DOKTORSAVHANDLINGAR
VID
CHALMERS TEKNISKA HÖGSKOLA

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THE FORMATION AND STRUCTURE OF PEROXY COMPOUNDS OF GROUP II a AND II b ELEMENTS

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NILS-GÖSTA VANNERBERG

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To my Wife

Preface

In this paper the formation and structures of peroxides, peroxide hydrates and peroxide hydroperoxidates of Group IIa and IIb elements will be reviewed. The discussion is based upon a number of investigations including the following communications by the present author.

N1 Formation and structure of magnesium peroxide. Arkiv för Kemi *14*, 99–105 (1959).

N2 Formation and structure of zink peroxide. Arkiv för Kemi *14*, 119–124 (1959).

N3 On the formation and structure of cadmium peroxides. Arkiv för Kemi *10*, 455–459 (1956).

N4 Formation and structure of mercuric peroxides. Arkiv för Kemi *13*, 515–521 (1959).

N5 On the system SrO_2–H_2O–H_2O_2.
2. The crystal structure of strontium peroxide octahydrate. Arkiv för Kemi *14*, 17–30 (1959).

N6 On the system BaO_2–H_2O–H_2O_2.
1. Investigation of the existing phases and their preparation.
2. The structure of $BaO_2 \cdot H_2O_2$. Arkiv för Kemi *14*, 147–160 (1959).

N7 On the system SrO_2–H_2O–H_2O_2.
1. The crystal structure of α- and β-$SrO_2 \cdot 2H_2O_2$. Arkiv för Kemi *13*, 29–41 (1958).

N8 On the system BaO_2–H_2O–H_2O_2.
3. The crystal structure of α-, β- and γ-$BaO_2 \cdot 2H_2O_2$ and $BaO_2 \cdot H_2O_2 \cdot 2H_2O$. Arkiv för Kemi *14*, 125–145 (1959).

N9 The infrared spectra of some peroxide hydrates and peroxidates. Arkiv för kemi *14*, 107–113 (1959).

Introduction

Catenation is a phenomenon which commonly occurs among the Group IVb elements. The elements in the nitrogen group also exhibit tendency to form self-linkages. In the oxygen group, however, it is more unusual. Except for the bonds in the different modifications of the pure element, such bonds between oxygen atoms are only encountered in peroxides, in superoxides and ozonides.

These compounds contain groups O_2^{2-}, O_2^- or O_3^-. To the first two, the following electronic structure formulae are attributed (1).

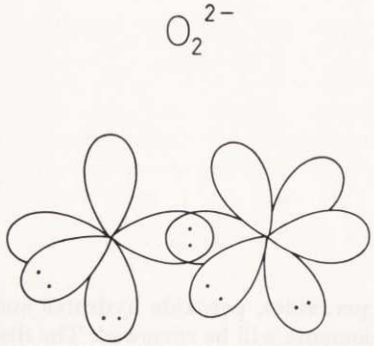


Fig. 1. Schematic representation of the electronic structure of O_2^{2-}.

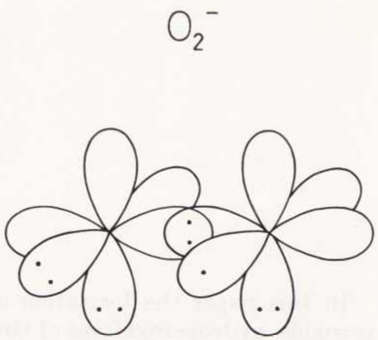


Fig. 2. Schematic representation of the electronic structure of O_2^-.

$$[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4] \quad O_2^{2-}$$

$$[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^3] \quad O_2^-$$

For comparison, the electronic structure of O_2 is given by

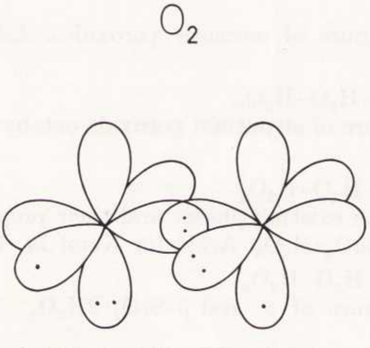
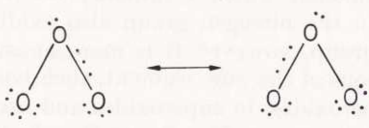


Fig. 3. Schematic representation of the electronic structure of O_2.

$$[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2] \quad O_2$$

According to the valency bond theory, the two oxygen atoms form a single covalent bond in a peroxide ion; a single covalent and a three electron bond in the superoxide ion; and a single covalent and two three-electron bonds in the oxygen molecule (2).

