The Crystal Structure of Hydrogen Peroxide Dihydrate *

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The crystal structure of hydrogen peroxide dihydrate, $H_2O_2 \cdot 2H_2O$, has been determined from single crystal X-ray data. Exposures at $-70°$ and $-190°C$ indicate the same structure. The crystals are monoclinic (space group $C2/c$) with four molecules in a unit cell of dimensions: $a = 9.400$, $b = 9.479$, $c = 4.51$ Å and $\beta = 121.33°$ at $-190°C$. The structure contains planar chains of water molecules connected by hydrogen bonds of 2.74 Å. The chains are crosslinked by the hydrogen peroxide molecules into a three-dimensional network by hydrogen bonds of 2.76 and 2.69 Å. Peaks in a difference synthesis suggest the positions of the hydrogen atoms in these bonds, and indicate slight displacements from the lines joining the oxygen atoms. These positions correspond to a dihedral angle of about 130°, in the hydrogen peroxide molecule, between the planes defined by the peroxide link and the hydrogen atoms.

T^he melting point diagram of the system hydrogen peroxide-water indicates only one intermediary compound, $H_2O_2 \cdot 2H_2O$. The existence of a crystalline phase of this composition has also been confirmed by X-ray powder diffraction data (Natta and Rigamonti [1]). They concluded that the lattice had a low symmetry but were unable to index the photographs. The melting point of the dihydrate has been reported as: —51°C (Maass and Herzberg [2]), —52.10° (Foley and Giguère [3]), —50.2° (Mironov [4]). These investigations also indicate that solid solutions are absent.

The present work involves the determination of the crystal structure of $H_2O_2 \cdot 2H_2O$ from single crystal X-ray diffraction data obtained at —190°C. X-ray photographs taken at —70°C indicate the same structure.

EXPERIMENTAL

The crystals were grown from solutions of hydrogen peroxide and water sealed in glass capillaries (diameter 0.1—0.2 mm. and wall thickness 0.01—0.02 mm.). The hydrogen peroxide (Becco's hydrogen peroxide of 90 %) was distilled in a vacuum system

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and the middle fraction taken out and mixed with distilled water to the desired composition. The analysis was made by titration with permanganate. The sample used had a composition of 48.8 wt. % H_2O_2, corresponding to 1.98 moles per mole of hydrogen peroxide.

The single crystals were grown in the ordinary way in a modified Weissenberg camera (Olovsson and Templeton [5]). As the crystal was grown it was apparent that the melting point was in reasonable agreement with the earlier-published data cited above. It was very difficult to get crystals that were not twinned. The crystal chosen was composed of two twins related by reflexion in the bc plane or rotation about c, but it was quite easy to get each reflection uniquely indexed. Equi-inclination Weissenberg photographs, layers 0 to 3, were taken with rotation around the c axis using Cu-K radiation. The results below refer to the data from $-190°C$ but the photographs from $-70°C$ indicate the same structure. The relative intensities were estimated visually by using multiple-film technique (four films) and comparing with an intensity scale. The data were corrected for the Lorentz and polarization effects.

UNIT CELL AND SPACE GROUP

The data showed the diffraction symmetry $2/m$. The systematic absences require an I-centered monoclinic cell with almost orthogonal axes ($a' = 8.038$ Å, $b' = 9.479$ Å, $c' = 4.51$ Å, $\beta' = 92.70°$) or a C-centered cell with $\beta \sim 120°$. The C-centered cell was chosen in order to be in agreement with the International Tables [6]. The unit cell parameters are then*:

$a = 9.400 \pm 0.002$ Å, $b = 9.479 \pm 0.002$ Å,

$c = 4.51 \pm 0.01$ Å, $\beta = 121.33° \pm 0.03°$. ($t = -190°C$)

a, b and c were determined from rotation and quartz-calibrated zero-layer Weissenberg photographs ($a = 4.913$ Å for α-quartz; $\lambda_{\text{Cu-}K\alpha_1} = 1.54051$ Å, $\lambda_{\text{Cu-}K\alpha_2} = 1.54433$ Å), β was obtained by the method of angular lag [7].

