -molecule. Two locally disordered structures where the H_2O_2 -molecules exist in the usual skew conformation (*vide infra*) can be constructed that are difficult to reject from the X-ray data only. We will show that these structures can be ruled out by means of the proton magnetic resonance data.

1. *Dynamic disorder.* The H_2O_2 -molecules might rotate around the O—O bond, and due to the presence of the close oxalate oxygen neighbor the rotation will not be uniform, but the hydrogen atoms will mainly sit on the lines marking the shortest oxygen-oxygen distances. Such a rotation will most probably be thermally activated, and the rotation frequency will increase with temperature. Hence, this process should in some temperature region have a pronounced effect on the proton magnetic resonance line shape, and also on the proton spin lattice relaxation time.¹²

2. *Static disorder.* If the dynamic process described in the last paragraph was suddenly stopped, then the structure obtained would be statically disordered with only one hydrogen bond formed per H_2O_2 -molecule. In the skew conformation we assume for simplicity that all bonds are orthogonal, that the O—O distance = 1.48 Å and the O—H distance = 1.0 Å, the intramolecular H—H distance will then be 2.04 Å. From eqn. (1) it follows that this short distance will contribute 5.9 G² to the second moment. Hence, if the structure is statically disordered, the second moment of the proton magnetic resonance spectrum will be at least 5.9 G².

Both of these proposals will give only 1/2 hydrogen at the position where the hydrogen has been located by X-ray diffraction data, and 1/2 hydrogen atom should sit on top of each peroxide oxygen looking along the a -axis. As the position of the hydrogen atom has been deduced solely on the basis of the difference map in Fig. 2, these proposals can hardly be rejected on the basis of the X-ray data. It is difficult to integrate the scattering density in the hydrogen peak with sufficient accuracy to judge between 1/2 or 1 electron, and the lack of peaks in the difference map in Fig. 2 at the peroxide oxygen

positions can be due to the B -factor or atomic form factor used for the oxygen atom at that position.

The proton magnetic resonance spectrum of the powdered compound (washed with ethyl alcohol and air dried) was recorded on a Varian Associate Dual Purpose NMR-spectrometer operating at 60 Mc/sec. The experimental second moment of the spectrum was determined to $1.90 \pm 0.16 \text{ G}^2$ by graphical integration (average of nine spectra corrected for modulation broadening).¹³ The signal was easily saturated so we had to work at low power levels, $H_1 = 0.7 \text{ mG}$, to avoid saturation effects. The signal to noise ratio was correspondingly poor, about 8/1. The spin lattice relaxation time, T_1 , was measured by saturating the signal and observing the recovery directly. T_1 was found to increase monotonically from about 150 sec at room temperature to 300 sec at -100°C .

The T_1 -data rule out the possibility of dynamically disorder. In solids, where the molecules are rotating, T_1 has been found to have a sharp temperature dependence and to have a minimum value below 1 sec.¹⁴ The observed value of the second moment, 1.9 G^2 , rules out the possibility of static disorder, as this demands a second moment of at least 5.9 G^2 .

The second moment can be calculated from the proton structure by means of Van Vleck's formula. The intermolecular contributions from the protons are found to be 0.72 G^2 , and the contribution from the sodium atoms is 0.36 G^2 , using the atomic coordinates in Table 1. The protons and the sodium atoms are the only nuclei with non-zero magnetic moment. The total intermolecular contribution to the second moment is therefore 1.08 G^2 . The difference $1.90 - 1.08 \text{ G}^2$ must be the intramolecular contribution. From Van Vleck's formula, the intramolecular proton-proton distance which corresponds to this difference, $0.72 \pm 0.18 \text{ G}^2$, is $2.81 \pm 0.14 \text{ \AA}$. This is somewhat larger than the X-ray value, 2.45 \AA , but remembering the large uncertainties inherent in both methods, the agreement must be regarded as satisfactory.

DISCUSSION OF THE STRUCTURE

The structure of $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ is shown in Fig. 3, and the calculated interatomic distances, based on the coordinates in Table 1, are given in Table 4.

