unusually tight packing. The packing is illustrated in Fig. 3. There are no opportunities for hydrogen bonding and no overall dipolar attractions. There are only a few intermolecular distances less than 3·6 Å (Fig. 3). However, each atom interacts with several atoms from neighboring molecules at distances only slightly longer (3·6 to 3·8 Å). The molecules mesh together neatly, accounting for the relatively high density.

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The Crystal Structure of Ammonium Oxalate Monoperhydrate

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The crystal structure of ammonium oxalate monoperhydrate $(NH_4)_2C_2O_4.H_2O_2$, has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the orthorhombic space group $P2_12_12$, with two molecules per unit cell. 6% of the H_2O_2 molecules are found to be exchanged with H_2O molecules occupying randomly distributed sites. Both the oxalate ion and the hydrogen peroxide molecule are situated on twofold axes. The interatomic dimensions of the oxalate ion are normal, but the ion is *non-planar*. The planes of the two $C-C-O_2$-groups of the ion are inclined at an angle of 28·15 (9)°. The hydrogen peroxide molecule has a skew conformation with a dihedral angle of 121 (3)°, the acceptor angle being 127·77 (9)°. The interatomic dimensions are of normal values. All available hydrogen atoms are engaged in hydrogen bonds; $O-H\cdots O$ is 2·625 (1) Å and the $N-H\cdots O$ average distance is 2·860 (1) Å. Single crystals of the perhydrate transform to single crystals of the hydrate over a period of several months. No variation in unit-cell dimensions is found for different batches of crystals, and no gradual variation in unit-cell dimensions seems to accompany the transformation from the perhydrate to the hydrate.

Introduction

Investigations are being carried out at this institute to study the structure and bonding of the hydrogen peroxide molecule in solids (Pedersen, 1969a). Previously it has been found that the hydrogen peroxide molecule forms stoichiometric compounds with all the alkali metal oxalates. The crystal structures of the following compounds have been determined: $Li_2C_2O_4.H_2O_2$ (Pedersen, 1969b), $Na_2C_2O_4.H_2O_2$ (Pedersen & Pedersen, 1964) $K_2C_2O_4.H_2O_2$ and $Rb_2C_2O_4.H_2O_2$ (Pedersen, 1967). Evidence has been found that caesium oxalate also forms a perhydrate. In this paper the crystal structure of ammonium oxalate monoperhydrate will be described in detail. A preliminary note (Pedersen, 1969c) has been published, but as indications of non-stoichiometry were found in this compound, a detailed discussion was postponed until more accurate intensity data were available.

The crystal structure of ammonium oxalate monoperhydrate is closely related to the structure of ammonium oxalate monohydrate (Robertson, 1965). A similar analogy has been observed previously for the potassium and rubidium oxalates, which also form

both monohydrates and monoperhydrates (Pedersen, 1967). The crystal structure of ammonium oxalate monohydrate, which has previously been carefully refined from three-dimensional X-ray data at 30°K (Robertson, 1965), shows all available hydrogen atoms to be engaged in hydrogen bonds and the oxalate ion to be *non-planar*, the dihedral angle between the two $C-C-O_2$ planes being 26·6 (4)°. The non-planarity is believed to be caused by the hydrogen bonding network.

By substituting the water molecule by a molecule of hydrogen peroxide, one would expect changes in the crystal structure. Slight changes in packing and hydrogen bonding possibilities may lead to changes in the unusual twisted conformation of the oxalate ion, which hitherto has been observed only for the hydrogen oxalate ion (Haas, 1964; Pedersen, 1968; Follner, 1970; Tellgren & Olovsson, 1971).

The hydrogen peroxide molecule in the gas phase has a dihedral angle of 111·5°. The molecule has, however, been found to show great variation in dihedral angle, from 90 to 180°, in the solids that so far have been studied in detail. As ammonium oxalate contains only light atoms, it was hoped that the dimensions deter-

mined for the H_2O_2 molecule in this compound would be of high accuracy, supplementing existing information on the hydrogen peroxide molecule in solids.

Experimental

Ammonium oxalate monoperhydrate, $(NH_4)_2C_2O_4 . H_2O_2$ was prepared by dissolving the monohydrate (*pro analysi* Merck) in perhydrol (30% H_2O_2 in H_2O). By slow evaporation of the solution at room temperature, colourless, long prismatic (**c**), crystals of the monoperhydrate separated. Chemical analysis of the compound was difficult, as it decomposed during the analysis. Infrared spectra recorded for this compound and for the monohydrate showed a number of absorption lines, and although there were some significant differences the two spectra were similar.

The symmetry of the crystals determined from oscillation and Weissenberg diagrams was found to be orthorhombic; absent spectra are ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$) which determine the space group to be $P2_12_12$ (No. 18). The measured density, 1·51(1) g.cm^{-3}, agreed reasonably well with the value of

1·53 g.cm^{-3} calculated for a two-molecule unit cell.