Giguère, Knop and Falk [8] report a preliminary value of 1.20 for the density at the melting point. With four molecules per unit cell, the calculated density at $-190°C$ is 1.36. Systematic absences were, in addition to the extinctions due to the C-centering: ($h0l$) for l odd. These data suggest the space groups Cc or $C2/c$, assuming that the absences are space group extinctions. As shown below, the structure is well described in $C2/c$ (C_{2h}^6) with the atoms in the general 8-fold positions: $(0,0,0$ and $\frac{1}{2},\frac{1}{2},0) + (x,y,z); (\overline{x},\overline{y},\overline{z}); (\overline{x},y,\frac{1}{2}-z); (x,\overline{y},\frac{1}{2}+z).$

DETERMINATION OF THE ATOMIC COORDINATES

A comparison of the unit cell dimensions for ice ($a = 4.51$ Å, $c = 7.34$ Å; Megaw [9]), ammonia monohydrate ($a = 4.51$ Å, $b = 5.587$ Å, $c = 9.700$ Å; Olovsson and Templeton [5]), and hydrogen peroxide dihydrate ($a = 9.400$ Å, $b = 9.479$ Å, $c = 4.51$ Å) shows that they all have one axis in common, 4.51 Å. In the first two compounds this corresponds to the unit length of a planar zig-zag chain of tetrahedrally hydrogen bonded water molecules (distance O—H————O = 2.76 Å). This immediately suggests that the present structure also contains such chains, oriented along the c axis. The atoms in the chain then must be related to each other by the c glide, and the y coordinate

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* A different choice of C-centered cell, gives $a = 9.030$ Å and $\beta = 117.23°$.

of a water oxygen can be estimated to 0.084. The subsequent interpretation of the three-dimensional Patterson maps was based on the four-fold positions in space group Cc. In the structure obtained, the oxygen atoms in a H_2O_2 molecule were not symmetry-related to each other and the same refers to the oxygen atoms in the two water molecules. The coordinates of this structure were subjected to about 6 cycles of Fourier and least-squares refinement. After suitable choice of the origin (the x and z coordinates for one atom are arbitrary), these partly refined oxygen coordinates were for H_2O_2: O (1), $(-0.009, 0.184, 0.089)$; O (2), $(0.008, -0.181, -0.061)$ and for H_2O: O (3), $(0.299, 0.084, 0.271)$; O (4), $(-0.298, -0.081, -0.299)$. If the space group were $C2/c$, the atoms O (1) and O (2) as well as O (3) and O (4) would be related by the centre of symmetry at $(0,0,0)$, and this is obviously very nearly the case here. The centrosymmetric space group $C2/c$ was therefore chosen for the further work, which means only two independent oxygen atoms per asymmetric unit. In this structure, according to the interpretation given below, the dihedral angle H-O-O-H of the hydrogen peroxide molecule is about 130°. This seemed somewhat disturbing and other structural solutions were then looked for. However, in a systematic study of the Patterson maps, using both Cc and $C2/c$, no other structure could be found than the one already obtained.

The coordinates and isotropic temperature factors for oxygen and an over-all scale factor were refined by least-squares methods on the IBM 650 computer (the interlayer scale factor was then based on the relative exposure time). R_3 (see below) was the quantity actually minimized. The weighting factor w in this expression and some other details of the program are described elsewhere (Olovsson and Templeton [5]). For reflections too weak to be observed, the quantity $F_o - F_c$ was set equal to zero in the sums when $F_c < F_{min}$ and equal to $F_{min} - F_c$ when $F_c > F_{min}$. In the »LS II» program, modified for the space group $C2/c$, the only crossterms used were those between the x and z coordinates of the same atom. The scattering factors used for oxygen (uncharged) are those published by Berghuis et al.[10] The shifts in the coordinates in the final cycles were less than 0.0001. The results, together with the standard deviations, after about 20 cycles of refinements are given in Table 1. The »unreliability factors» at this point were:

$$R_1 = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right| = 0.091$$
$$R_2 = [\Sigma (\left| F_o \right| - \left| F_c \right|)^2 / \Sigma \left| F_o \right|^2]^{\frac{1}{2}} = 0.086$$
$$R_3 = \Sigma [w(\left| F_o \right| - \left| F_c \right|)^2 / \Sigma w \left| F_o \right|^2]^{\frac{1}{2}} = 0.092$$

The observed and calculated structure factors are compared in Table 2. Hydrogen atoms are omitted from these calculations.

Table 1. Atomic parameters and standard deviations.

