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Hydrogen Bond Studies. X. The Crystal Structure of Ammonium Hydrogenperoxide

BY JÖRGEN TEGENFELDT AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

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The crystal structure of NH_4OOH has been determined from three-dimensional single-crystal X-ray data, recorded at -36 and -170°C . The data indicate that the same structure occurs at both temperatures. The structure belongs to the space group $P2_1/c$ and has four molecules in each unit cell. The unit-cell dimensions at -160°C are: $a = 6.580$, $b = 6.767$, $c = 6.143$ Å; $\beta = 121.73^\circ$. The assignment of the hydrogen atoms to the bonds indicates clearly that the structure contains ammonium ions and hydrogenperoxide ions and the compound in the solid state should accordingly be written as NH_4OOH . The hydrogenperoxide ions are linked by short hydrogen bonds (2.54 Å) to form parallel infinite chains. The ammonium ions form links between these chains (hydrogen bonds of length 2.72 and 2.85 Å) giving a three-dimensional network.

Introduction

The melting point diagram for the system $\text{NH}_3\text{-H}_2\text{O}_2$ has been studied by Maas & Hatcher (1922) and Mironov (1959). The diagram has a very pronounced maximum which corresponds to a compound with the composition $\text{NH}_3 \cdot \text{H}_2\text{O}_2$, melting at 24.5°C . According to Mironov there is also a compound with the composition $2\text{NH}_3 \cdot \text{H}_2\text{O}_2$.

From the Raman spectrum (Simon & Kriegsmann, 1955) and the infrared spectrum (Knop & Giguère, 1959) of the crystalline 1:1 compound it has been concluded that the solid contains ammonium and hydrogenperoxide ions. In the liquid state, however, the

Raman spectra recorded by Simon & Marchand (1950) and Simon & Uhlig (1952) gave no indication that such ions exist to a measurable extent.

The present account concerns an X-ray investigation of the crystalline compound $\text{NH}_3 \cdot \text{H}_2\text{O}_2$.

Experimental

Two series of investigations were undertaken with two different crystals.

In one instance dry ammonia was distilled into a weighed capillary containing a known amount of water-free hydrogen peroxide (see below). The capillary was sealed off and then weighed again to determine the

amount of ammonia. By trial and error a sample was obtained containing ammonia and hydrogen peroxide in the proportion 1.015 ± 0.005 moles of hydrogen peroxide per mole of ammonia. The part of the capillary later exposed to the X-ray beam had a diameter of about 0.2 mm.

In the other case dry ammonia was bubbled into a vessel containing water-free hydrogen peroxide at about 0°C. The liquid was protected from contact with the atmosphere (Maas & Hatcher, 1922). The crystals which separated were partly freed from adhering hydrogen peroxide by suction on a sintered glass filter funnel in an atmosphere of dry nitrogen, and were finally recrystallized from absolute alcohol. The dried crystals were melted and capillaries with an approximate diameter of 0.15 mm were filled with the liquid and sealed in a flame.

In both preparations the ammonia was dried over calcium sulphate (Drierite); in the first preparation it was also purified by distillation under vacuum. The water-free hydrogen peroxide was prepared from 90% hydrogen peroxide by distillation under vacuum to 98% followed by repeated recrystallization of this product until it contained between 99.9 and 100.0% of hydrogen peroxide (Maas & Hatcher, 1922).

Single crystals were grown in a low-temperature camera described earlier (Olovsson, 1960). Equi-inclination Weissenberg photographs were taken at -36°C with both of the above types of capillary, and at -170°C with the second of these types. The crystals were rotated in the first instance about the diagonal $[01\bar{1}]$ (9 layers) and in the second instance about the b axis (7 layers). The radiation used was Cu K , and in the second instance about 90% of the reflexions within the copper reflexion sphere were recorded. The total number of reflexions recorded was 465 of which 116 were too weak to be measured.

The relative intensities were estimated visually by comparison with a calibrated intensity scale, and were corrected for Lorentz and polarization effects. No absorption correction was applied since the linear absorption coefficient is 10.8 cm^{-1} and the diameter of the crystal was 0.15 mm.

The final refinements employed only data from the second crystal taken at -170°C .

No structural differences could be detected on comparison of data for the two crystals recorded at -36°C . Similarly, no structural changes could be detected from diffraction patterns of the second crystal on cooling from -36°C to -170°C .

Unit-cell dimensions and space group

Preliminary values for the cell dimensions and a diffraction symmetry of $2/m$ indicated a monoclinic unit cell. Accurate cell dimensions were obtained from the second crystal at -35 and -162°C . Zero-layer oscillation photographs gave the a and c dimensions and the angle β . The b dimension was obtained from rotation

photographs. Each of these photographs was calibrated with a quartz single crystal at 22°C , and all exposures, including those at the two temperatures, were recorded on the same film without removing the film from the cassette. The dimensions a and c and the angle β were fitted to the measured θ -values, using the method of least squares. The unit-cell dimensions together with their standard deviations are as follows:

$$a = 6.580 \pm 0.001, \quad b = 6.767 \pm 0.009, \quad c = 6.143 \pm 0.002 \text{ \AA} \\ \beta = 121.73 \pm 0.02^\circ \quad (\text{at } -162^\circ\text{C})$$

$$a = 6.583 \pm 0.001, \quad b = 6.763 \pm 0.009, \quad c = 6.147 \pm 0.002 \text{ \AA} \\ \beta = 121.66 \pm 0.02^\circ \quad (\text{at } -35^\circ\text{C})$$

$$(\text{Cu } K\alpha_1 \lambda = 1.54051 \text{ \AA}, \text{ Cu } K\alpha_2 \lambda = 1.54433 \text{ \AA}, \\ \text{Cu } K\beta \lambda = 1.39217 \text{ \AA};$$

$$a = 4.913 \text{ \AA} \text{ and } c = 5.4045 \text{ \AA} \text{ for } \alpha \text{ quartz at } 22^\circ\text{C})$$

With four molecules in the unit cell the calculated density of the solid is 1.457 g.cm^{-3} . An experimental determination of the density has not been made, but the mean value of the densities of solid ammonia and solid hydrogen peroxide gives an estimated density of about 1.2 g.cm^{-3} .