The electronic structure of the O_3^- ion is not known with certainty (3, 4). However, as the ion is paramagnetic, the formula might be



to be compared with the formula for ozone

Among the ozonides, only the potassium compound has been characterized (3, 4), but its chemical behaviour is very slightly known. All alkali metals are known to form superoxides (5, 6). Moreover, the alkaline earth metals (7, 8), magnesium, zinc and cadmium, are able to form small quantities of superoxide (9, 10). Superoxide groups are also found in certain coordination compounds, such as

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{5-} \qquad (11)$$

The peroxy compounds have been subjected to several investigations. In most cases the work has been preparative and analytical. On the other hand, only very few structural investigations have been performed. The purpose of the present investigation has been to fill this gap and to give a uniform treatment of certain classes at least of peroxy compounds.

In general, the inorganic peroxy compounds can be divided into four main groups:

1. Ionic peroxides
2. Covalent peroxides
3. Complex peroxides
4. Peroxoacids

Ionic peroxides are formed by the elements in Group Ia and IIa in the Periodic Table (Table 1). Covalent peroxides are formed by elements in Group Ib, IIb and by hydrogen. The elements in the Groups IIIa–VIII form complex peroxides, while the elements in Group IIIb–VIb form peroxoacids. However, the boundary-lines between the different groups are indistinct. For instance, the peroxides of the rare earth metals form an intermediate link between ionic and complex peroxides, while zinc and cadmium peroxides form a transition between ionic and covalent peroxides. The boundary between the complex peroxides and peroxoacids is still more vague. Nevertheless, the above classification basis is very useful. In Table 1, the most important inorganic peroxy compounds are tabulated in such a way that for each element a characteristic peroxy compound has been listed.

In the following text only the ionic and covalent peroxy compounds will be discussed.

The ionic peroxides occur as single salts, but also form addition compounds with water and with hydrogen peroxide (5, 12). The latter are called hydroperoxidates (5) and are formed by the following peroxides: Li_2O_2, Na_2O_2, K_2O_2 and CaO_2, SrO_2, BaO_2 (5, 12). The latter three compounds also form a hydrate with eight molecules of water (12). Of the alkali peroxides, the sodium compound, which is the one most thoroughly investigated, seems to form hydrates with two, six and eight molecules of water (13). Some peroxidate hydrates have also been reported, such as $Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$ and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ (5, 12) (see Table 2). The covalent peroxides have also been reported to form several hydrates and hydroperoxidates, though less precisely characterized.

Below, the formation and structure of the peroxides, peroxide hydrates and hydroperoxidates of the elements in Group IIa and IIb will be described. As an introduction, the chemical behaviour of the Group IIa and IIb elements will be shortly reviewed.

Generally, the elements of Group IIa and IIb have the valency +2 in chemical compounds. The heavier elements in Group IIa form typical ionic compounds, but

Table 1. Peroxy

Ionic peroxides		Complex peroxides				
I a	II a	III a	IV a	V a	VI a	VII a
Li_2O_2	—					
Na_2O_2	MgO_2					
K_2O_2	CaO_2	—	$TiO_3 \cdot 2\,H_2O$	K_3VO_8	K_3CrO_8	—
Rb_2O_2	SrO_2	$Y_4O_9 \cdot xH_2O$	$ZrO_3 \cdot 2\,H_2O$	K_3NbO_8	Na_2MoO_6	—
Cs_2O_2	BaO_2	$La_2O_5 \cdot xH_2O$	$HfO_3 \cdot 2\,H_2O$	K_3TaO_8	K_2WO_8	Re_2O_8
		—	$ThO_3 \cdot 2\,H_2O$		$UO_4 \cdot 2\,H_2O$	

Table 2. Some hydrates and peroxidates of Group Ia and IIa elements.