Oxygen (O$_I$) in H$_2$O$_2$	Oxygen (O$_1$) in H$_2$O
$x = -0.0075 \pm 0.0003$	$x = 0.2980 \pm 0.0003$
$y = 0.1809 \pm 0.0003$	$y = 0.0822 \pm 0.0003$
$z = 0.0785 \pm 0.0009$	$z = 0.2850 \pm 0.0008$
$B = 2.38$ Å^2	$B = 2.08$ Å^2

Table 2. Observed and calculated structure factors

h	k	$|F_o|$	$|F_c|$	h	k	$|F_o|$	$|F_c|$	h	k	$|F_o|$	$|F_c|$	h	k	$|F_o|$	$|F_c|$
l = 0				l = 1								5	1	11	12
2	0	6	9	− 9	1	6	4	4	6	3	2	7	1	<2	1
4	0	42	45	− 7	1	19	20	6	6	3	1	−10	2	6	5
6	0	22	22	− 5	1	3	3	− 9	7	7	6	− 8	2	2	1
8	0	<3	1	− 3	1	40	39	− 7	7	4	2	− 6	2	3	2
10	0	11	12	− 1	1	23	23	− 5	7	13	14	− 4	2	20	19
1	1	8	10	1	1	6	6	− 3	7	5	5	− 2	2	4	7
3	1	49	47	3	1	22	22	− 1	7	9	10	0	2	27	24
5	1	15	12	5	1	5	5	1	7	11	11	2	2	3	3
7	1	16	16	7	1	5	5	3	7	<2	1	4	2	5	5
9	1	<1	<1	−10	2	11	11	5	7	7	6	6	2	7	6
0	2	6	7	− 8	2	2	<1	7	7	1	1	−11	3	<1	<1
2	2	50	50	− 6	2	13	12	− 8	8	6	5	− 9	3	<3	1
4	2	14	14	− 4	2	30	34	− 6	8	4	2	− 7	3	4	4
6	2	8	9	− 2	2	21	18	− 4	8	5	3	− 5	3	8	7
8	2	12	10	0	2	56	56	− 2	8	13	14	− 3	3	12	13
10	2	<1	<1	2	2	10	10	0	8	9	10	− 1	3	14	14
1	3	44	45	4	2	6	7	2	8	9	8	1	3	14	12
3	3	30	32	6	2	6	7	4	8	1	<1	3	3	11	10
5	3	20	20	8	2	6	5	6	8	4	2	5	3	8	6
7	3	9	10	− 9	3	8	8	− 7	9	10	10	7	3	4	4
9	3	6	6	− 7	3	12	12	− 5	9	6	5	−10	4	4	3
0	4	25	25	− 5	3	27	29	− 3	9	10	11	− 8	4	3	3
2	4	9	8	− 3	3	18	18	− 1	9	5	3	− 6	4	2	3
4	4	6	8	− 1	3	9	9	1	9	3	2	− 4	4	7	7
6	4	3	4	1	3	22	22	3	9	11	10	− 2	4	15	14
8	4	3	2	3	3	21	20	5	9	5	6	0	4	9	8
1	5	30	33	5	3	16	16	− 6	10	4	4	2	4	6	6
3	5	4	3	7	3	6	6	− 4	10	9	9	4	4	3	2
5	5	25	27	−10	4	<1	<1	− 2	10	<3	3	6	4	<2	1
7	5	<1	<1	− 8	4	16	14	0	10	12	12	− 9	5	6	5
9	5	7	7	− 6	4	11	12	2	10	2	2	− 7	5	16	14
0	6	4	4	− 4	4	3	3	4	10	2	3	− 5	5	8	9
2	6	37	37	− 2	4	41	47	− 3	11	3	3	− 3	5	14	16
4	6	7	8	0	4	13	14	− 1	11	<1	<1	− 1	5	10	11
6	6	7	6	2	4	28	26	1	11	3	2	1	5	4	2
8	6	12	11	4	4	3	3	l = 2				3	5	19	17
1	7	3	3	6	4	5	2	−10	0	9	7	5	5	2	2
3	7	14	13	8	4	6	6	− 8	0	8	9	−10	6	5	6
5	7	10	10	− 9	5	7	6	− 6	0	10	12	− 8	6	4	2
7	7	9	7	− 7	5	3	2	− 4	0	11	11	− 6	6	<2	<1
0	8	22	23	− 5	5	17	17	− 2	0	—	—	− 4	6	17	18
2	8	6	6	− 3	5	<1	<1	0	0	12	12	− 2	6	10	11
4	8	14	12	− 1	5	9	9	2	0	22	25	0	6	21	22
6	8	10	8	1	5	12	13	4	0	9	10	2	6	<1	<1
1	9	8	8	3	5	7	6	6	0	<2	<1	4	6	5	4
3	9	8	7	5	5	9	8	−11	1	<2	2	− 9	7	7	5
5	9	5	5	7	5	4	2	− 9	1	8	9	− 7	7	9	9
0	10	10	8	− 8	6	3	3	− 7	1	15	15	− 5	7	11	11
2	10	<1	<1	− 6	6	5	5	− 5	1	26	26	− 3	7	5	5
4	10	6	4	− 4	6	7	6	− 3	1	8	8	− 1	7	<2	1
1	11	6	5	− 2	6	6	5	− 1	1	5	3	1	7	9	8
3	11	12	11	0	6	6	6	1	1	22	23	3	7	9	8
0	12	7	9	2	6	3	3	3	1	10	10	5	7	5	6