Unit-cell dimensions at 18 °C are: $a_0 = 8·531$ (1), $b_0 = 10·476$ (1), $c_0 = 3·8228$ (8) Å. These were determined by a least-squares fit of the χ, φ, and 2θ values of 64 general reflexions, all measured at $\pm 2\theta$ on a manual Picker diffractometer (take off angle, 0·4°; $\lambda_{Cu K\beta} = 1·39217$, $\lambda_{Cu K\alpha} = 1·54178$, $\lambda_{Cu K\alpha_1} = 1·54050$ Å). The intensities were measured by the $\omega/2\theta$ scan method on an automated Picker four-circle diffractometer, using a graphite monochromater, a pulse height discriminator and Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). The scanning range used of 2° was selected based on the trace of some high angle peaks, the background being measured for 20 sec on each side of the peak. The crystal used for intensity measurements was approximately a parallelepiped of height 0·56 mm and cross section $0·26 \times 0·20$ mm. As the perhydrates normally are fairly unstable crystals the intensities of reflexions with $2\theta < 55°$ were measured first and then the range $55° < 2\theta < 70°$ was covered, the intensities of three selected standard reflexions being measured after every 50 reflexions. The intensities were constant well within 1 % for the first range, but toward the end of the measurements of the second range, the intensities had
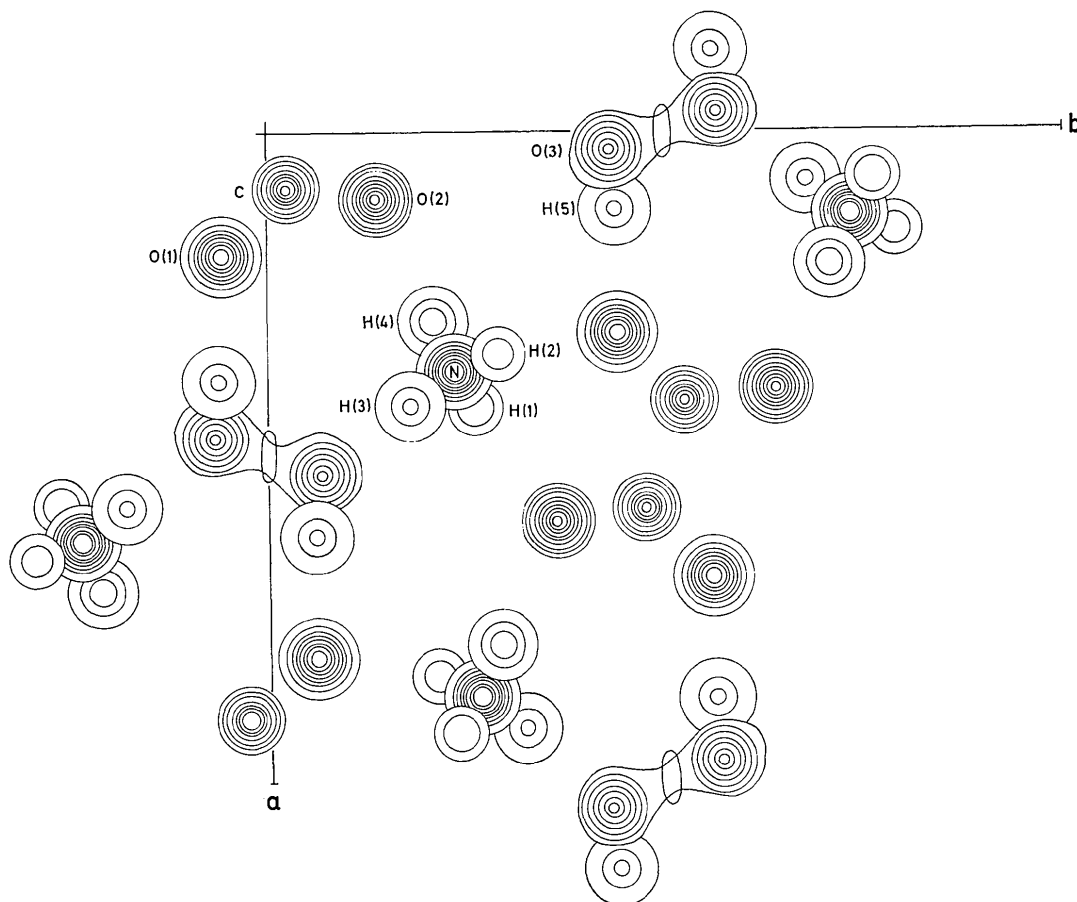

Fig. 1. Composite Fourier synthesis. Contours for the heavy atoms C, N and O are 2, 4, 6 e.Å^{-3} *etc.*; contours for the hydrogen atoms are 0·4, 0·6, 0·8 e.Å^{-3} and are traced from the difference Fourier synthesis.