Li_2O_2	K_2O_2	SrO_2
$Li_2O_2 \cdot H_2O_2 \cdot 3H_2O$	$(K_2O_2 \cdot H_2O)$	$SrO_2 \cdot 8H_2O$
$Li_2O_2 \cdot H_2O_2 \cdot 2H_2O$	$K_2O_2 \cdot 2H_2O_2$	$SrO_2 \cdot 2H_2O_2$
$Li_2O_2 \cdot 2H_2O_2$	$(K_2O_2 \cdot 4H_2O_2)$	

Na_2O_2	CaO_2	BaO_2
		$BaO_2 \cdot 8H_2O$
$Na_2O_2 \cdot 2H_2O$	$CaO_2 \cdot 8H_2O$	$BaO_2 \cdot H_2O_2$
$Na_2O_2 \cdot 6H_2O$	$CaO_2 \cdot 2H_2O_2$	$BaO_2 \cdot 2H_2O_2$
$Na_2O_2 \cdot 8H_2O$		
$Na_2O_2 \cdot H_2O_2$		
$Na_2O_2 \cdot 2H_2O_2$		
$Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$		

Table 3. Some physical and chemical properties of elements in Group II a and II b.

	Be	Mg	Ca	Sr	Ba	Zn	Cd	Hg
Electronegativity (2)	1.5	1.2	1.0	1.0	0.9	(1.7)	(1.7)	(1.7)
Ionic radii Å Goldschmidt (16)	0.34	0.78	1.06	1.27	1.43	0.83	1.03	1.12
Ionic radii Å, Pauling (2)	0.31	0.65	0.99	1.13	1.35	0.74	0.97	1.10
Atomic radii Å (17)	0.89	1.36	1.74	1.91	1.98	1.25	1.41	1.44
Tetrahedral covalent radii Å (2)	1.06	1.40	—	—	—	1.31	1.48	1.48
Ionisation energies $Me \rightarrow Me^{2+}$ kcal/mole (14, 15)	634	523	414	384	349	629	595	670

this is not so pronounced for the lighter atoms. From the ionisation potentials (14, 15) of these atoms it appears that large energy amounts are needed to completely remove two electrons (Table 3). This energy sacrifice is partly compensated by energies liberated when the ions formed are hydrated or built into an ionic lattice.

compounds (H_2O_2).

	Covalent peroxides		Peroxo acids				
VIII	Ib	IIb	IIIb	IVb	Vb	VIb	VIIb
			(HBO_3)	$H_2C_2O_6$	HNO_4	—	—
			H_4AlO_6	—	H_3PO_5	$H_2S_2O_8$	—
($FeO_2 \cdot xH_2O$ $CoO_2 \cdot xH_2O$ $NiO_2 \cdot xH_2O$)	CuO_2	ZnO_2	—	$H_2Ge_2O_7$	—	—	—
—	—	CdO_2	—	$H_2Sn_2O_7$	—	—	—
—	—	HgO_2	Tl_2O_4	$Pb_2O_5 \cdot xH_2O$	—	—	—

However, the following general rule applies: As the elements in Group IIa become lighter and smaller, the covalent character grows more pronounced.

Zinc and cadmium have many chemical resemblances to beryllium and magnesium, although the enhanced deformability of the underlying 18-electron arrangement renders all compounds of the former elements more covalent.

Mercury differs markedly in chemical respect from zink and cadmium. The mercuric (II) compounds are generally typically covalent.

Experimental methods

Preparation methods

The various compounds were prepared by conventional methods. Generally the compounds were precipitated from a metal salt solution in hydrogen peroxide by adding alkali. The concentrations of metal salt, hydrogen peroxide or alkali, as well as the temperature were varied to obtain the compound desired. In some cases peroxides were prepared by treating an oxide with hydrogen peroxide solution.

X-ray methods

X-ray powder diffraction methods as well as single crystal methods were used (18, 19, 20, 21, 22, 23, 24). Intensities were measured visually and in some cases photometrically or by Geiger counter tubes.

Usual corrections were applied (18, 22, 23, 24). The intensities were thus corrected by the appropriate Lorenz and polarization factor, in some cases also by an absorption factor (25). When comparing the structure factors, the observed factor was corrected for thermal vibration by an empirical factor.

Fourier summations were carried out by means of a Hägg-Laurent machine (26) and of an Alwac 3-E digital computer (27, 28). Structure factors (29) were generally computed by desk counting machines. In some cases, however, the Alwac 3-E computer (30, 31) was employed. Atomic form factors were taken from Landolt-Börnstein (32, 33, 34) and from Vand *et al.* (35).

The accuracy was calculated using Cruickshank's method (36) in two cases (N5, N7), and by the least square method in one case (37) (N1).

Table 4. Peroxy compounds of Group IIa and IIb elements established by the present author.