Table. 2 (cont.)

h	k	$|F_o|$	$|F_c|$	h	k	$|F_o|$	$|F_c|$	h	k	$|F_o|$	$|F_c|$	h	k	$|F_o|$	$|F_c|$
− 8	8	3	3	− 9	1	15	14	1	3	9	8	− 2	6	6	7
− 6	8	4	4	− 7	1	6	6	3	3	11	12	0	6	6	5
− 4	8	<2	<1	− 5	1	26	26	5	3	2	4	2	6	5	4
− 2	8	13	12	− 3	1	17	17	−10	4	12	12	− 9	7	3	3
0	8	<1	<1	− 1	1	13	14	− 8	4	9	8	− 7	7	14	12
2	8	8	8	1	1	18	19	− 6	4	8	8	− 5	7	6	6
4	8	5	4	3	1	4	3	− 4	4	28	30	− 3	7	12	12
− 7	9	<2	<1	5	1	6	8	− 2	4	3	1	− 1	7	12	11
− 5	9	2	2	−10	2	<1	<1	0	4	22	23	1	7	5	4
− 3	9	3	3	− 8	2	10	11	2	4	8	7	3	7	7	8
− 1	9	4	3	− 6	2	19	19	4	4	4	4	− 8	8	<2	1
1	9	5	4	− 4	2	<1	<1	− 9	5	<1	<1	− 6	8	<1	<1
3	9	4	3	− 2	2	35	33	− 7	5	12	12	− 4	8	10	10
− 6	10	2	1	0	2	1	<1	− 5	5	3	2	− 2	8	6	5
− 4	10	2	2	2	2	9	12	− 3	5	9	10	0	8	8	8
− 2	10	6	5	4	2	7	8	− 1	5	10	10	2	8	<1	<1
0	10	4	2	−11	3	5	5	1	5	<2	1	− 7	9	3	3
2	10	3	3	− 9	3	7	7	3	5	9	8	− 5	9	10	11
− 1	11	2	2	− 7	3	18	18	−10	6	3	3	− 3	9	4	3
				− 5	3	8	9	− 8	6	6	4	− 1	9	2	2
	$l = 3$			− 3	3	9	10	− 6	6	7	6	− 4	10	<1	<1
−11	1	4	4	− 1	3	11	11	− 4	6	7	6	− 2	10	9	11

DISCUSSION OF THE STRUCTURE AND HYDROGEN POSITIONS

The structure is shown in Fig. 1. The bond distances and angles with their standard deviations are given in Table 3 and Fig. 2. The correlations between symmetry-related atoms and the uncertainty of the unit cell dimensions were considered in the calculations of these standard deviations.