dropped about 5%, showing that decomposition had started. This drop in intensity was, however, corrected for. A standard deviation (σ) was calculated for each reflexion from counter statistics, including a 2% uncertainty in scaling and fluctuation of diffractometer stability. If an intensity was less than 2σ, it was considered unobserved. In the 2θ range covered, 0–70°, 1034 independent intensities were measured out of which only 28 were considered unobserved. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was considered necessary (linear absorption coefficient for Mo $K\alpha$ radiation is 1·6 cm^{-1}). The scattering factors for C, N and O were those given by Hanson, Herman, Lea & Skillman (1964), whereas the values given by Stewart, Davidson & Simpson (1965) were used for H. All calculations were performed using a set of computer programs written or modified for use on a CDC 3300 computer (Dahl, Gram, Groth, Klewe & Rømming, 1970).

Structure refinement

Initial positions of all atoms, including hydrogen, were determined from Patterson and Fourier syntheses (Pedersen, 1969c), but as already pointed out indications of non-stoichiometry in this compound were evident. From the appearance of the Fourier map there seemed too much scattering density at the position of the oxygen atom of H_2O_2, as the thermal parameter for this atom was significantly larger than for the other atoms; furthermore the length of the O–O bond was determined to be less than 1·40 Å which seemed unreasonable. As the crystal structure of the monoperhydrate and hydrate of ammonium oxalate are closely related, a possible explanation for the observations could be that water molecules occupy a fraction of the hydrogen peroxide sites. This would lead to systematic errors in the parameter values for the oxygen atom and could also account for the relatively low electron density at this oxygen site. Initial refinement using film data indicated that approximately 10% of the hydrogen peroxide molecules were randomly replaced by

water molecules (Pedersen, 1969a). The model derived from film data was refined by full-matrix least-squares analyses based on the new diffractometer data.

Table 1. *Final fractional positional parameters and their standard deviations*

See Fig. 1 for the identities of the atoms. The e.s.d. given in parentheses is in the units of the least significant digit given for the corresponding parameter.

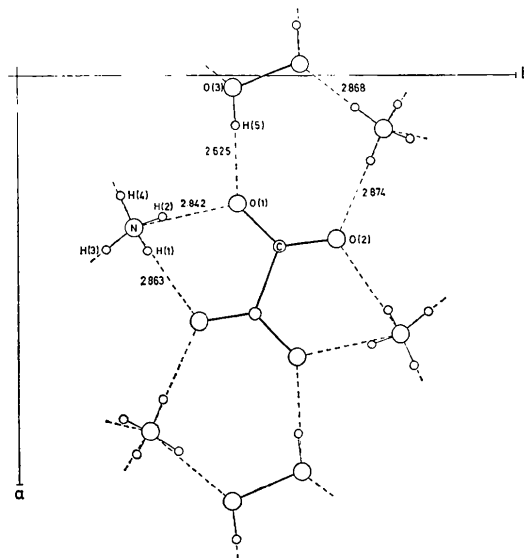|	x	y	z
C	0·08616 (11)	0·02533 (9)	0·0829 (3)
O(1)	0·19046 (9)	−0·05388 (8)	0·1545 (3)
O(2)	0·10637 (10)	0·14068 (8)	0·0128 (3)
O(3)	0·03082 (12)	0·43540 (10)	0·1350 (3)
N	0·37112 (13)	0·23519 (10)	0·3988 (3)
O_w	0	0·50000	0·256 (10)
H(1)	0·4381 (27)	0·2722 (21)	0·235 (10)
H(2)	0·3313 (26)	0·2971 (21)	0·528 (6)
H(3)	0·4232 (27)	0·1654 (23)	0·515 (6)
H(4)	0·2751 (29)	0·2069 (18)	0·308 (7)
H(5)	0·1142 (29)	0·4485 (19)	0·029 (6)

Fig. 2. Hydrogen bonding environment of the oxalate and ammonium ions and the hydrogen peroxide molecule.

Table 2. *Thermal vibration parameters and their standard deviations*

See Fig. 1 for the identities of the atoms. The e.s.d. given in parentheses is in the units of the least significant digit given for the corresponding parameter.