Mg
MgO_2

Ca
CaO_2
$CaO_2 \cdot 8H_2O$
$\alpha\text{-}CaO_2 \cdot 2H_2O_2$
$\beta\text{-}CaO_2 \cdot 2H_2O_2$*

Sr
SrO_2
$SrO_2 \cdot 8H_2O$
$SrO_2 \cdot H_2O_2$*
$\alpha\text{-}SrO_2 \cdot 2H_2O_2$
$\beta\text{-}SrO_2 \cdot 2H_2O_2$*

Ba
BaO_2
$BaO_2 \cdot 8H_2O$
$BaO_2 \cdot H_2O_2$
$BaO_2 \cdot H_2O_2 \cdot 2H_2O$*
$\alpha\text{-}BaO_2 \cdot 2H_2O_2$
$\beta\text{-}BaO_2 \cdot 2H_2O_2$*
$\gamma\text{-}BaO_2 \cdot 2H_2O_2$*

Zn
ZnO_2

Cd
CdO_2

Hg
$\alpha\text{-}HgO_2$
$\beta\text{-}HgO_2$*

Infrared methods

Infrared absorption spectra of some peroxide compounds were obtained by a Perkin-Elmer infrared spectro-photometer (N9). The samples were either suspended in hexachlorobutadiene or mixed with potassium bromide and pressed to a disc (38).

The formation of the peroxy compounds formed by elements in Group IIa and IIb

The compounds were prepared as described in the original papers N1–N7.

The existence of the peroxy compounds listed in Table 4 was proved. Those not earlier established are marked with an asterisk. Other peroxy compounds in these systems, though mentioned in literature, probably do not exist.

The structures of the peroxy compounds formed by elements in Group IIa and IIb

The structures of the anhydrous peroxides of Group IIa and IIb elements

Among the elements in Group IIa, barium, strontium and calcium peroxides crystallize with the calcium carbide structure (39, 40, 41, 42, 43).

This structure has a tetragonal body-centered elementary cell, space group I 4/mmm No. 139 (41). (To show the resemblance to the rock salt structure some authors quote a larger face centered cell (41)). The metallic ions can be placed in the position 0,0,0, while the metalloid atoms are placed in $\frac{1}{2},\frac{1}{2},z$ and $\frac{1}{2},\frac{1}{2},\bar{z}$. The elementary cell dimensions of the three peroxides are given in Table 5. The metallic ions are surrounded by six peroxide ions, forming an octahedron (see Fig. 4). The metallic

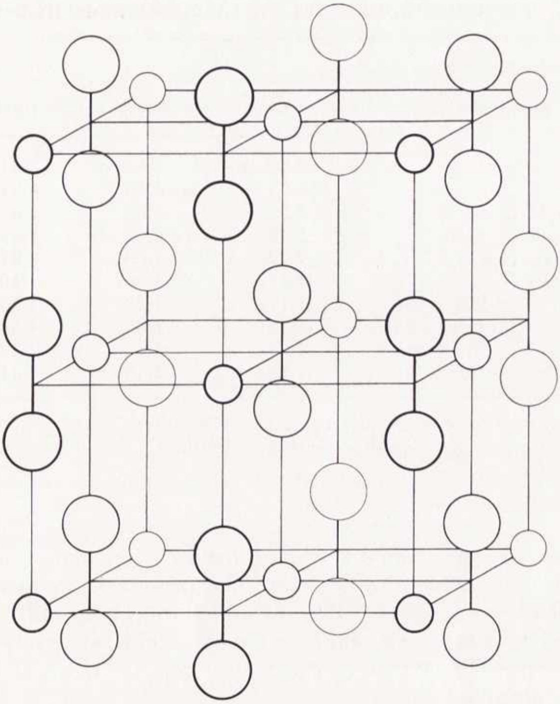


Fig. 4. The calcium carbide structure. Face centered cell.

ions are then in contact with ten oxygen atoms. The distance from the metallic ion to two of the latter is somewhat shorter than to the other eight (41). (See Table 5.)

An ionic structure with coordination number ten is stable only if all ions have about the same size (2). In this case only the heavier elements of Group IIa can form peroxides with the calcium carbide crystal structure. In the series BaO_2–SrO_2–CaO_2, the structure stability decreases markedly from Ba to Ca, which appears i.a. when comparing the dissociation pressures of the compounds. At 100°C it is about 10^{-13} atm for BaO_2 (44), about 0.1 atm for SrO_2 (45) and about 80 atm for CaO_2 (46).

The *a*-axes of calcium peroxide and strontium peroxide are of the same length (see Table 5). This possibly indicates contact between the oxygen atoms in the calcium peroxide lattice, and explains the high dissociation pressure of the compound and its reactivity (43).