The H_2O_2 -molecule is found in a planar *trans* conformation. This is not the stable conformation for an isolated molecule. Penney and Sutherland¹⁵ pointed out that in the stable conformation the two O—H bonds would be nearly orthogonal to minimize the repulsion between the two unshared electron pairs on the two oxygen atoms. This skew conformation has been found in solid H_2O_2 ^{16,17}, in $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$,¹⁸ and in the addition compound hyperol, urea- H_2O_2 .¹⁹ Abrahams¹⁶ could not locate the hydrogen atoms from the X-ray data in solid H_2O_2 , but by assuming that the hydrogen atoms lie on the lines of shortest intermolecular O—O contacts, the following data were derived: the angle H—O—O 97° and the dihedral angle 94° . The value of the dihedral angle thus derived, is also found by Busing and Levy, as quoted by Pauling¹⁷ in a neutron diffraction study of crystals of hydrogen peroxide. Busing and Levy were also able to determine the positions of the hydrogen atoms and, hence, could calculate the true dihedral angle: $89^\circ \pm 2^\circ$ and the H—O—O angle

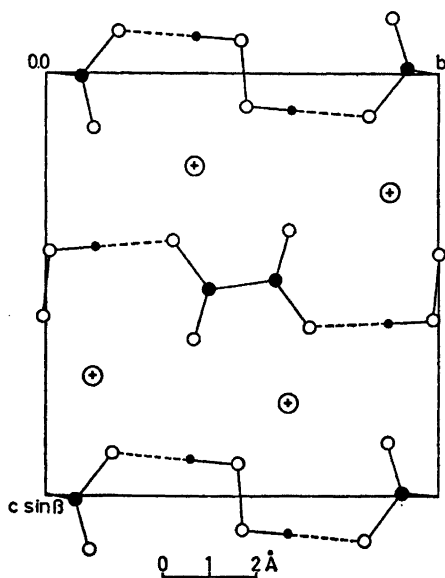


Fig. 3. Packing relations in $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ displayed in projection on (100).

$101.5^\circ \pm 0.5^\circ$. Apparently, the hydrogen atoms are not located on the lines of the shortest intermolecular O—O contacts. Olovsson and Templeton¹⁸ found from their X-ray data on $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ a very large dihedral angle of 130° .

Many theoretical and experimental investigations have been made in order to determine the potential energy of the isolated molecule as the two hydroxyl groups are rotated relative to each other around the O—O bond.

Table 4. Interatomic distances and valence angles \pm standard deviations

Distances in the H_2O_2 molecule:

$$\text{O}-\text{O} = 1.466 \text{ \AA} \pm 0.009 \text{ \AA}$$

$$\text{O}-\text{H} = 0.89 \text{ \AA} \pm 0.05 \text{ \AA}$$

$$\angle \text{H}-\text{O}-\text{O} = 97^\circ \pm 3^\circ$$

Distances in the oxalate ion:

$$\text{C}-\text{O}_1 = 1.270 \text{ \AA} \pm 0.007 \text{ \AA}$$

$$\text{C}-\text{O}_2 = 1.259 \text{ \AA} \pm 0.007 \text{ \AA}$$

$$\text{C}-\text{C} = 1.570 \text{ \AA} \pm 0.011 \text{ \AA}$$

$$\angle \text{C}-\text{C}-\text{O}_1 = 115.1^\circ \pm 0.5^\circ$$

$$\angle \text{C}-\text{C}-\text{O}_2 = 118.2^\circ \pm 0.5^\circ$$

$$\angle \text{O}_1-\text{C}-\text{O}_2 = 126.7^\circ \pm 0.5^\circ$$

Hydrogen bond distance $\text{O}_2-\text{O}_1 = 2.588 \text{ \AA} \pm 0.006 \text{ \AA}$

Interionic distances;