I Carbon, oxygen and nitrogen

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

	10^5b_{11}	10^5b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}
C	518 (9)	387 (7)	354 (6)	− 7 (1)	−17 (4)	10 (3)
O(1)	575 (9)	567 (7)	751 (9)	14 (1)	19 (4)	140 (4)
O(2)	737 (10)	390 (6)	762 (8)	−21 (1)	−121 (4)	71 (4)
O(3)	714 (14)	595 (11)	804 (12)	9 (1)	100 (6)	148 (5)
N	793 (12)	437 (7)	412 (6)	−14 (1)	− 7 (5)	18 (4)

II Hydrogen and water oxygen

	B		B
O_w	8·0 (5)	H(3)	4·1 (4)
H(1)	5·6 (6)	H(4)	4·8 (5)
H(2)	3·8 (5)	H(5)	3·3 (4)

Table 3. *Observed and calculated structure factors*

H	K	L	FOBS.	FCAL
0	2	0	26.27	24.18
0	4	0	15.39	15.51
0	6	0	12.10	11.39
0	8	0	2.12	2.10
0	10	0	17.23	17.98
0	12	0	3.17	3.25
1	13	0	3.48	3.46
1	11	0	2.40	2.72
1	10	0	9.63	9.97
1	7	0	22.74	21.94
1	6	0	14.44	13.79
1	5	0	4.06	4.04
1	4	0	31.65	29.46

(Remainder of table comprises extensive columns of H, K, L, FOBS., FCAL structure-factor values, not individually legible.)

Table 3 (cont.)

The quantity minimized was:

$$\sum W_h^2(k \cdot F_{oh} - |F_{ch}|)^2 \quad \text{where} \quad W_h = \frac{1}{\sigma_{hkl}}.$$

The refinement was first performed isotropically then anisotropically, excluding the hydrogen atoms in the least-squares refinement, but including them in the structure factors calculations. In the last cycles of refinement the hydrogen atom parameters, including an isotropic thermal parameter, were also varied.

Two procedures were used in the final cycles of the least-squares refinement. Firstly, variable fractions of oxygen atoms from H_2O_2 and H_2O molecules were included, and secondly no water was included. The results are:

H_2O_2 and H_2O: $R_w = 4\cdot6\%$, $R = 4\cdot2\%$,

$$r(O-O) = 1\cdot452 \ (1) \ \text{Å}$$

H_2O_2 only: $R_w = 5\cdot5\%$, $R = 4\cdot8\%$,

$$r(O-O) = 1\cdot434 \ (1) \ \text{Å}$$

$$R_w = [\sum W^2(|F_o| - |F_c|)^2 / \sum W^2|F_o|^2]^{1/2},$$

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

The oxygen–oxygen bond is significantly longer if water molecules are included. The fraction of H_2O_2 oxygen atoms in H_2O_2 sites in the lattice was found to be $88\cdot9$ (7)%, and the fraction of H_2O oxygen atoms $6\cdot4$ (4)%. Accordingly approximately 6% of the H_2O_2 sites is occupied by water molecules. This means that there is one water molecule in every 8 unit cells. Since super-structure reflexions were not observed, the water molecules appear to be randomly distributed over the cells.

The final positional and thermal parameters with standard deviations are given in Table 1 and Table 2 respectively. Table 3 gives the observed and calculated structure factors. A composite Fourier map including the hydrogen atoms from a difference map is shown in Fig. 1. Geometrical features are given in Fig. 2 and in Tables 5 to 8. Different sections of the final difference map are given in Figs. 3 and 4 which show the residual electron density in the bonds of the oxalate ion and in the H_2O_2 molecule.

Thermal motion

Table 4 gives the results of an analysis of the thermal motion of the oxalate ion in terms of the rigid body tensors of translations $|T|$, libration $|L|$, and screw motion $|S|$ (Schomaker & Trueblood, 1968). The r.m.s. discrepancy between observed and calculated U_{ij} serves as a measure of the applicability of this analysis, and thus of the rigidity of the ion. The rigid body parameters of the oxalate ion are given in Table 4. The r.m.s. value of ΔU_{ij} is $5 \cdot 10^{-4}$ Å^2. Hence, the fit is excellent and the oxalate ion can be properly described as a rigid body.

Table 4. *Rigid body thermal parameters for the oxalate ion*

Axes of reference are a,b,c. E.s.d. of components of L are given in parentheses, in units of last digit shown.

$L[\times 10^{-1}(°)^2]$	768 (77)	279 (62)	0 (7)
		73 (76)	0 (7)
			110 (7)

Principal axes of L

	r.m.s. Amplitude	Direction cosines ($\times 10^3$)		
$L1$	9·3°	943	332	0
$L2$	3·3	0	0	1000
$L3$	(0)*	332	−943	0

Principal axes of reduced T

r.m.s. Amplitude		Direction cosines ($\times 10^3$)	
0·16	0	1000	0
0·14	974	0	225
0·14	225	0	−974

Displacement of libration axes from intersecting (Å)†
Effective screw translations (Å)

Parallel to $L1$	0·018
Parallel to $L2$	0·049
Parallel to $L3$	†
$(\Delta U^2_{ij})^{1/2}$ (Å^2)	0·0005

* The eigenvalue of $L3$ was slightly negative.
† These quantities are not meaningful because the eigenvalue of $L3$ was negative.