In Table 5, the size of the peroxide group has been calculated by using the ionic radii of Goldschmidt (10) and Pauling (2). No correction has been made for the change in coordination number from the standard value of six (2). The oxygen radii calculated from SrO_2 and BaO_2 according to Goldschmidt show the best agreement, but the absolute values obtained are certainly too small. On the other hand, the agreement between the corresponding values obtained according to Pauling is not so good, but they are of the correct magnitude. Further, from these values it appears that there is in fact anion contact in calcium peroxide, the observed oxygen–oxygen packing distance being 2.92 Å, while the predicted distance is $(1.49 + 1.44) = 2.93$, if the radius in the *a*-direction only is used in the calculation.

Table 5. Crystallographic data for the alkaline earth peroxides.

Unit cell dimensions, interatomic distances and ionic radii		CaO_2	SrO_2	BaO_2
a		3.56 Å	3.55 Å	3.81 Å
c		5.95	6.55	6.84
Me–O	(2 dist.)	2.23	2.53	2.68
Me–O	(8 dist.)	2.62	2.62	2.79
O–O	(4 dist.)	2.92	3.08	3.31
O–O	(1 dist.)	(1.49)	(1.49)	1.49
r_0*	(c-direction)	(1.17)	1.26	1.25
r_0*	(a-direction)	(1.56)	1.35	1.36
r_0**	(c-direction)	(1.24)	1.40	1.33
r_0**	(a-direction)	(1.63)	1.49	1.44

* Ionic radius of oxygen calculated according to Goldschmidt.

** Ionic radius of oxygen calculated according to Pauling.

The interatomic distances in CaO_2 and SrO_2 are calculated on the assumption of an oxygen–oxygen distance of 1.49 Å in a peroxide group.

The calcium peroxide structure can be stabilized by replacing some of the peroxide ions by superoxide ions, which are shorter. The presence of superoxide ions in the peroxide lattice has been shown by Brosset and Vannerberg (43).

The limiting radius ratio for a stable calcium carbide structure is not very easy to calculate. However, if contacts in the z-direction are disregarded, the following expression can be obtained

$$r_{\text{kation}} + r_{\text{anion}} = \sqrt{\frac{a^2}{2} + \frac{d^2}{4}}$$

$$2 \cdot r_{\text{anion}} < \sqrt{\frac{a^2}{2} + \left(\frac{c}{2} - d\right)^2}\,.$$

a and c being the lengths of the axes and d the distance between the oxygen atoms in a peroxide group.

$$\frac{r_k}{r_a} > 2\sqrt{\frac{2+\left(\frac{d}{a}\right)^2}{2+\left(\frac{c}{a}-\frac{2d}{a}\right)^2}} - 1; \quad \frac{r_k}{r_a} > 0.70 \quad \begin{array}{l} \frac{c}{a} = 1.84 \\ \frac{d}{a} = 0.42. \end{array}$$

The values for c/a and d/a correspond to SrO_2. If r_a is assumed to be 1.46 Å then r_k must be larger than 1.02 Å, i.e. somewhat greater than the crystal radius of calcium.

The formula can be tested on the superoxides of the heavier alkali metals, which also crystallize with the calcium carbide structure (47, 48, 49), while sodium superoxide crystallizes with a disordered pyrite structure (50, 51, 52). The limiting radius ratio for a stable alkali superoxide with calcium carbide structure would be

$$\frac{r_k}{r_a} > 0.66 \qquad \frac{c}{a} = 1.66 \qquad \frac{d}{a} = 0.32.$$

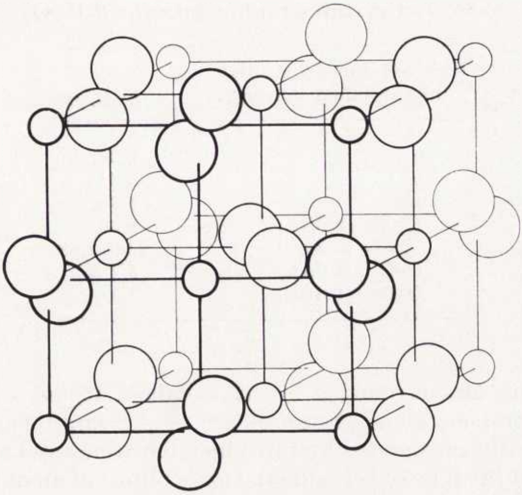


Fig. 5. The pyrite structure.