$$\text{Na}-\text{O}_2 = 2.435 \text{ \AA} \pm 0.006 \text{ \AA}$$

$$\text{Na}-\text{O}_3' = 2.423 \text{ \AA} \pm 0.006 \text{ \AA}$$

$$\text{Na}-\text{O}_1' = 2.481 \text{ \AA} \pm 0.006 \text{ \AA}$$

$$\angle \text{O}_2-\text{Na}-\text{O}_3' = 93.8^\circ \pm 0.2^\circ$$

$$\text{Na}-\text{O}_1' = 2.370 \text{ \AA} \pm 0.006 \text{ \AA}$$

$$\text{Na}-\text{O}_2 = 2.363 \text{ \AA} \pm 0.006 \text{ \AA}$$

$$\text{Na}-\text{O}_3 = 2.402 \text{ \AA} \pm 0.006 \text{ \AA}$$

The most recent experimental investigation appears to be a high resolution infrared study of the molecule in the gas phase by Redington, Olson and Cross.²⁰ These authors find a skew equilibrium structure with a dihedral angle of 119.8° and a H—O—O angle of 94.8°. They further find that the *trans* conformation is associated with an energy maximum 0.9 kcal/mole (300 cm⁻¹) above the equilibrium conformation. The highest barrier hindering internal rotation is due to the *cis* conformation which is about 4 kcal/mole (1300 cm⁻¹) above the equilibrium conformation. The energy gain by the formation of one hydrogen bond from a water molecule in hydrates is about 3–4 kcal/mole.¹⁴ The energy of hydrogen bonds formed by hydrogen peroxide seems to be of the same magnitude as the ones formed by water.²¹ Hence, the formation of two hydrogen bonds per molecule, as in the compound under study, can more than account for the twisting of the hydrogen peroxide molecule from the skew to the *trans* conformation which requires only 0.9 kcal/mole. The hydrogen atom is, within the experimental uncertainty on the line connecting the peroxide oxygen to the oxalate oxygen. This oxygen-oxygen distance is fairly short, 2.588 Å, indicating a relatively strong hydrogen bond. The *trans* conformation is further stabilized in the lattice by two close sodium contacts for each peroxide oxygen, 2.43 Å away and with Na—O—Na angle = 94°. Each perhydrate oxygen is therefore approximately tetrahedrally surrounded by two sodium cations, one other perhydrate oxygen and one hydrogen atom. From these considerations it follows quite generally that the conformation of the hydrogen peroxide molecule found in solids can be heavily influenced by intercrystalline forces.

The bond lengths in the *trans* conformation, shown in Table 4 are not significantly different from the corresponding bond lengths found for the skew conformation. Redington, Olson and Cross²⁰ in their infrared study find the O—O distance equal to 1.475 Å and the O—H distance equal to 0.950 Å. Our values are 1.466 Å for the former and 0.9 Å for the latter. The value found for the H—O—O angle, 97°, is somewhat smaller than the value found by Busing and Levy for the corresponding angle in solid H₂O₂, 101.5° ± 0.5°, but a little larger than the infrared value 94.8°.

Table 5. Observed bond lengths (Å) and angles (°) in the oxalate ion.

	C—C	C—O ₁	C—O ₂	O—C—O	C—C—O ₁	C—C—O ₂	planar
(NH ₄) ₂ C ₂ O ₄ ·H ₂ O a)	1.56	1.25	1.23	125	116	119	no
Na ₂ C ₂ O ₄ b)	1.54	1.23	1.23	124	115	121	yes
Li ₂ C ₂ O ₄ c)	1.561	1.264	1.252	127	116	116	yes
Na ₂ C ₂ O ₄ ·H ₂ O ₂ d)	1.570	1.259	1.270	127	115	118	yes
α-H ₂ C ₂ O ₄ e)	1.56	1.194	1.289	128	109	123	yes
H ₂ C ₂ O ₄ ·2H ₂ O f)	1.53	1.19	1.29	126	113	122	yes

a) Jeffrey, G. A. and Parry, G. S. *J. Chem. Soc.* 1952 4864.

b) Jeffrey, G. A. and Parry, G. S. *J. Am. Chem. Soc.* 76 (1954) 5283.

c) Beagley, B. *Private Communication*.

d) Present work.

e) Cox, E. G. Doughill, M. W. and Jeffrey, G. A., *J. Chem. Soc.* 1952 4854.

f) Ahmed, F. R. and Cruickshank, D. W. J. *Acta Cryst.* 6 (1953) 385.