The absence of reflexions $h0l$ for $l=2n+1$ and $0k0$ for $k=2n+1$ (the latter condition detectable only in the data from the first crystal, since the second was rotated about the b axis) indicated uniquely the space group $P2_1/c$, assuming that the diffraction symmetry is correct and that the absences are not accidental.

The structure gave a good agreement with the data when refined in this space group, demonstrating that the space group had been correctly assigned.

The atoms occupy the general positions:

$$(x, y, z), (\bar{x}, \bar{y}, \bar{z}), (x, \frac{1}{2} - y, \frac{1}{2} + z), (\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z) .$$

Determination of the atomic coordinates

The structure was determined from three-dimensional Patterson maps. The orientations of the hydrogen peroxide molecules were deduced from the short 1.5 Å oxygen–oxygen vectors, and their positions in the unit cell were derived from the Harker vectors. When the oxygen positions had been found, the oxygen–nitrogen vectors could be identified; the positions of the nitrogen atoms were then derived. The atomic coordinates were refined in two F_o syntheses, after which the atomic coordinates, individual scale factors and isotropic temperature factors were refined by the least-squares method using a block-diagonal approximation. Finally the structure was refined on an IBM 7090 computer with the full matrix least-squares program, ORFLS, written by Busing, Martin & Levy (1962). In both cases the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used was that due to Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). In this $w = 1/(a + |F_o| + c|F_c|)^2$, where the constants a and c were chosen as follows: $a = 1.4$ ($\approx 2|F_{o(\min)}|$) and $c = 0.04$

($\approx 2/|F_o|_{\max}$). Reflexions too weak to be observed were given zero weight.

When isotropic temperature factors were used and the hydrogen atoms were neglected, the reliability coefficients after three cycles of refinement with the full-matrix least-squares program were:

$$R_1 = \Sigma | |F_o| - |F_c| | / \Sigma |F_o| = 0.114$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.162.$$

At this point the shifts in all parameters were less than one-tenth of the standard deviations.

The hydrogen atoms were then included and the coordinates and isotropic temperature factors of the oxygen and nitrogen atoms together with the individual scale factors were refined, the hydrogen atoms being retained in fixed positions with a constant temperature factor of 6.0 \AA^2 . The hydrogen atoms were assigned to the nitrogen and oxygen atoms in accordance with the discussion below. They were placed on the lines between the hydrogen-bonded atoms at distances of 1.05 \AA from one oxygen atom in the $\text{O-H}\cdots\text{O}$ bond and 1.07 and 1.04 \AA from the nitrogen atoms in the short and long $\text{N-H}\cdots\text{O}$ bonds respectively. These distances were selected on the basis of data given in chapter 9-3 in the book by Pimentel & McClellan (1960). When the hydrogen atoms had been included in this way, the reliability factor R_1 decreased to 0.101 after three cycles. When the hydrogen atoms were shifted somewhat ($< 0.2 \text{ \AA}$) so as to correspond to the observed maxima in a difference synthesis based on nitrogen and oxygen only, R_1 decreased to 0.100 after two cycles.

When anisotropic temperature factors of the form $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hll_{13} + 2klb_{23})]$ were employed the final reliability coefficients were:

$$R_1 = 0.109 \quad R_2 = 0.154 \quad (\text{neglecting hydrogen atoms})$$

$$R_1 = 0.096 \quad R_2 = 0.133 \quad (\text{including hydrogen atoms on the lines joining the hydrogen-bonded atoms as described above}).$$

During the anisotropic refinements (three cycles with hydrogen atoms neglected and three cycles with hydrogen atoms included) the relative inter-layer scale factors were kept constant and only the over-all scale factor was refined. The atomic parameters at different stages of refinement are given in Table 1. Table 2 lists structure factors after the last cycle of refinement, including hydrogen atoms and anisotropic temperature factors.

The atomic scattering factors used are those for neutral N, O and H, given in *International Tables for X-ray Crystallography* (1962, p. 202).

Description and discussion of the structure

The structure is shown in Fig. 1, where the hydrogen atoms have been assigned to the oxygen and nitrogen atoms according to the text following. Fig. 2 gives a

projection of the structure on a plane perpendicular to the b axis.

Bond distances and angles are given in Table 3 together with their standard deviations; the bond configurations are illustrated in Figs. 3 and 4. The distances and angles have been computed from the atomic coordinates given in Table 1(d). The standard errors of the distances and angles were computed with the program ORFFE (Busing, Martin & Levy, 1964) from the errors of the atomic coordinates; these were obtained in the form of a variance-covariance matrix from the final least-squares cycle with the use of ORFLS. When

Table 1. *Atomic parameters and standard deviations (based on data from the second crystal, recorded at -170°C)*

(a) After isotropic refinements omitting hydrogen atoms			
	Oxygen O(1)	Oxygen O(2)	Nitrogen
x	0.6675 ± 0.0006	0.8247 ± 0.0006	0.7445 ± 0.0008
y	0.6759 ± 0.0007	0.6766 ± 0.0006	0.1181 ± 0.0008
z	0.1635 ± 0.0007	0.8656 ± 0.0007	0.9990 ± 0.0008
$B(\text{\AA}^2)$	1.39	1.30	1.37
(b) After isotropic refinements with hydrogen atoms on the lines joining hydrogen-bonded atoms (see text)			
	Oxygen O(1)	Oxygen O(2)	Nitrogen
x	0.6679 ± 0.0005	0.8247 ± 0.0005	0.7442 ± 0.0007
y	0.6759 ± 0.0006	0.6763 ± 0.0006	0.1186 ± 0.0007
z	0.1642 ± 0.0006	0.8647 ± 0.0006	0.9990 ± 0.0007
$B(\text{\AA}^2)$	1.42	1.37	1.40
(c) After anisotropic refinements omitting hydrogen atoms			
	Oxygen O(1)	Oxygen O(2)	Nitrogen
x	0.6671 ± 0.0006	0.8245 ± 0.0006	0.7445 ± 0.0008
y	0.6763 ± 0.0006	0.6763 ± 0.0006	0.1175 ± 0.0007
z	0.1630 ± 0.0006	0.8656 ± 0.0006	0.9991 ± 0.0007
b_{11}	0.0136	0.0122	0.0138
b_{22}	0.0081	0.0073	0.0057
b_{33}	0.0091	0.0090	0.0126
b_{12}	-0.0017	0.0013	-0.0001
b_{13}	0.0066	0.0061	0.0078
b_{23}	-0.0014	0.0021	0.0006
(d) After anisotropic refinements with hydrogen atoms as in (b)			
	Oxygen O(1)	Oxygen O(2)	Nitrogen
x	0.6673 ± 0.0005	0.8244 ± 0.0005	0.7444 ± 0.0007
y	0.6764 ± 0.0006	0.6760 ± 0.0005	0.1180 ± 0.0006
z	0.1635 ± 0.0005	0.8648 ± 0.0005	0.9991 ± 0.0006
b_{11}	0.0140	0.0126	0.0137
b_{22}	0.0084	0.0077	0.0059
b_{33}	0.0090	0.0096	0.0132
b_{12}	-0.0014	0.0012	-0.0001
b_{13}	0.0064	0.0065	0.0079
b_{23}	-0.0008	0.0016	0.0007
(e) Root mean square components of thermal vibration along principal axes of the ellipsoids of vibration, calculated from the b_{ij} values in (d)			
Atom	Principal axis	Component	
Oxygen O(1)	1	0.10 \AA	
	2	0.13	
	3	0.15	
Oxygen O(2)	1	0.10	
	2	0.13	
	3	0.15	
Nitrogen	1	0.11	
	2	0.13	
	3	0.15	