The water molecules are hydrogen-bonded to each other into planar chains oriented along the c axis and in the planes $x = 0.20$, 0.30, 0.70 or 0.80, respectively. The chains are cross-linked by the hydrogen peroxide molecules into a three-dimensional network. It appears that the hydrogen peroxide molecules are not bonded to each other; the two-fold axis passes through the centre of the O-O bond. The oxygen-oxygen distance in the water chain (2.741 Å with a standard deviation $\sigma = 0.005$ Å) is slightly different from the corresponding distances in ammonia monohydrate (2.759 Å, $\sigma = 0.005$ Å; Olovsson and Templeton [5]) and ice (2.755 Å, $\sigma = 0.008$ Å; Tables of interatomic distances [11]). One of the oxygen-oxygen distances between water and hydrogen peroxide is 2.761 Å ($\sigma = 0.004$ Å), while the other is significantly shorter, 2.685 Å ($\sigma = 0.004$ Å). When refining the structure, the atomic coordinates were repeatedly changed by hand in trials to make both of these distances equal, but the subsequent least-squares treatment invariably shifted them back again. The O-O distance in hydrogen peroxide, 1.481 Å ($\sigma = 0.009$ Å), is in agreement with the value 1.48 ± 0.01 Å given in Tables of interatomic distances [11].

The bond angle in the water chain is close to the tetrahedral value but the deviations of other angles from their normal values when these water chains and the hydrogen peroxide molecules are linked together (Fig. 2)
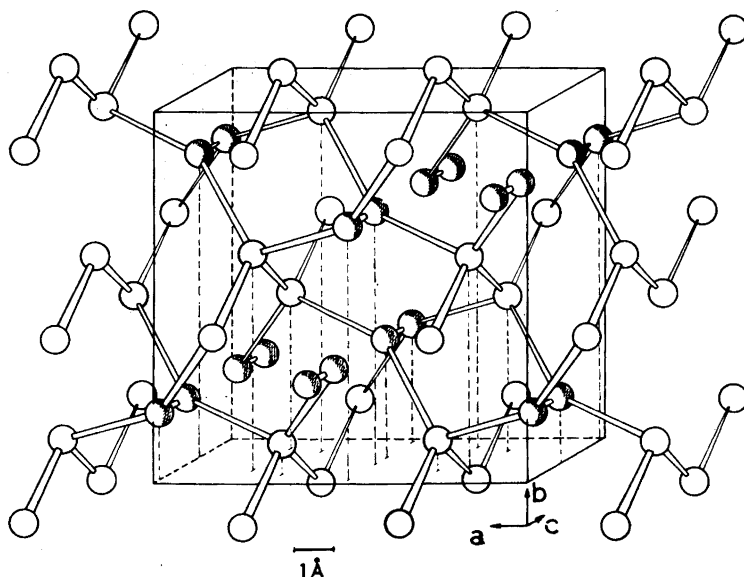
Fig. 1. The crystal structure of hydrogen peroxide dihydrate. The peroxide groups are shaded.

indicate some strain in the structure. The low melting point is another indi-
cation of low stability. The following arguments about the locations of the
hydrogen atoms are similar to those presented in the case of ammonia mono-
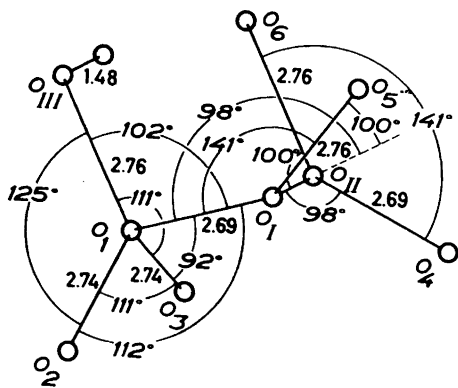hydrate (Olovsson and Templeton [5]). One of the hydrogen atoms in water

Fig. 2. Bond distances and angles to the neighbors of a water molecule and a hydrogen peroxide molecule (the orientation is the same as in Fig. 1.).
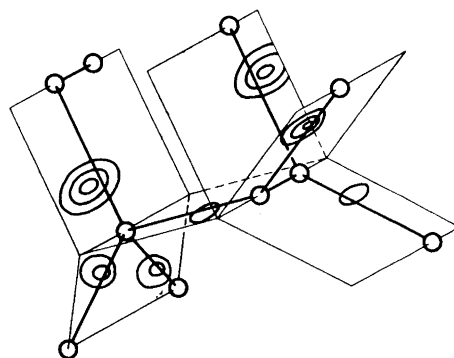
Fig. 3. Schematic representation of the difference synthesis in various sections. The contours are drawn at 0.70, 0.85 and 1.00 e · Å⁻³. The atoms are the same as in Fig. 2.

Table 3. Bond distances and angles with their standard deviations (*cf.* Fig. 2).