Table 6. Observed and calculated structure factors. Structure factors calculated less than the minimum observable value are omitted.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	8.1	7.5	0	6	1	8.8	-9.1
0	0	4	13.1	-11.8	0	6	2	1.9	1.2
0	0	6	20.0	-20.0	0	6	3	19.6	21.0
0	0	8	11.2	11.3	0	6	4	12.5	-13.3
0	0	10	12.8	11.9	0	6	5	13.0	-13.8
0	1	1	10.0	10.2	0	6	6	14.3	-14.5
0	1	2	3.3	-2.4	0	6	7	3.4	-2.9
0	1	3	7.2	7.7	0	6	8	6.4	-5.5
0	1	4	23.5	23.9	0	6	9	5.2	4.4
0	1	5	7.5	-7.4	0	7	1	11.0	-11.1
0	1	6	13.8	-14.6	0	7	2	19.4	20.2
0	1	7	26.1	30.4	0	7	3	2.6	-2.1
0	1	9	1.3	2.3	0	7	5	6.6	-6.7
0	1	10	10.4	-8.6	0	7	6	1.2	-1.1
0	1	11	2.3	2.7	0	7	7	9.8	7.6
0	2	0	20.5	21.7	0	7	8	10.4	-7.5
0	2	1	25.9	25.1	0	8	0	15.3	15.3
0	2	2	15.8	16.1	0	8	1	2.8	2.1
0	2	3	28.7	-29.2	0	8	2	10.4	-10.5
0	2	4	6.5	6.1	0	8	3	2.9	2.7
0	2	5	17.8	19.2	0	8	4	2.7	2.5
0	2	6	2.6	-2.3	0	8	5	2.2	-1.7
0	2	7	6.0	-6.7	0	8	6	6.0	-4.7
0	2	8	3.7	-3.9	0	9	1	5.5	-4.8
0	2	9	11.5	-9.5	0	9	2	6.0	-4.8
0	2	11	2.7	2.5	0	9	3	1.9	1.8
0	3	1	40.8	-39.8	0	9	4	5.8	4.6
0	3	2	25.8	-26.2	0	10	0	10.6	8.8
0	3	3	2.4	1.6	0	10	2	6.0	4.1
0	3	4	11.5	11.9	0	10	3	13.5	-11.8
0	3	5	32.2	36.8					
0	3	6	4.4	-4.5	1	0	8	3.2	-3.5
0	3	7	5.0	-5.7	1	0	6	3.7	2.2
0	3	8	6.3	5.8	1	0	4	19.5	-21.1
0	3	10	12.7	-11.1	1	0	2	43.4	45.0
0	4	0	37.6	-39.3	1	0	2	76.6	78.7
0	4	1	13.5	-14.2	1	0	4	33.0	-33.3
0	4	2	22.4	26.2	1	0	6	14.1	-15.3
0	4	3	18.1	-18.8	1	0	8	5.6	6.2
0	4	4	9.2	-9.4	1	0	10	12.6	12.7
0	4	6	4.8	-4.7	1	1	10	4.2	4.2
0	4	7	6.3	6.5	1	1	9	7.5	8.4
0	4	8	13.5	-12.5	1	1	8	19.1	-19.4
0	4	10	3.6	-3.5	1	1	7	1.9	1.2
0	5	1	13.5	-14.8	1	1	6	2.2	0.6
0	5	2	5.6	5.9	1	1	5	26.7	27.0
0	5	3	12.1	-12.0	1	1	4	5.8	3.6
0	5	4	11.2	-11.1	1	1	3	14.9	-15.0
0	5	5	8.1	7.7	1	1	2	25.6	26.6
0	5	6	7.4	7.8	1	1	1	16.2	-15.3
0	5	7	11.5	-11.4	1	1	0	22.8	-24.5
0	5	8	6.0	-4.4	1	1	1	12.8	13.4
0	5	9	5.7	4.5	1	1	2	39.3	-40.1
0	5	10	3.3	3.4	1	1	3	8.6	8.6
0	6	0	10.3	9.1	1	1	4	16.1	16.7