Table 2. Observed and calculated structure factors

Data taken at -170°C . Asterisks indicate reflexions which were too weak to be measured. The F_o values for these are given as F_{min} .

H	K	L	F_o	FC	H	K	L	F_o	FC
1	0	0	6.1	6.9	1	0	0	6.1	6.9
1	0	0	17.8	17.2	2	0	0	17.8	17.2
1	0	0	6.5	6.4	3	0	0	6.5	6.4
1	0	0	9.9	8.6	4	0	0	9.9	8.6
1	0	0	2.0	1.3	5	0	0	2.0	1.3
1	0	0	6.6	6.6	6	0	0	6.6	6.6
1	0	0	5.7	5.5	7	0	0	5.7	5.5
1	0	0	2.4	2.7	8	0	0	2.4	2.7
1	0	0	5.2	4.4	9	0	0	5.2	4.4
1	0	0	11.6	11.4	10	0	0	11.6	11.4
1	0	0	5.9	6.1	11	0	0	5.9	6.1
1	0	0	23.4	25.8	12	0	0	23.4	25.8
1	0	0	8.1	9.8	13	0	0	8.1	9.8
1	0	0	15.3	17.5	14	0	0	15.3	17.5
1	0	0	4.4	4.3	15	0	0	4.4	4.3
1	0	0	5.8	15.9	16	0	0	5.8	15.9
1	0	0	7.3	7.0	17	0	0	7.3	7.0
1	0	0	19.9	20.5	18	0	0	19.9	20.5
1	0	0	8.1	8.0	19	0	0	8.1	8.0
1	0	0	9.7	9.3	20	0	0	9.7	9.3
1	0	0	1.1	1.7	21	0	0	1.1	1.7
1	0	0	8.8	7.6	22	0	0	8.8	7.6
1	0	0	2.5	2.5	23	0	0	2.5	2.5
1	0	0	2.7	9.5	24	0	0	2.7	9.5
1	0	0	8.5	8.5	25	0	0	8.5	8.5
1	0	0	1.3	1.1	26	0	0	1.3	1.1
1	0	0	1.8	0.8	27	0	0	1.8	0.8
1	0	0	1.3	0.6	28	0	0	1.3	0.6
1	0	0	8.0	5.9	29	0	0	8.0	5.9
1	0	0	0.0	0.0	30	0	0	0.0	0.0
1	0	0	2.2	2.2	31	0	0	2.2	2.2
1	0	0	23.2	23.8	32	0	0	23.2	23.8
1	0	0	1.7	0.9	33	0	0	1.7	0.9
1	0	0	1.8	0.1	34	0	0	1.8	0.1
1	0	0	8.5	8.9	35	0	0	8.5	8.9
1	0	0	5.3	5.9	36	0	0	5.3	5.9
1	0	0	8.2	7.1	37	0	0	8.2	7.1
1	0	0	2.1	2.4	38	0	0	2.1	2.4
1	0	0	0.5	1.1	39	0	0	0.5	1.1
1	0	0	12.8	12.3	40	0	0	12.8	12.3
1	0	0	1.2	1.9	41	0	0	1.2	1.9
1	0	0	1.1	2.0	42	0	0	1.1	2.0
1	0	0	1.4	1.2	43	0	0	1.4	1.2
1	0	0	7.6	5.9	44	0	0	7.6	5.9
1	0	0	4.0	3.3	45	0	0	4.0	3.3
1	0	0	7.4	6.3	46	0	0	7.4	6.3
1	0	0	6.4	6.6	47	0	0	6.4	6.6
1	0	0	6.1	6.9	48	0	0	6.1	6.9
1	0	0	3.8	3.5	49	0	0	3.8	3.5
1	0	0	1.9	2.0	50	0	0	1.9	2.0
1	0	0	6.6	5.2	51	0	0	6.6	5.2
1	0	0	9.9	9.5	52	0	0	9.9	9.5
1	0	0	3.5	5.6	53	0	0	3.5	5.6
1	0	0	1.9	1.6	54	0	0	1.9	1.6
1	0	0	4.8	3.9	55	0	0	4.8	3.9
1	0	0	1.9	1.7	56	0	0	1.9	1.7
1	0	0	3.2	2.7	57	0	0	3.2	2.7
1	0	0	1.4	2.3	58	0	0	1.4	2.3
1	0	0	4.5	4.7	59	0	0	4.5	4.7
1	0	0	1.6	0.3	60	0	0	1.6	0.3
1	0	0	4.5	4.4	61	0	0	4.5	4.4
1	0	0	11.4	10.1	62	0	0	11.4	10.1
1	0	0	4.9	2.1	63	0	0	4.9	2.1
1	0	0	3.0	2.1	64	0	0	3.0	2.1
1	0	0	1.7	0.5	65	0	0	1.7	0.5
1	0	0	5.0	4.4	66	0	0	5.0	4.4
1	0	0	20.9	21.0	67	0	0	20.9	21.0
1	0	0	6.3	6.6	68	0	0	6.3	6.6
1	0	0	1.8	1.0	69	0	0	1.8	1.0
1	0	0	1.9	0.7	70	0	0	1.9	0.7
1	0	0	2.1	1.2	71	0	0	2.1	1.2
1	0	0	4.9	4.5	72	0	0	4.9	4.5
1	0	0	4.2	4.3	73	0	0	4.2	4.3
1	0	0	9.8	9.7	74	0	0	9.8	9.7