The translational motion is reasonably isotropic, 0·16, 0·14, 0·14 Å while libration is quite anisotropic, the most appreciable motion corresponding to an r.m.s.

amplitude of 9·3° about an axis $|L_1|$ only 0·4° away from the C–C bond. Of the two other libration axes, one is along the twofold axis of the molecule $|L_2|$ with an amplitude of 3·3°, and the other orthogonal both to C–C and to the twofold axis $|L_3|$, with an amplitude approximately zero. The close similarity between this pattern and that found for the oxalate ion in some other crystals (Coppens & Sabine, 1969) attests to its physical reality.

The bond lengths were corrected (Cruickshank, 1956, 1961) for the effects of thermal motion indicated by the rigid body analysis.

Discussion

(a) The molecular structure

The structure of ammonium oxalate monoperhydrate is built up of oxalate ions, hydrogen peroxide molecules and ammonium ions. The packing of the constituents is similar to that observed in ammonium oxalate monohydrate. The oxalate ion is twisted also in the monoperhydrate. The angle of twist between the two C–C–O_2 planes is found to be 28·15 (9)° compared with 26·6 (4)° observed in the corresponding hydrate. The normally observed conformation of the oxalate ion is centrosymmetric and planar. The hydrogen oxalate ion, however, has previously been found to be twisted in four different compounds, KHC_2O_4 (Pedersen, 1968); $LiHC_2O_4.H_2O$ (Follner, 1970); $NaHC_2O_4.H_2O$ (Tellgren & Olovsson, 1971); $KHC_2O_4.H_2C_2O_4.2H_2O$ (Haas, 1964); whereas it is planar in $(NH_4)HC_2O_4.H_2C_2O_4.2H_2O$ (Currie, Speakman & Curry, 1967). These findings may be accounted for if the energy loss by deviations from planarity, i.e. the conjugation energy of the ion, is of the same magnitude as the energy gain by hydrogen bond formation. If the

ion can form suitable hydrogen bonds and retain planarity, this of course is preferred. But the above mentioned examples seem to indicate that hydrogen bond formation is preferred to the retainment of planarity. These results are in accordance with Kitaigorodskii's (1961) statement that a molecule will give up symmetry rather than packing efficiency.

The dimensions of the oxalate ion in ammonium oxalate monoperhydrate, as given in Table 5, conform to earlier results (Pedersen, 1969a). The C–O bonds are equal to within the experimental uncertainty: 1·2469 (13) Å and 1·2497 (13) Å, the C–C bond is long 1·5629 (20) Å, the C–C–O angles are: 117·27° (0·11) and 116·43° (0·11), the O–C–O angle is 126·30° (10); hence the twisting of the ion does not seem to influence the intramolecular dimensions. This may seem surprising in view of the lack of resonance in the ion, but the C–C bond has invariably been found to be longer than the value normally accepted for $C(sp^2)$–$C(sp^2)$ bonds and a satisfactory explanation of this effect is still lacking.

The hydrogen peroxide molecule in the present compound is found to have the skew conformation, but with a rather large dihedral angle of 120·9° (3·1). The acceptor dihedral angle is 127·77° (9). Although for the isolated molecule in the gas phase the dihedral angle is 111·5° (Hunt, Leacock, Peters & Hecht, 1965), previous studies have shown a wide variation of this angle in solids, from 90° in solid H_2O_2 to 180° in Li- and $Na_2C_2O_4.H_2O_2$. The angle seems to be determined by the hydrogen-bond acceptors (Pedersen, 1969d), and also in this case the observed dihedral angle is insignificantly different from the dihedral angle defined by the acceptor atoms. The intramolecular dimensions determined for H_2O_2 are given in Table 6, which also contains comparable values for solid and gaseous H_2O_2.

Table 5. *Intramolecular bond lengths* (Å) *and angles*(°)

	Distance				Angle	
	Uncorrected	Corrected			Uncorrected	Corrected
C–C	1·563 (2)	1·565 (2)	C——C–O(1)		116·43 (11)	116·20 (11)
C–O(1)	1·2469 (13)	1·2584 (13)	C——C–O(2)		117·27 (11)	117·05 (11)
C–O(2)	1·2497 (13)	1·2610 (13)	O(1)–C–O(2)		126·30 (10)	126·77 (10)

Angle of twist of oxalate ion: 28·15 (9)°

N–H(1)	0·93 (3)	H(1)–N–H(2)	107·8 (2·0)	
N–H(2)	0·88 (2)	H(2)–N–H(4)	95·9 (1·8)	
N–H(3)	0·96 (3)	H(4)–N–H(3)	109·5 (1·9)	
N–H(4)	0·94 (2)	H(3)–N–H(1)	110·1 (2·0)	
		H(1)–N–H(4)	114·7 (2·7)	
		H(2)–N–H(3)	118·4 (2·3)	

Table 6. *Intramolecular parameters in* (Å) *and* (°) *for the* H_2O_2 *molecule*

	r(O–O)	r(O–H)	O–O–H	O–O–O	ϕ	ϕ acceptor
This comp.	1·452 (2)	0·83 (2)	99·0 (1·4)	106·74 (9)	120·9 (3·1)	127·77 (9)
H_2O_2 (solid)*	1·453 (7)	0·988 (5)	102·7 (3)	94·8 (2)	90·2 (6)	93·4 (3)
H_2O_2 (gas)†	1·475 (4)	0·950 (5)	94·8 (20)		111·5 (5)	

* Busing & Levy (1965).
† Redington, Olson & Cross (1962); Hunt, Leacock, Peters & Hecht (1965).