SODIUM OXALATE PERHYDRATE

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<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
1	1	$\bar{5}$	22.0	23.0	1	4	$\bar{4}$	4.0	4.3
1	1	$\bar{6}$	4.7	- 3.9	1	4	$\bar{5}$	2.1	- 2.5
1	1	$\bar{7}$	2.2	- 3.4	1	4	$\bar{6}$	8.4	- 7.6
1	1	$\bar{8}$	9.6	10.0	1	4	$\bar{7}$	9.0	- 9.5
1	1	$\bar{9}$	15.7	17.2	1	4	$\bar{8}$	6.1	- 6.0
1	1	$\bar{10}$	7.2	- 7.7	1	4	$\bar{9}$	3.4	- 3.0
1	1	$\bar{11}$	1.6	- 1.0	1	4	$\bar{10}$	1.9	- 2.5
1	2	9	4.5	- 4.9	1	5	8	7.4	8.1
1	2	8	4.5	- 5.0	1	5	7	5.9	6.6
1	2	7	13.9	-12.7	1	5	6	5.0	- 4.7
1	2	5	14.3	-12.9	1	5	5	18.2	-18.2
1	2	4	7.9	6.8	1	5	3	2.4	1.3
1	2	3	38.9	40.1	1	5	2	13.4	-13.3
1	2	2	12.3	10.7	1	5	0	4.4	4.6
1	2	1	37.9	-40.6	1	5	$\bar{1}$	16.8	-16.3
1	2	0	12.0	12.6	1	5	$\bar{2}$	11.9	10.8
1	2	$\bar{1}$	5.9	- 4.7	1	5	$\bar{3}$	9.2	- 9.3
1	2	$\bar{2}$	14.3	14.3	1	5	$\bar{4}$	14.2	-13.9
1	2	$\bar{3}$	26.5	-27.4	1	5	$\bar{5}$	9.6	-10.0
1	2	$\bar{4}$	5.0	5.1	1	5	$\bar{6}$	3.2	3.3
1	2	$\bar{5}$	22.6	23.9	1	5	$\bar{7}$	12.9	12.7
1	2	$\bar{6}$	4.4	- 4.3	1	5	$\bar{8}$	5.9	- 5.8
1	2	$\bar{7}$	2.6	- 3.0	1	5	$\bar{9}$	6.9	- 7.3
1	2	$\bar{8}$	4.2	- 4.1	1	5	$\bar{10}$	5.9	5.7
1	2	$\bar{9}$	7.1	- 6.6	1	6	8	2.3	- 3.1
1	2	$\bar{10}$	1.9	1.5	1	6	6	11.6	-13.0
1	2	$\bar{11}$	2.9	3.1	1	6	5	4.0	3.8
1	3	9	4.2	- 5.0	1	6	4	11.3	-10.4
1	3	8	13.4	-14.1	1	6	3	15.7	-16.6
1	3	7	15.3	15.2	1	6	2	7.4	6.3
1	3	6	4.4	3.6	1	6	1	21.8	-21.6
1	3	4	7.9	- 7.0	1	6	0	13.7	-13.0
1	3	3	13.4	10.8	1	6	$\bar{1}$	10.5	10.3
1	3	2	3.8	3.2	1	6	$\bar{2}$	4.7	4.5
1	3	1	27.0	-25.5	1	6	$\bar{3}$	7.7	7.4
1	3	0	21.5	-20.2	1	6	$\bar{4}$	16.6	-16.3
1	3	$\bar{1}$	35.0	-35.6	1	6	$\bar{5}$	10.3	-10.1
1	3	$\bar{2}$	16.1	-16.0	1	6	$\bar{6}$	12.6	-12.0
1	3	$\bar{3}$	13.1	11.7	1	6	$\bar{7}$	7.2	6.6
1	3	$\bar{4}$	18.7	18.4	1	6	$\bar{8}$	3.7	- 3.2
1	3	$\bar{5}$	13.6	12.2	1	6	$\bar{9}$	4.1	3.5
1	3	$\bar{6}$	13.4	-13.6	1	7	6	3.2	- 3.8
1	3	$\bar{7}$	19.4	19.5	1	7	5	7.1	8.2
1	3	$\bar{8}$	2.3	2.4	1	7	4	7.4	8.1
1	3	$\bar{9}$	13.4	-13.8	1	7	3	9.3	- 9.7
1	3	$\bar{10}$	4.2	- 4.5	1	7	2	4.4	4.5
1	4	8	2.1	- 2.9	1	7	1	10.6	-11.3
1	4	7	2.6	0.1	1	7	0	6.8	6.0
1	4	6	18.1	-18.2	1	7	$\bar{1}$	6.0	- 5.7
1	4	5	5.9	- 5.1	1	7	$\bar{2}$	2.3	- 2.2
1	4	4	8.1	6.7	1	7	$\bar{3}$	6.0	- 5.4
1	4	3	18.1	-15.7	1	7	$\bar{4}$	14.2	-13.7
1	4	2	5.6	- 5.4	1	7	$\bar{5}$	5.9	5.8
1	4	1	15.5	-13.5	1	7	$\bar{6}$	9.6	10.4
1	4	0	33.5	34.8	1	7	$\bar{7}$	5.5	- 6.3
1	4	$\bar{1}$	7.7	6.5	1	7	$\bar{8}$	3.5	3.0
1	4	$\bar{2}$	34.7	-35.0	1	8	6	4.5	4.6
1	4	$\bar{3}$	12.4	11.2	1	8	5	1.7	1.4