1	0	0	3.4	3.9	75	0	0	3.4	3.9
1	0	0	6.1	6.0	76	0	0	6.1	6.0
1	0	0	1.9	1.7	77	0	0	1.9	1.7
1	0	0	10.7	10.7	78	0	0	10.7	10.7
1	0	0	2.8	2.0	79	0	0	2.8	2.0
1	0	0	2.8	2.0	80	0	0	2.8	2.0
1	0	0	0.7	0.3	81	0	0	0.7	0.3
1	0	0	2.4	2.4	82	0	0	2.4	2.4
1	0	0	3.6	3.2	83	0	0	3.6	3.2
1	0	0	17.6	18.5	84	0	0	17.6	18.5
1	0	0	2.2	2.2	85	0	0	2.2	2.2
1	0	0	9.3	7.8	86	0	0	9.3	7.8
1	0	0	1.4	1.4	87	0	0	1.4	1.4
1	0	0	2.4	2.6	88	0	0	2.4	2.6
1	0	0	1.1	0.1	89	0	0	1.1	0.1
1	0	0	1.7	1.7	90	0	0	1.7	1.7
1	0	0	13.9	14.2	91	0	0	13.9	14.2
1	0	0	2.3	2.2	92	0	0	2.3	2.2
1	0	0	8.5	8.6	93	0	0	8.5	8.6
1	0	0	6.0	6.8	94	0	0	6.0	6.8
1	0	0	2.0	1.7	95	0	0	2.0	1.7
1	0	0	1.6	1.5	96	0	0	1.6	1.5
1	0	0	1.9	0.8	97	0	0	1.9	0.8
1	0	0	1.9	0.7	98	0	0	1.9	0.7
1	0	0	1.8*	0.4	99	0	0	1.8*	0.4
1	0	0	5.3	4.2	100	0	0	5.3	4.2
1	0	0	3.0	2.2	101	0	0	3.0	2.2
1	0	0	3.0	2.2	102	0	0	3.0	2.2
1	0	0	1.9*	1.2	103	0	0	1.9*	1.2
1	0	0	10.0	10.8	104	0	0	10.0	10.8
1	0	0	1.9*	1.2	105	0	0	1.9*	1.2
1	0	0	5.4	5.4	106	0	0	5.4	5.4
1	0	0	1.9	0.5	107	0	0	1.9	0.5
1	0	0	1.8	0.8	108	0	0	1.8	0.8
1	0	0	17.1	18.4	109	0	0	17.1	18.4
1	0	0	8.7	8.4	110	0	0	8.7	8.4
1	0	0	8.7	8.4	111	0	0	8.7	8.4
1	0	0	3.2	3.1	112	0	0	3.2	3.1
1	0	0	1.7*	0.8	113	0	0	1.7*	0.8
1	0	0	6.3	6.3	114	0	0	6.3	6.3
1	0	0	4.1	1.1	115	0	0	4.1	1.1
1	0	0	0.9	0.5	116	0	0	0.9	0.5
1	0	0	1.1	1.6	117	0	0	1.1	1.6
1	0	0	3.5	2.8	118	0	0	3.5	2.8
1	0	0	3.9	3.3	119	0	0	3.9	3.3
1	0	0	2.1	1.7	120	0	0	2.1	1.7
1	0	0	4.4	4.8	121	0	0	4.4	4.8
1	0	0	4.2	4.0	122	0	0	4.2	4.0
1	0	0	6.4	6.0	123	0	0	6.4	6.0
1	0	0	2.9	3.5	124	0	0	2.9	3.5
1	0	0	1.7*	1.4	125	0	0	1.7*	1.4
1	0	0	5.3	3.8	126	0	0	5.3	3.8
1	0	0	3.8	3.7	127	0	0	3.8	3.7
1	0	0	12.3	11.9	128	0	0	12.3	11.9
1	0	0	5.3	5.8	129	0	0	5.3	5.8
1	0	0	17.8	19.6	130	0	0	17.8	19.6
1	0	0	6.4	7.3	131	0	0	6.4	7.3
1	0	0	5.5	6.2	132	0	0	5.5	6.2
1	0	0	2.0	1.9	133	0	0	2.0	1.9
1	0	0	3.0	2.4	134	0	0	3.0	2.4
1	0	0	1.5	1.9	135	0	0	1.5	1.9
1	0	0	2.7	2.1	136	0	0	2.7	2.1
1	0	0	1.5	0.6	137	0	0	1.5	0.6
1	0	0	3.1	3.0	138	0	0	3.1	3.0
1	0	0	3.1	3.0	139	0	0	3.1	3.0

the standard deviations in the cell parameters were taken into account no significant changes were observed in the standard deviations of the bond lengths and angles. In the discussion following, the distances uncorrected for anisotropic thermal motion are used, since no experimental scaling has been done, and thus part of the anisotropy has probably been accounted for by refinement of individual scale factors for the separate layers.