Around O_I:		Around O_1:	
Bond	Distance (Å)	Bond	Distance (Å)
$O_I - O_{II}$	1.481 ± 0.009	$O_1 - O_2$	2.741 ± 0.005
$O_1 - O_1$	2.685 ± 0.004	$O_1 - O_3$	2.741 ± 0.005
$O_I - O_5$	2.761 ± 0.004	$O_1 - O_I$	2.685 ± 0.004
		$O_1 - O_{III}$	2.761 ± 0.004

Bonds	Angle (deg.)	Bonds	Angle (deg.)
$O_{II} - O_1 - O_1$	97.7 ± 0.2	$O_I - O_1 - O_2$	111.7 ± 0.1
$O_{II} - O_1 - O_5$	100.4 ± 0.2	$O_I - O_1 - O_3$	91.5 ± 0.1
$O_1 - O_I - O_5$	140.5 ± 0.2	$O_I - O_1 - O_{III}$	101.8 ± 0.1
		$O_2 - O_1 - O_3$	110.7 ± 0.2
		$O_2 - O_1 - O_{III}$	125.0 ± 0.2
		$O_3 - O_1 - O_{III}$	110.6 ± 0.2

is obviously involved in the hydrogen bonds of the water chain. The question is then to which one of the two oxygen atoms the hydrogen atom should be pointed. The two directions are not equivalent when regard is paid to the distribution of the other nearest neighbors (in contrast to the situation in ammonia monohydrate). But it is not entirely obvious from a structural point of view which orientation should be preferred. The three-dimensional $F_o - F_c$ synthesis (based on the oxygen coordinates only) seemed to give a definitive answer, as a well resolved »hydrogen peak» appeared in one direction but not in the other. The difference synthesis * is shown schematically in Fig. 3, where all the other hydrogen atoms also seem to be visible. All »hydrogen peaks» in the difference maps are close to the lines connecting the heavier atoms; the approximate coordinates are (0.305, 0.040, 0.105) and (0.385, 0.155, 0.345) for the »hydrogen atoms» bonded to O_1 and (0.105, 0.135, 0.120) for the »hydrogen atom» bonded to O_I. These peaks correspond to O-H
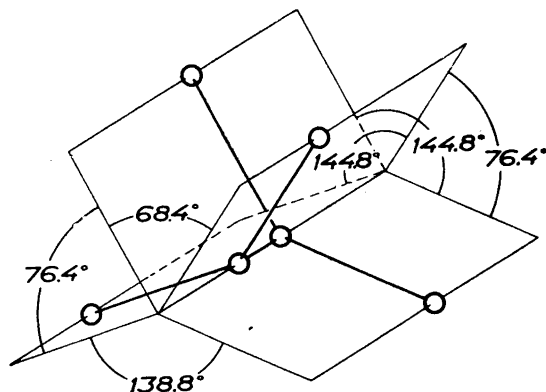

Fig. 4. Dihedral angles with the peroxide group and the nearest oxygen neighbors.

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* The Fourier calculations were made on the IBM 701 computer at University of California Computer Center.

bond distances of about 1.0 Å, as expected. The apparent deviations from the connecting lines are such that they make the angles H-O-H in water and O-O-H in hydrogen peroxide closer to the values in the pure compounds ($\wedge$ O-O-H is according to a neutron diffraction investigation by Busing and Levy [12] close to 102°). The dihedral angles between planes defined by the peroxide group and the nearest oxygen neighbors are shown in Fig. 4. If the two-fold symmetry applies to the hydrogen atoms there are obviously only two values possible for the dihedral angle H-O-O-H, namely about 139° or 68° (if hydrogen is on the connecting lines) and the former was definitely indicated by the difference synthesis. The same dihedral angle is about 10° less with the experimental hydrogen positions. The same angle in solid hydrogen peroxide itself is about 90° (Busing and Levy [12]). For the urea-hydrogen peroxide addition compound $CO(NH_2)_2 \cdot H_2O_2$ Lu, Hughes and Giguère [13] report this angle to be 106° (assuming that the hydrogen atoms are on the connecting lines). Spectroscopic evidence indicates that the restoring force for twisting about the O-O bond is rather small (Giguère and Harvey [14]). And infra-red investigation of the crystalline dihydrate at low temperature actually indicates that the peroxide molecule is somewhat distorted in this compound [8].

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