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
1	8	4	3.8	— 3.0	2	2	0	5.1	4.9
1	8	3	2.0	— 1.4	2	2	$\bar{1}$	40.6	— 39.8
1	8	2	4.2	4.4	2	2	$\bar{2}$	5.4	4.4
1	8	1	4.2	4.5	2	2	$\bar{3}$	6.6	— 6.3
1	8	0	13.6	— 13.6	2	2	$\bar{5}$	8.7	— 7.3
1	8	$\bar{1}$	3.9	3.2	2	2	$\bar{6}$	4.8	— 3.7
1	8	$\bar{2}$	14.2	14.3	2	2	$\bar{7}$	9.5	9.8
1	8	$\bar{4}$	4.8	— 5.0	2	2	$\bar{8}$	4.3	— 3.9
1	8	$\bar{6}$	4.4	— 4.1	2	2	$\bar{9}$	3.7	— 2.7
1	8	7	2.7	2.6	2	3	9	2.8	3.3
1	9	5	10.5	11.8	2	3	8	4.0	4.1
1	9	3	4.1	— 4.1	2	3	7	3.6	4.2
1	9	2	3.2	3.6	2	3	6	11.7	— 14.0
1	9	1	9.5	— 9.6	2	3	5	14.1	16.5
1	9	$\bar{1}$	1.6	— 2.0	2	3	4	3.0	— 3.0
1	9	$\bar{3}$	3.2	3.2	2	3	3	14.9	— 15.1
1	9	4	6.1	5.8	2	3	2	6.4	— 5.6
1	9	$\bar{5}$	9.6	8.6	2	3	1	16.7	— 18.3
1	9	6	3.4	— 4.4	2	3	0	3.0	— 2.6
1	10	2	2.7	3.0	2	3	$\bar{1}$	3.0	— 3.0
1	10	1	7.9	— 8.0	2	3	$\bar{2}$	8.8	— 7.9
1	10	0	6.0	5.2	2	3	$\bar{4}$	19.7	— 19.8
1	10	$\bar{1}$	9.3	8.7	2	3	$\bar{5}$	20.9	20.2
1	10	$\bar{2}$	5.6	5.0	2	3	$\bar{6}$	8.4	9.2
					2	3	$\bar{7}$	4.5	— 3.9
2	0	8	4.6	— 6.3	2	3	$\bar{8}$	8.0	— 8.6
2	0	6	16.3	— 21.7	2	4	6	4.6	4.4
2	0	4	15.8	14.3	2	4	5	6.8	— 7.5
2	0	2	8.0	7.7	2	4	4	14.2	— 14.3
2	0	0	50.0	44.8	2	4	3	13.6	— 14.2
2	0	$\bar{2}$	26.0	— 24.6	2	4	2	13.9	14.7
2	0	4	9.1	7.5	2	4	1	6.7	— 6.2
2	0	$\bar{6}$	12.4	— 10.3	2	4	0	6.1	— 4.9
2	0	$\bar{10}$	13.6	11.3	2	4	$\bar{1}$	4.4	4.2
2	1	7	6.1	7.0	2	4	$\bar{2}$	23.1	21.7
2	1	6	13.8	— 15.8	2	4	$\bar{3}$	3.8	2.3
2	1	5	7.4	— 6.7	2	4	$\bar{4}$	22.8	— 23.6
2	1	4	8.9	8.0	2	4	$\bar{5}$	7.7	— 6.9
2	1	3	12.6	11.0	2	4	$\bar{6}$	7.1	— 6.1
2	1	2	8.9	7.5	2	4	$\bar{7}$	8.2	— 8.5
2	1	1	9.3	— 9.9	2	4	$\bar{9}$	3.0	— 3.3
2	1	0	6.4	— 5.2	2	5	8	3.5	— 4.6
2	1	$\bar{1}$	17.4	— 17.8	2	5	6	6.1	7.0
2	1	$\bar{2}$	21.8	— 19.6	2	5	5	4.2	3.0
2	1	$\bar{3}$	18.4	16.1	2	5	4	7.0	— 7.2
2	1	4	20.6	— 20.4	2	5	3	13.8	— 14.3
2	1	$\bar{5}$	7.4	5.9	2	5	2	6.5	— 5.4
2	1	6	21.3	21.3	2	5	$\bar{1}$	7.7	6.0
2	1	7	19.5	17.4	2	5	$\bar{3}$	13.0	— 12.9
2	1	8	4.3	— 4.0	2	5	4	7.4	6.5
2	2	9	6.3	— 5.5	2	5	$\bar{6}$	13.8	— 14.7
2	2	8	3.6	— 4.8	2	5	7	2.9	— 3.1
2	2	7	7.8	— 10.2	2	5	9	8.1	7.8
2	2	5	3.7	— 3.2	2	6	6	4.6	— 6.2
2	2	4	4.2	4.5	2	6	4	4.0	— 5.2
2	2	3	13.7	— 13.8	2	6	3	11.1	10.5
2	2	2	6.7	6.4	2	6	2	6.3	6.3
2	2	1	26.7	29.6	2	6	1	16.1	— 17.1