The data are obtained from the crystal structure of KO_2 (49). From this structure the oxygen radius in the x-direction is found to be $(2.92 - 1.33) = 1.59$ Å. Hence the cation radius must be larger than $0.66 \cdot 1.59 = 1.05$ Å. This value is larger than the ionic radius of sodium, which is only 0.95 Å. Accordingly sodium superoxide cannot be expected to crystallize with the calcium carbide structure.

The ionic radii of magnesium, zinc and cadmium are still smaller than that of calcium. The peroxides consequently cannot crystallize with the calcium carbide structure. Instead, magnesium, zinc and cadmium peroxide are isostructural with pyrite (N1, N2, N3).

The elementary cell of pyrite is cubic (53). The space group is Pa3 No. 205. The metallic atoms can be placed in the positions $0,0,0$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$ or $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; $0,\frac{1}{2},0$; $0,0,\frac{1}{2}$; the metalloid atoms in $\pm\,(x,x,x;\ \frac{1}{2}+x,\frac{1}{2}-x,\bar{x};\ \bar{x},\frac{1}{2}+x,\frac{1}{2}-x;\ \frac{1}{2}-x,\bar{x},\frac{1}{2}+x)$ (see Fig. 2 and Table 6).

Table 6. Crystallographic data for MgO_2, ZnO_2 and CdO_2

Unit cell dimensions, interatomic distances, ionic and covalent radii	MgO_2		ZnO_2		CdO_2	
a	4.84 Å		4.87 Å		5.27 Å	
Me–O (6 dist.)	2.08		2.10		2.29	
O–O (3 dist.)	2.88	3.01	2.90	3.02	3.18	3.29
O–O (1 dist.)	1.50		1.48		1.50	
r_0*	1.30		1.27		1.26	
r_0**	1.43		1.36		1.32	
r_0*** (Me–O)	0.68		0.79		0.81	
r_0*** (O–O)	0.75		0.74		0.75	

* Ionic radius of oxygen calculated according to Goldschmidt.

** Ionic radius of oxygen calculated according to Pauling.

*** Tetrahedral covalent radius of oxygen.

Table 7. Crystallographic data for β-HgO_2

Unit cell dimensions and interatomic distances	β-HgO_2
a	6.08 Å
b	6.01
c	4.80
Hg–O (2 dist.)	2.06
Hg–O (4 dist.)	2.66–2.68
O–O (4 dist.)	3.2–3.5
O–O (1 dist.)	1.5

The metallic atoms are surrounded by six metalloid atoms, which form an octahedron. All six metal–metalloid distances are of the same length. The metalloid atoms are tetrahedrally surrounded by three metallic atoms and one metalloid atom. If it is assumed, that in an ionic peroxide the ionic radius of an oxygen atom is 1.4 Å, only metals with ionic radii larger than $1.4 \cdot (\sqrt{2} - 1) = 0.6$ Å can be expected to crystallize with the pyrite structure. As is clear from Table 3, magnesium, zinc and cadmium have ionic radii greater than this value but less than the ionic radius of calcium. As mentioned above, the latter is the smallest cation found in a peroxide with calcium carbide structure.

The anhydrous peroxide of magnesium, zink or cadmium has not been obtained. By preparation from water solutions, precipitates have been obtained, which have small crystallite sizes and great ability to adsorb water (N1, N2, N3).

Beryllium has an ionic radius much smaller than 0.6 Å needed for the pyrite structure. Nor has any beryllium peroxide with the pyrite structure been reported. Beryllium does not seem to form any kind of peroxides at all (54).

Mercury forms two peroxides, α- and β-HgO_2 (N4). Of these, only the structure of the latter is known in detail (N4).

β-Mercuric peroxide crystallizes with orthorhombic symmetry. The space group is Pbca No. 61. The unit cell dimensions and interatomic distances are given in Table 7. The mercury atoms and the peroxide groups form infinite zig-zag chains extended along the c-axis. The different chains are bonded together by van der Waals' forces and possibly by weak ionic bonds.

In the series BaO_2–SrO_2–CaO_2–MgO_2–ZnO_2–CdO_2–HgO_2 there is a smooth transition in bond character from ionic to covalent bonds.

The first three peroxides crystallize with the calcium carbide structure. The bonds in such a structure must be predominantly ionic. The peroxides of magnesium, zinc and cadmium crystallize with the pyrite structure. This structure admits resonance between ionic and covalent bonds. In magnesium peroxide the bonds are certainly ionic but in the peroxides of zinc and cadmium there may be a considerable contribution of covalent bonds. β-Mercuric peroxide, on account of its structure, is certainly dominated by covalent bonds.