It should be pointed out, however, that there still exist some uncertainties in the gas phase values.

From Table 6 we see that the intramolecular parameters $r(O-O)$, $r(O-H)$, and O–O–H are about the same for the molecule in the two solids, but there seems to be a shortening of $r(O-O)$ compared with the gas phase value. This point has been discussed in detail in a separate paper (Pedersen, 1972).

This structure reveals another example of the ability of the hydrogen peroxide molecule to be able to adjust the dihedral angle to conform to the immediate surroundings. Theoretical calculations of the dihedral angle in this compound, based on a point charge model of the structure gives a dihedral angle of 138° at the energy minimum (Pedersen, 1969a, 1969d).

The ammonium ion conformation is as expected, the nitrogen atom being tetrahedrally surrounded by four hydrogen atoms at distances of 0·88–0·96 (2) Å and with angles of values, 95·9–118·4 (2·0)°, which are almost tetrahedral. The distances and angles are given in Table 5.

(b) Hydrogen bonding

The packing of the molecules and ions, described in detail above, is governed by hydrogen bond formation. Fig. 2 shows the packing in ammonium–oxalate monoperhydrate viewed along c. The bond lengths are given in Table 7. There can be no doubt that it is the strong hydrogen bonding that is responsible for the twisted configuration of the oxalate ion and very favourable conditions for the formation of hydrogen bonds exist.

bond, and approximately in the plane of the $C-C-O_2$ group.

The hydrogen peroxide molecule is hydrogen bonded both to the oxalate ion, $O-H \cdots O = 2·625$ (1) Å and to the ammonium ion $N-H \cdots O = 2·868$ (1) Å. The hydrogen peroxide molecules and the oxalate ions are tied together in infinite zigzag chains parallel to a and spaced $b/2$ apart. These chains are interconnected by ammonium ions situated between them, being bonded to three different oxalate ions and one hydrogen peroxide molecule, forming an intricate three-dimensional network.

The coordination around the hydrogen peroxide oxygen atom is somewhat different from earlier observations, where it normally has a tetrahedral coordination. There are two nearest oxygen neighbours, the oxalate oxygen which is the acceptor of the hydrogen bond, and the other oxygen atom within the molecule. However, the two lone pairs which normally coordinate to cations in the structure must be somewhat differently arranged here. The O(3) oxygen is situated between two nitrogen atoms, $O(3)-N = 2·868$ (1) and 3·035 (2) Å. However, both the difference Fourier map and the least-squares refinements give as a result that H(3) is situated close to the shortest interatomic distance, 2·868 (1) Å. This means that there is a definite hydrogen bond $N-H(3)-O(3)$, with $H(3)-O(3) = 1·94$ Å and $N-H(3)-O(3) = 162·1$ (2·0)°.

The other $O(3) \cdots N$ distance of 3·035 Å, (Table 8) but with no intermediate hydrogen atom, is longer than

Table 7. Hydrogen bond lengths (Å) and angles (°)

H(5)–O(1)	1·81 (2)	O(3)–H(5)–O(1)	167·7 (2·1)
H(4)–O(2)	1·96 (2)	N——H(4)–O(2)	165·6 (2·4)
H(2)–O(1)	1·99 (2)	N——H(2)–O(1)	162·7 (2·0)
H(3)–O(3)	1·94 (2)	N——H(3)–O(3)	162·1 (2·0)
H(1)–O(2)	1·95 (3)	N——H(1)–O(2)	166·8 (3·0)

Donor-acceptor bond lengths (Å) and angles (°).*

O(3)–O(1)	2·625 (1)	O(2)–N–O(1)	115·54 (5)
N——O(2)	2·874 (1)	O(1)–N–O(2)	96·12 (4)
N——O(1)	2·842 (1)	O(2)–N–O(3)	106·95 (5)
N——O(3)	2·868 (1)	O(3)–N–O(2)	118·54 (5)
N——O(2)	2·863 (1)	O(2)–N–O(2)	115·17 (5)
N——O_w	3·00 (2)	O(1)–N–O(3)	101·47 (6)
O(1)–O_w	3·12 (2)		

* The angles are given in the same order as the H–N–H angles of Table 5.