The structure contains infinite chains of hydrogen peroxide molecules held together by hydrogen bonds. The chains are parallel to the c axis. The individual chains are linked together by ammonia molecules to form a three-dimensional network. Each nitrogen atom is then approximately tetrahedrally surrounded by four oxygen atoms [Fig. 3(a) and (b)]. These are two oxygen atoms which belong to different hydrogen peroxide molecules within the same chain (N...O distances: 2.72 and 2.84 Å), and an oxygen atom from each of two adjacent chains (distances 2.73 and 2.86 Å). Each oxygen atom is also approximately tetrahedrally coordinated [Fig. 4(a) and (b)] by two nitrogen atoms [distances 2.72 and 2.73 Å from oxygen O(1), 2.84 and

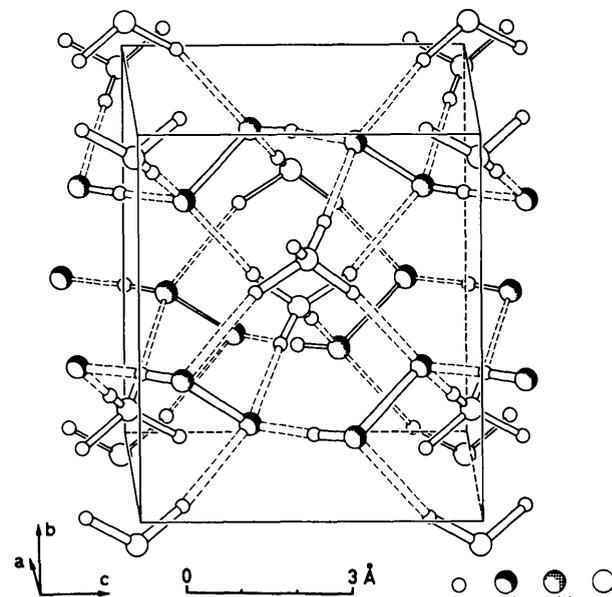


Fig. 1. The crystal structure of ammonium hydrogenperoxide.

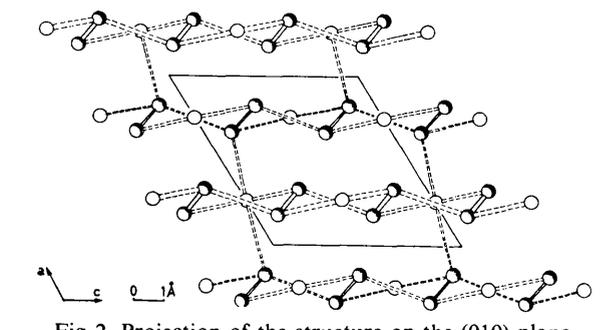


Fig. 2. Projection of the structure on the (010) plane.

2.86 Å from oxygen O(2)] and two oxygen atoms (2.54 and 1.50 Å). One of these oxygen neighbours belongs to the same peroxide group as the oxygen under consideration.

In this compound there are five hydrogen atoms and five free electron pairs available for hydrogen bonding per formula unit of $\text{NH}_3 \cdot \text{H}_2\text{O}_2$. It is therefore one of the very few examples where the number of hydrogen atoms is the same as the number of free electron pairs available for hydrogen bonding (Olovsson, 1960). Ice is, of course, the most obvious example of this group. In such cases all the lone pairs are naturally expected to be involved in hydrogen bonding. In the structure under discussion the neighbouring atoms are so favourably arranged that this is very probably the case here also. There still remains, however, the problem of assigning the hydrogen atoms to the oxygen and nitrogen atoms. It turns out that there are only two main possibilities; thus the structure is built up either from (1) ions, NH_4^+ and OOH^- , or (2) molecules without net charge, namely NH_3 and H_2O_2 .

These two possibilities are discussed separately below.

The ionic possibility: NH_4^+ and OOH^-

In this case there are hydrogen bonds of only the two main types $\text{N-H} \cdots \text{O}$ and $\text{O-H} \cdots \text{O}$; there are no bonds of the type $\text{N} \cdots \text{H-O}$ since the ammonium nitrogen atoms have no electron pairs available for hydrogen bonding. Thus the assignment of the hydrogen atoms in the bonds involving nitrogen is clear and only the assignment in the $\text{O-H} \cdots \text{O}$ bonds remains to be discussed.

Discussion of the $\text{O-H} \cdots \text{O}$ bonds

In each chain of hydrogenperoxide ions there will be two different types of oxygen atom, one of which has lost its hydrogen and one has its hydrogen left. It is therefore clear that the assignment of a hydrogen atom to one particular oxygen atom within the chain determines the assignment of hydrogen atoms for the rest of the chain, since there are only $\text{O-H} \cdots \text{O}$ bonds within the chains, and no such bonds between two chains:

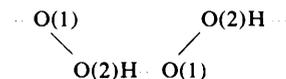


Table 3. Bond distances and angles with their standard deviations (cf. Figs. 3 and 4)

The distances are not corrected for thermal motion. This correction, assuming independent motion of the atoms, lies between +0.010 and +0.014 Å, except for the 1.500 Å O-O distance, where it is +0.024 Å. The corrections, assuming 'riding motion' are all less than 0.001 Å.

(a) Distances and angles around the ammonium ion

Bond	Distance	Bond	Distance
N-O(1)	2.715 ± 0.005 Å	N-O(2')	2.835 ± 0.005 Å
N-O(1''')	2.725 ± 0.005	N-O(2'')	2.863 ± 0.005
Bonds	Angle	Bonds	Angle
O(1) — N-O(1''')	110.1 ± 0.2°	O(1''') — N-O(2')	112.5 ± 0.2°
O(1) — N-O(2'')	109.9 ± 0.2	O(1) — N-O(2')	88.3 ± 0.2
O(1''') — N-O(2'')	120.0 ± 0.2	O(2'') — N-O(2')	111.6 ± 0.2

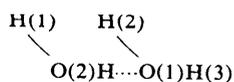
(b) Distances and angles around oxygen O(1)

Bond	Distance	Bond	Distance
O(1)-O(2)	1.500 ± 0.005 Å	O(1)-N	2.715 ± 0.005 Å
O(1)-O(2')	2.536 ± 0.005	O(1)-N''	2.725 ± 0.005
Bonds	Angle	Bonds	Angle
O(2')-O(1)-O(2)	103.3 ± 0.2	O(2)-O(1)-N''	94.8 ± 0.2°
O(2')-O(1)-N''	116.1 ± 0.2	O(2)-O(1)-N	95.2 ± 0.2
O(2')-O(1)-N	124.3 ± 0.2	N — O(1)-N''	113.9 ± 0.2

(c) Distances and angles around oxygen O(2)