The structures of the peroxide hydrates of Group IIa and IIb elements

Only one kind of peroxide hydrate has been well characterized, namely the octahydrate (N5). This is formed by calcium, strontium and barium but not by magnesium or any of the Group IIb elements.

The octahydrate structure consists of chains

$$-O_2^{2-}-(H_2O)_8-O_2^{2-}$$

held together by strong hydrogen bonds (N5). These chains are linked into a three-dimensional network by the metallic ions and by weak hydrogen bonds.

Every peroxide group is bonded by hydrogen bonds to eight water molecules, while the water molecules are bonded by hydrogen bonds to one peroxide group and to two other water molecules. Furthermore, every water molecule is bonded to a strontium ion.

Each water molecule accordingly forms three hydrogen bonds and is in addition bonded to a strontium atom. This is to be expected. An oxygen atom in a peroxide group, however, forms four hydrogen bonds of equal strength. An attempt to explain this has been made in the original paper (N5).

The metallic ions are situated at the centre of a nearly regular Archimedean antiprism, formed by eight water molecules.

The reason for the non-existence of $MgO_2 \cdot 8H_2O$ is certainly due to the smallness of the Mg^{2+} ion. In the discussed structure, the relation between the metallic ion radius and the radius of the water molecule must be

$$\frac{r_{M}^{2+}}{r_{H_2O}} > \sqrt{2 + \frac{\sqrt{2}}{2}} - 1 \qquad \frac{r_{M}^{2+}}{r_{H_2O}} > 0.645$$

to prevent contact between the water molecules. Thus, if 1.40 Å is the radius of a water molecule (55) no cation with a radius less than $1.40 \cdot 0.645 = 0.90$ Å can form a stable peroxide octahydrate with the $SrO_2 \cdot 8H_2O$ structure; this excludes the Mg^{2+} ion.

It is interesting to note that if the metallic ions really were cubically surrounded by eight water molecules, as suggested by Natta (56), the stability limit would be $1.40 \cdot 0.732 = 1.02$ Å. Calcium peroxide octahydrate could then be expected to be unstable, which is not the case.

The peroxide octahydrates are rather stable compounds. The calcium peroxide octahydrate decomposes at atmospheric conditions in a couple of days, but the strontium or barium compounds are stable for years in normal air. This is in agreement with the structure. Here, the cations are surrounded by a suitable number of water molecules. The water molecules and the peroxide ions are firmly bonded to each other by hydrogen bonds. The angles between the bonds seem favourable. But the main reason for the stability is the effective isolation of every peroxide group. There can be no effective electron transport from one peroxide group to another and hence no decomposition of the peroxide groups.

Magnesium, zinc and cadmium have been reported to form a number of peroxide hydrates (N1, N2, N3). The present author has showed, however, that such "hydrates" contain no strong hydrogen bonds (N9) and that the corresponding powder photographs contain only the pattern of the anhydrous peroxide, with very broad lines, indicating a small crystallite size (N1, N2, N3). It can then be concluded that the "hydrates" consist of small crystallites of the peroxides, which have adsorbed water molecules on the surface.

The structures of the peroxide hydroperoxidates

The peroxide monohydroperoxidates

Only the strontium and barium monohydroperoxidates (Sr or $BaO_2 \cdot H_2O_2$) have been characterized (N6, N7). They are probably isomorphous, as their X-ray powder patterns show great resemblance. The structure of the barium compound has been determined (N6).

The structure consists of barium and hydroperoxide ions. The latter are linked by hydrogen bonds into helix chains. All hydrogen atoms are involved in bond formation. The periodic unit of the chains contains four HO_2^- ions. The length of the periodic unit is equal to the length of the b-axis, i.e. 9.46 Å. Illustrations of the helix chain can be found in N6. The formula of the chain can be written $(HO_2)_{4n}^{4n-}$. Bond lengths and angles between bonds are tabulated in Table 9.

The helix chains are linked into a three-dimensional network by the barium ions.