Around the ammonium group there are eight oxygen atoms very roughly forming a cube. Four of these, in tetrahedral orientation, are at an average distance of 2·862 Å, while the other four are at about 3·21 Å. This situation implies the existence of definite hydrogen bonds, which are also supported by the hydrogen atom peaks in the difference map, Fig. 1. The distribution of hydrogen bonds around the oxalate ion is shown in Fig. 2. Each carboxyl oxygen receives two hydrogen bonds at approximately 120° to the C–O

(a)

(b)
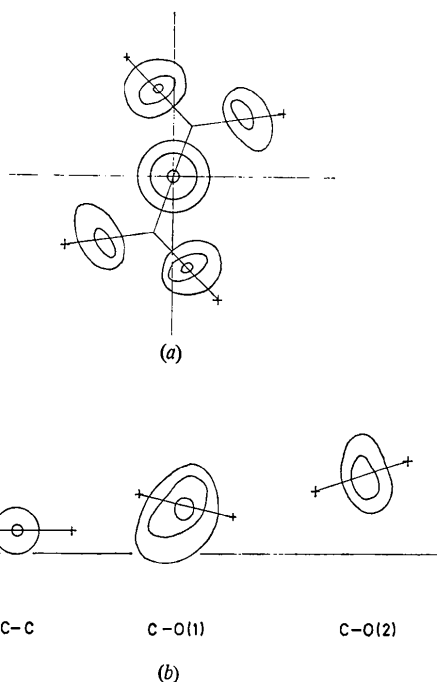
Fig. 3. Residual electron density in the bonds of the oxalate ion, contours are 0·2, 0·3, 0·4 e.Å⁻³. (a) is a section in the planes of the $C-C-O_2$ groups. (b) shows orthogonal sections through the three different bonds of the exalate ion.

the van der Waals distance between oxygen and nitrogen, 2·9 Å, and cannot be regarded as a close contact. We must therefore conclude that the O(3) atom in this structure has threefold coordination, contrary to the tetrahedral arrangement normally found.

Table 8. Non-bonded interatomic distances

N–O(1')	3·103 (1)
N–O(2')	3·283 (1)
N–O(3')	3·035 (2)
N–O(2'')	3·405 (1)

The hydrogen bonds are not linear, the deviation from linearity being smallest for the bond formed by H(5) and largest for the bond formed by H(3). The N–H$\cdots$O angles range from 162·1–166·8 (2·3)°, and the O–H$\cdots$O angle is 167·7 (2·1)°.

As pointed out previously, the ammonium oxalate monoperhydrate phase seems to tolerate the interchange of some of the H_2O_2 molecules with water molecules. These water molecules will fit rather nicely into the structure having tetrahedral coordination. The water molecule can donate two hydrogen bonds to oxalate oxygens 3·12 (2) Å away and accept two hydrogen bonds from ammonium ions 3·00 (2) Å away. These hydrogen-bond distances are of course somewhat longer than the corresponding distances in the monohydrate, 2·743 and 2·879 Å, but are still possible hydrogen bonding contacts.

The observation of water molecules in the lattice of a perhydrate may also have an impact on similar compounds and may be one source for an apparent shortening of the O–O bond in perhydrates. This

(a)

(b)

Fig. 4. Section of difference Fourier map (a) along and (b) orthogonal to the twofold axis of the H_2O_2 molecule. The heavier traced peaks are the oxygen atoms taken from the Fourier map.

question, however, is discussed in more detail in a separate paper (Pedersen, 1971).

(c) Residual electron density

Fig. 3 shows two sections of the final difference map of the compound. (a) is a section in the planes of the C–C–O_2-groups and (b) shows orthogonal sections through the three different bonds of the oxalate ion. The only peaks above a general background of ± 0·1 e.Å^{-3} are hydrogen atom peaks, the water oxygen atom and residual electron density in the bonds of the oxalate ion. Residual electron density has been observed in several accurately determined crystal structures (Beagley & Small, 1963, 1964; O'Connell, Rae & Maslen, 1966; Hodgson & Ibers, 1969) and is attributed to bonding electrons. The residual electron density in the bonds of the oxalate ion is centred on the bonds and the observed electron densities are: ϱ[C–C]=0·3, ϱ[C–O(1)]=0·4, ϱC–O(2)]=0·3 e.Å^{-3}. The standard deviation $\sigma(\varrho)$ is calculated to be 0·05 e.Å^{-3}, and hence the electron density peaks in the bonds are significantly above background.

Peaks attributable to the bonding electrons in the ammonium ion are not well enough resolved from the hydrogen atom peaks to be clearly visualized.