Bond	Distance	Bond	Distance
O(2)-O(1)	1.500 ± 0.005 Å	O(2)-N'	2.835 ± 0.005 Å
O(2)-O(1')	2.536 ± 0.004	O(2)-N''	2.863 ± 0.005
Bonds	Angle	Bonds	Angle
O(1) — O(2)-O(1')	103.3 ± 0.2°	O(1)-O(2)-N''	93.7 ± 0.2°
O(1') — O(2)-N''	120.4 ± 0.2	O(1)-O(2)-N'	93.1 ± 0.2
O(1') — O(2)-N'	126.7 ± 0.2	N' — O(2)-N''	108.4 ± 0.2

This bond can be compared with the corresponding bond in ice:



It is to be expected that the substitution of H(1) by the more electronegative oxygen will increase the positive net charge on the hydrogen atom involved in the hydrogen bond and accordingly lead to a shortened O-H...O bond. This effect, however, would be counteracted by the substitution of H(2) by OH, leading to a decrease in the negative charge on oxygen O(1) and to a longer bond. The net effect of these two substitutions is expected, empirically, to be about zero. [Substitution of H(1) and H(2) in ice as described gives roughly the same bond situation as is found in solid hydrogen peroxide, where the bond is 2.78 Å, *i.e.* about the same as in ice (Olovsson, 1960)]. In addition to these substitutions, H(3) is also removed, leaving a lone pair on the oxygen atom O(1) in the compound

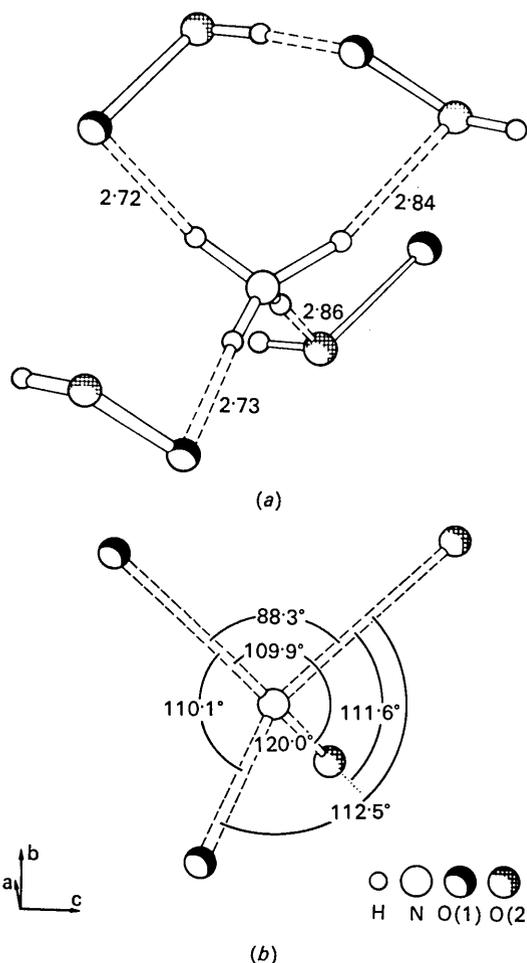


Fig. 3. (a) Bond distances and (b) angles involving the ammonium ion and its neighbours. In (a) the hydrogen atoms have been assigned to the oxygen and nitrogen atoms according to the text.

under discussion. The negative charge on O(1) will then be strongly increased, and this will cause a considerable shortening of the bond O-H...O. The experimental value in the ammonium compound is 2.54 Å as compared with 2.76 Å in ice.

Discussion of the N-H...O bonds

From a consideration of the N-H...O bonds, at least two types are to be expected, one involving an oxygen atom that has lost its hydrogen atom, and a second with an oxygen atom which has retained its hydrogen. The bond should be shorter in the first case than in the second owing to the higher negative charge on the first oxygen atom. As described above, two of the neighbours coordinating nitrogen are oxygen atoms belonging to hydrogen peroxide molecules within the same chain. There are accordingly two possible ways of assigning the hydrogen atoms (numbers have the same meaning as in Tables 1 and 3):

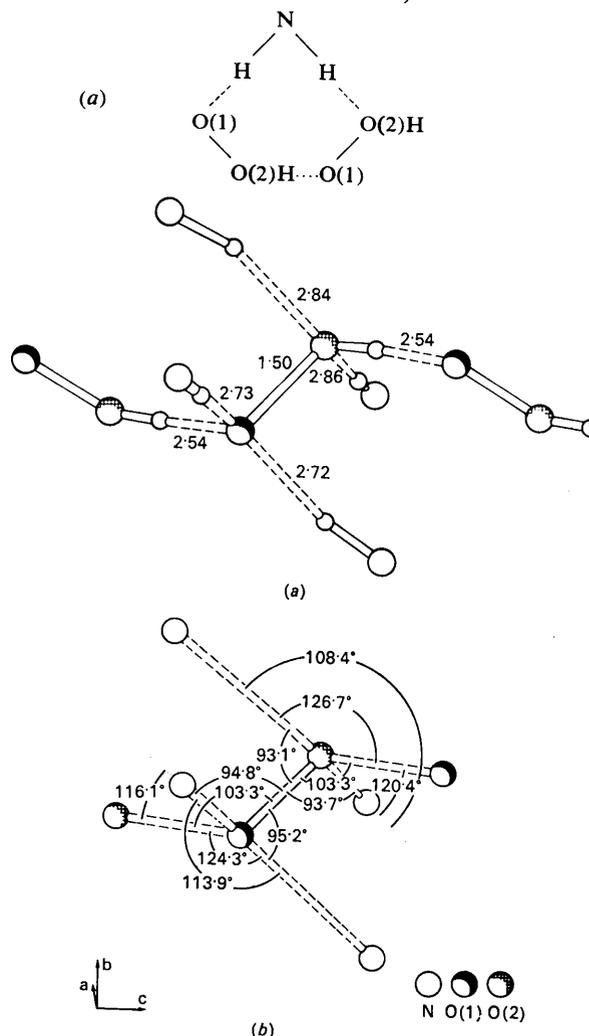
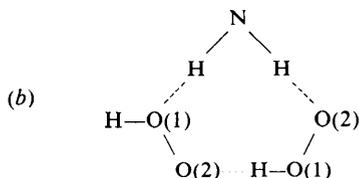


Fig. 4. (a) Bond distances and (b) angles involving the hydrogenperoxide group and its neighbours. In (a) the hydrogen atoms have been assigned to the oxygen and nitrogen atoms according to the text.