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
2	6	0	11.8	11.5	2	8	4	9.1	9.2
2	6	$\bar{1}$	13.8	12.8	2	8	3	4.4	4.1
2	6	$\bar{3}$	4.7	- 4.0	2	8	2	5.1	- 4.2
2	6	4	14.1	-14.3	2	8	0	4.2	4.1
2	6	$\bar{5}$	5.7	5.9	2	8	$\bar{1}$	3.8	3.6
2	6	$\bar{6}$	10.1	-10.1	2	8	$\bar{2}$	9.2	- 9.1
2	6	$\bar{7}$	2.6	- 3.5	2	8	$\bar{3}$	5.1	4.6
2	7	6	5.9	7.2	2	8	4	8.8	8.7
2	7	4	5.6	6.1	2	8	$\bar{5}$	4.6	3.8
2	7	2	6.7	6.5	2	8	$\bar{6}$	3.1	- 3.4
2	7	1	7.1	- 7.9	2	9	2	2.1	1.9
2	7	0	3.6	- 2.6	2	9	1	8.0	- 7.4
2	7	$\bar{1}$	9.8	- 9.3	2	9	0	4.0	4.3
2	7	$\bar{2}$	3.6	- 4.0	2	9	$\bar{1}$	8.7	- 8.2
2	7	$\bar{3}$	4.3	4.4	2	9	$\bar{2}$	6.5	5.1
2	7	4	7.3	7.4	2	9	$\bar{3}$	7.3	7.0
2	7	7	5.4	4.6					

The commonly observed conformation for the oxalate ion is centrosymmetric and planar. In $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, however, the ion is centrosymmetric, but not planar.²² The bond lengths and angles observed in the oxalate ions in a series of accurately determined oxalates are given in Table 5 together with the results of this investigation. From the data in Table 5 it is seen that the results found for $\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}_2$ are in accordance with earlier investigations, and the ion is found to be planar within the experimental uncertainty. The equation of the plane containing the centre of symmetry $(0, \frac{1}{2}, \frac{1}{2})$, O_1 and O_2 is: $x + 0.9873y - 1.4121z + 0.2124 = 0$, and the C atom is 0.005 Å out of this plane.

It follows from the data in Table 5 that the oxalate ion is not as regular as one should expect. The observed C—C bond is definitely longer than expected for a $\text{Csp}^2\text{—Csp}^2$ single bond, 1.48 Å, and even longer than a $\text{Csp}^3\text{—Csp}^3$ bond, 1.53 Å.²³ The angle O—C—O is also significantly larger than 120°. The same changes have also been observed in related molecules like the oxamate ion⁹ and in the isoelectronic compound N_2O_4 .²⁴ These deformations have very recently been thoroughly discussed by Beagley and Small,⁹ and for N_2O_4 by Bent,²⁵ but at present an adequate explanation for these deformations from the expected regular structure of the oxalate ion seems to be lacking.

The configuration around the sodium ion is a somewhat distorted octahedron built up of four oxalate oxygens at Na—O distances of 2.481 Å, 2.370 Å, 2.363 Å, and 2.482 Å and two peroxide oxygens at 2.435 Å and 2.422 Å. The found configuration correspond closely to the one in $\text{Na}_2\text{C}_2\text{O}_4$,²⁶ where the mean Na—O distance in the octahedron is 2.48 Å.

Acknowledgements. This work has been supported in part by *The Royal Norwegian Council for Scientific and Industrial Research*. Our thanks are also due to Mrs. T. L. Rolfsen and Miss M. Lange for extensive technical assistance, and to other members of the staff for many valuable discussions.

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Received March 23, 1964.