Sections along and orthogonal to the twofold axis of the H_2O_2 molecule are shown in Fig. 4. In contrast to the residual electron density peaks in the oxalate bonds this peak is definitly not centred on the O–O bond. A peak of electron density ϱ=0·5 e.A^{-3} is centred at z=0·20, at a distance of 0·25 Å from the bond, and on the opposite side of the hydrogen atoms of the molecule. The peak is not symmetrical and may be a combination of two peaks, one caused by residual electron density in the bond and another which is believed to represent a fraction of a water oxygen atom and which is not centred on the bond. The z coordinate for the water oxygen atom obtained from the least-squares refinement is 0·26 (1). As both the water molecule and the hydrogen peroxide molecule are supposed to be hydrogen bonded to the same acceptor and donor atoms the z parameter values of the two oxygen atoms must be different, otherwise the acceptor angle of the water molecule will be 135°. The z parameter value determined for the water oxygen atom, z=0·26 (1), gives an acceptor angle of 120°, and O–H$\cdots$O and N–H$\cdots$O hydrogen bonds of 3·12 Å and 3·00 Å. A z parameter value of 0·344 would be needed to get an acceptor angle of 109·5°, but in this case the O–H$\cdots$O and N–H$\cdots$O distances would be 3·31 and 2·87 Å, and the O–H$\cdots$O interaction would be extremely weak.

(d) The water content of $(NH_4)_2C_2O_4 . H_2O_2$

The fraction of water molecules in the specific crystal investigated in detail is determined to be 6·4 (4) %. The water molecules are not found to be ordered regularly in the structure. Several batches of crystals were made and their unit-cell dimensions determined to see if a
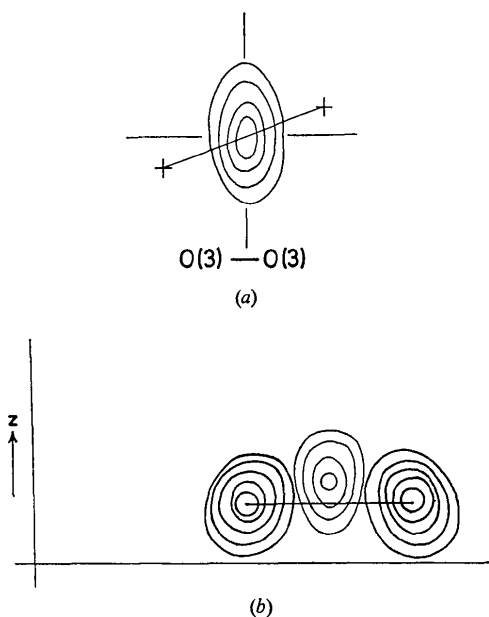
possible difference could be detected in this way. However, the results revealed no difference in unit-cell dimensions. Unit-cell constants measured with a diffractometer for a crystal decomposing within 10 hours were not significantly different from those given here. The preliminary film intensity data, however, indicated a larger fraction of water molecules than does the present investigation. This may still be correct, since it may be the size of the hydrogen peroxide molecule that determines the lattice dimensions, and the structure may contain water molecules up to a certain limit before collapsing. The water molecules will of course be looser bonded in this crystal than in the hydrate, but can still fit into the hydrogen peroxide positions and have normal coordination.

(e) Decomposition of $(NH_4)_2C_2O_4(H_2O_2)_{0.88}(H_2O)_{0.06}$

The crystal that was used for data collection on the diffractometer was stored in a Lindemann glass capillary for seven months. The crystal was then mounted in a Weissenberg camera and both oscillation and Weissenberg diagrams were recorded. The crystal was originally transparent and colourless, but had become white and opaque, showing signs of decomposition. The films showed powder lines which could be identified as the hydrate (ASTM card No. 14–801) and single-crystal reflexions. These reflexions, however, were not perhydrate reflexions. By comparing the Weissenberg film with corresponding films for the perhydrate and the hydrate, the intensity distribution on the films was found to resemble the hydrate film intensities. This conclusion was based on the intensity difference for several reflexions which were known to be very weak or absent in one phase, and medium to strong in the other. The measured lattice dimensions for the crystal were:

$a = 8.03$, $b = 10.31$, $c = 3.82$ Å, compared to:

Perhydrate: $a = 8.53$, $b = 10.48$, $c = 3.82$ Å

Hydrate: $a = 8.03$, $b = 10.31$, $c = 3.81$ Å.

The reflexions were somewhat elongated and blurred making accurate measurements impossible.

In addition, $hk0$ Weissenberg data were recorded for one particular crystal, twice a day over a period of two months. After six days the reflexions with the largest $\sin \theta/\lambda$ values became increasingly deformed especially those with high h indices, as the a axis shows the largest difference in the two compounds. One set of reflexions became weaker whereas the intensity of the other set increased. Apparently when the perhydrate single crystal decomposes, a hydrate single crystal is the end product. It is not a single crystal of superior quality, but it is, remarkably enough, a single crystal.

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