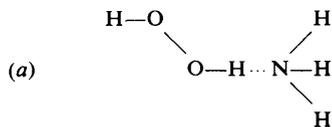
Differences between the two $\text{N}-\text{H}\cdots\text{O}$ bonds should be due mainly to the difference between the charges on O(1) and O(2). If one of these alternatives occurs throughout the crystal, *i.e.* if the structure is ordered with respect to the positions of the hydrogen atoms in neighbouring chains, the X-ray investigation should give different distances for $\text{N}-\text{O}(1)$ and $\text{N}-\text{O}(2)$. If, on the other hand, the structure is completely disordered, these distances should be the same; the Fourier maps, however, should then show considerably elongated peaks corresponding to the oxygen atoms. The experimental results for the bond lengths are 2.72 and 2.84 Å respectively. The oxygen peaks also show no sign of disorder. This indicates that oxygen O(1) has lost its hydrogen while oxygen O(2) has retained its hydrogen atom, and that this is the case throughout the crystal (case (a) above).

Evidence in support of these conclusions is provided by the short length (2.73 Å) of the bond to O(1) from the other nitrogen atom (which forms part of the linkage between the chain discussed above and one of the neighbouring chains) as compared with that to O(2) (2.86 Å).

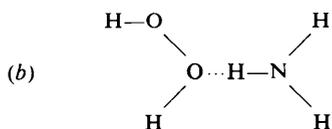
The non-ionic possibility: NH_3 and H_2O_2

In this case there will be bonds of the type $\text{N}\cdots\text{H}-\text{O}$ in addition to bonds of the types $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$. In this instance one would expect the $\text{O}-\text{H}\cdots\text{O}$ bonds to be rather similar in length to the hydrogen bonds in solid hydrogen peroxide. However, these latter bonds are considerably longer (2.80 Å according to Busing & Levy, 1965, and 2.78 Å according to Abrahams, Collin & Lipscomb, 1951). Even the bond $\text{O}-\text{H}\cdots\text{O}$ in $\text{H}_2\text{O}_2\cdot 2\text{H}_2\text{O}$ mentioned above, which should be shorter than the bond in the ammonia compound, is actually longer (2.69 Å).

When the bonds between oxygen and nitrogen are considered it can be stated immediately that the bond



in which the hydrogen atom is donated by oxygen, is expected to be shorter than the bond



where nitrogen is the donor. This is due in part to the higher electronegativity of oxygen, which will therefore be a better hydrogen donor, and in part to the greater basicity of ammonia by comparison with hydrogen peroxide, which should be accompanied by a greater attraction for protons. This would imply three long bonds and one shorter bond around each nitrogen. This difference should be detected in the X-ray investigation if the structure were ordered with respect to the orientation of the ammonia molecules. If the structure were completely disordered, however, only an average distance should be observed and the four bonds from the nitrogen should be similar in length. Neither of these two pictures conforms with the experimental result, namely that there are two short and two long bonds around nitrogen.

Further evidence supporting the ionic picture of the compound

It seems quite evident from the foregoing discussion of bond lengths that the compound consists of ammonium and hydrogenperoxide ions. This conclusion is further supported by a difference synthesis, based on the atomic parameters in Table 1(a). The difference synthesis showed maxima with coordinates in good agreement with those predicted for the hydrogen atoms on the basis of the assumptions (1) that the compound consists of ammonium and hydrogenperoxide ions and that the assignment of the hydrogen atoms is made in accordance with the foregoing discussion, (2) that the hydrogen atoms are situated close to the lines joining the hydrogen-bonded atoms and at distances from these as described above. Furthermore, use of the hydrogen coordinates from the difference synthesis gives

angles $\text{H}-\text{N}$ of the ammonium ion closer to the tetrahedral value than when the hydrogen atoms are assumed to lie exactly on the lines between the hydrogen bonded atoms. The synthesis showed no other maxima of a magnitude comparable to those assumed to correspond to hydrogen atoms.

The ionic picture of the compound also conforms with its high melting point, 24.5°C, as compared with the melting points of pure hydrogen peroxide, -0.4°C, and ammonia, -78°C. This difference indicates a much stronger interaction between the molecules in the compound than in the components.

The Raman spectrum (Simon & Kriegsmann, 1955) and the infrared spectrum (Knop & Giguère, 1959) have also been interpreted as indicating the presence of ammonium and hydrogenperoxide ions in the solid.

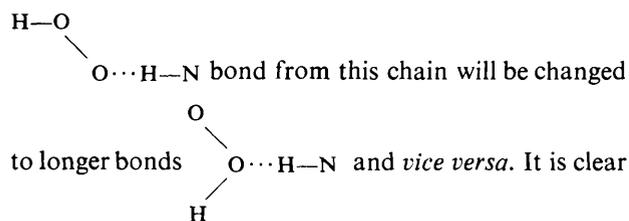
It is interesting to note that the $\text{O}-\text{O}$ bond in the hydrogenperoxide ion, 1.500 ± 0.005 Å, appears to be significantly longer than in the uncharged hydrogen peroxide molecule. In solid hydrogen peroxide the bond length has been reported as 1.45 Å (Busing &

Levy, 1965) and 1.49 Å (Abrahams, Collin & Lipscomb, 1951). In $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ the bond was found to be 1.48 Å (Olovsson & Templeton, 1960). Knop & Giguère (1959) report a decrease in the O–O stretching frequency from 880 cm^{-1} in solid hydrogen peroxide to 836 cm^{-1} in solid ammonium hydrogenperoxide. From these values they predict an increase in the O–O bond length of about 0.02 Å, which is in qualitative agreement with the increase reported here. Similar variations in the bond lengths are normally observed on altering the charges on the atoms involved (*cf. Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958).

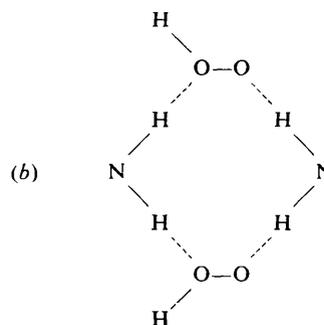
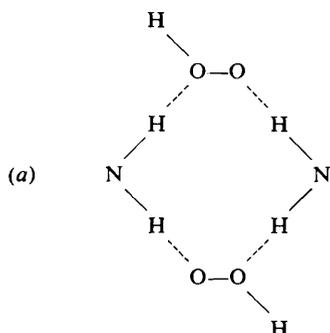
The structure of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (Olovsson & Templeton, 1959) is very similar to the structure of NH_4OOH ; both contain infinite chains of hydrogen-bonded water and hydrogen peroxide molecules, respectively, which are linked together by ammonia. However, the monohydrate contains *uncharged* water and ammonia molecules and the bonds are considerably weaker in this compound (melting point -79°C).

Order and disorder of hydrogen positions

It was mentioned in the preceding section that the structure seems to be ordered with respect to the hydrogen positions. It remains to decide whether or not this is to be expected. If hydrogen atoms in one chain are switched from one alternative to the other, this must have a rather drastic effect on the bonds forming the linkage between neighbouring chains. The short



that these two alternatives cannot be equivalent on comparison of two hydrogenperoxide ions from different chains, picked out of the structure together with the nitrogen atoms forming the linkage between them. The arrangements are



Arrangement (a) is the one actually observed. It is seen that the distribution of O–N bond lengths in the six membered ring is quite different in the two cases. In (a) it is short – long – short – long while in (b) it is short – short – long – long. A change from arrangement (a) to arrangement (b) cannot be made without changing some of the bond angles involved. An increase in strain energy will probably result and this may account for the instability of arrangement (b). This may be the reason why the structure appears to be ordered.

As was pointed out in the preceding section the structure of $\text{NH}_3 \cdot \text{H}_2\text{O}$ is very similar to the structure of this compound. In $\text{NH}_3 \cdot \text{H}_2\text{O}$ one of the hydrogen atoms associated with a water molecule in the water chains has a similar choice between two possible positions; *i.e.* it can be arranged to point to two different neighbouring oxygen atoms within the chain. Because of the symmetrical arrangement of the bonds which emerge from the water molecule to form part of the link to adjacent chains, an interchange of hydrogen between the two alternative positions will not affect the linkages to neighbouring nitrogen atoms and so to neighbouring chains. The hydrogen assignment in different chains should accordingly be rather independent and the structure may be disordered. It was, in fact, impossible to assign this special hydrogen atom to any one of the two positions within the chain, on the basis of the X-ray investigation.

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The Crystal Structure of β -Ca₂P₂O₇

BY NED C. WEBB

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239, U.S.A.

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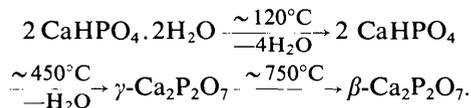
Crystals of β -Ca₂P₂O₇ are tetragonal, space group $P4_1$, with 8 formula units in a unit cell with $a=b=6.684$, $c=24.144$ Å. Each of the two independent pyrophosphate groups is in an essentially eclipsed configuration. The mean values for the bond lengths in the pyrophosphate groups are P-O (bridge) = 1.615 ± 0.017 Å and P-O = 1.518 ± 0.021 Å, and the P-O-P angles are 131 and 138°. Of the four independent calcium atoms two have seven nearest neighbor oxygen atoms, one has eight and one has nine. The structure exhibits a local, non-crystallographic center of symmetry.

Introduction

One of the objectives of the determination of the structure of sodium pyrophosphate decahydrate (MacArthur & Beevers, 1957; Cruickshank, 1964) was to establish the geometry of the pyrophosphate ion and, in particular, to determine the P-O-P angle. The P-O-P angle was found to be 134°, which is quite different from the value of 180° reported in cubic ZrP₂O₇ by Levi & Peyronel (1935). In ZrP₂O₇ the central oxygen atom lies on a center of symmetry, and in Na₄P₂O₇·10H₂O it lies on a twofold axis. In the β phase of calcium pyrophosphate, β -Ca₂P₂O₇, all atoms are in general positions, thereby providing an opportunity for studying the geometry of pyrophosphate groups free of symmetry restrictions. In other investigations of structures containing a pyro-group, X₂O₇, the X-O-X angle has been found to be 128° in Cl₂O₇ (Fonteyne, 1938), 124° in K₂S₂O₇ (Lynton & Truter, 1960) and 180° in Sc₂Si₂O₇ (Zachariasen, 1930; Cruickshank, Lynton & Barclay, 1962). In β -Mg₂P₂O₇ and β -Zn₂P₂O₇ the P-O-P group appears to be linear because of a thermal averaging of the position of the central oxygen atom (Calvo, 1965a, b).

Experimental

Heating dicalcium phosphate dihydrate to approximately 750°C produces β -Ca₂P₂O₇ which melts at approximately 1350°C:



A sample of CaHPO₄·2H₂O in a Vycor crucible was placed in a muffle oven and heated to ~1400°C. The oven was turned off but left closed to allow slow cooling of the melt. The solidified melt obtained in this way had a glassy appearance, but on shattering, the melt yielded small single crystals in the shape of rectangular solids. One of these crystals (0.25 × 0.17 × 0.10 mm) was mounted with its long axis (later found to be a) coincident with the axis of rotation.

Corbridge (1957) reported β -Ca₂P₂O₇ to crystallize in the tetragonal space group $P4_1$. We observed systematic absences ($00l$, $l \neq 4n$) on Weissenberg photographs indicating either space group $P4_1$ or $P4_12_2$, but the relationship observed in the intensity data, $|F(hkl)| \neq |F(h\bar{k}l)|$, eliminated $P4_12_2$ as a possibility. Precise values of the cell parameters b and c were obtained by least-squares refinement on data for seventeen $0kl$ reflections taken from measurements of a Straumanis-type rotation photograph. In adjusting the cell parameters to give the best fit between observed and calculated $\sin^2\theta$ values no allowance was made for eccentricity or absorption effects; each observational equation was weighted with $1/w = 1/\sin 2\theta$, and $\lambda(\text{Cu } K\alpha_1)$ was taken as 1.5405 Å. The results obtained here are listed in Table 1 along with those obtained by Corbridge (1957) and Keppler (1962); the standard deviations