The peroxide dihydroperoxidates

Peroxide dihydroperoxidates $MeO_2 \cdot 2H_2O_2$ are formed by calcium, strontium and barium. Three modifications, α, β and γ, have been established (Table 5) (N7, N8). The corresponding structures consist of metallic ions and peroxide groups. The peroxide groups seem to be bonded together by hydrogen bonds into short chains of the type

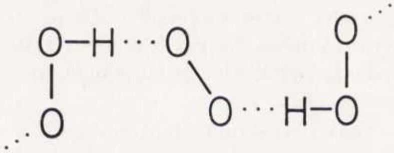


Fig. 6. The unit chain in the dihydroperoxidates.

The three modifications differ by the way these chains are linked together. The lengths of the hydrogen bonds and angles between bonds are tabulated in Table 9.

The α-arrangement

In this arrangement the short chains are bonded together to form double chains:

$$O_2^{2-}\cdots(H_2O_2)_2\cdots O_2^{2-}\cdots(H_2O_2)_2\cdots$$

In the crystals these chains are extended parallel with [110]. Illustrations of the chain can be found in N7, N8, and below.

All hydrogen atoms are involved in bond formation. The α-arrangement is formed by calcium, strontium as well as barium peroxide dihydroperoxidates.

Table 8. Space group, elementary cell dimensions and densities of the earth alkaline peroxide dihydroperoxidates.

Compound	Space group	a Å	b Å	c Å	γ	d g/cm^3
α-$CaO_2 \cdot 2\,H_2O_2$	C 2/c No. 15	8.145 ± 0.005	5.675 ± 0.003	8.059 ± 0.005	101° 58′ ± 4′	2.553
β-$CaO_2 \cdot 2\,H_2O_2$	—	—	—	—	—	—
α-$SrO_2 \cdot 2\,H_2O_2$	C 2/c No. 15	8.262 ± 0.006	6.024 ± 0.004	8.050 ± 0.005	100° 32′ ± 8′	3.164
β-$SrO_2 \cdot 2\,H_2O_2$	C 2/c No. 15	7.715 ± 0.004	8.754 ± 0.005	6.015 ± 0.003	93° 40′ ± 2′	3.074
α-$BaO_2 \cdot 2\,H_2O_2$	C 2/c No. 15	8.454 ± 0.006	6.398 ± 0.004	8.084 ± 0.005	96° 32′ ± 4′	3.629
β-$BaO_2 \cdot 2\,H_2O_2$	C 2/c No. 15	8.18 ± 0.03	9.03 ± 0.04	6.35 ± 0.03	95° 40′ ± 18′	3.38
γ-$BaO_2 \cdot 2\,H_2O_2$	Pbca No. 61	16.837 ± 0.014	6.407 ± 0.006	8.005 ± 0.007	—	3.651

The β-arrangement

In this arrangement the short peroxide chains are bonded together to form two-dimensional nets. In the crystals these peroxide layers are extended parallel with the (100) plane. Diagrams of the layers can be found in N8 and below. The β-arrangement is formed by strontium, barium and probably by calcium peroxide dihydroperoxidates.

The γ-arrangement

This arrangement is not so well established as those mentioned above. Actually there are two possible structures for this arrangement, but both contain short double chains linked into infinite layers. In the crystals these layers are parallel with the (001) plane. Diagrams of the layers can be found in N8 and below. The γ-arrangement is formed only by barium peroxide dihydroperoxidate.

From calculations of the densities (Table 8) it is obvious that the chains in α-arrangement are more densely packed than the layers in the β-arrangement. The layers of the γ-arrangement, however, seem to be as closely packed as that of the α-arrangement.

The hydrogen bonds

The hydrogen bond lengths, as well as the angles between the peroxide axes and the hydrogen bond directions found in these structures are tabulated in Table 9. In this table some of the azimuthal angles between two hydrogen bond directions are also included. In Table 10 the angles between two hydrogen bonds can be found.

As can be found from their lengths, the hydrogen bonds are of medium strength (57). The angles between the hydrogen bond directions and the peroxide axes make it probable that the bonds are formed in the direction of a free electron pair. This result is to be expected by purely electrostatic reasons (58) and also because it must increase the dislocation energy (59).

The peroxide group can form hydrogen bonds in several different ways.

The arrangement

$$\cdots\mathrm{O}\text{—}\mathrm{O}\cdots$$

Table 9. Hydrogen bond lengths and angles between bonds for the hydrogen bond type O–O ··· O–O.

Compound	Determination method	Bond length Å	Angle between hydrogen bond and peroxide axis	Azimuthal angle between hydrogen bond and hydrogen bond
$BaO_2 \cdot H_2O_2$	cryst.	2.3, 2,7	73°, 101°, 116°, 120°	110°, 118°
$BaO_2 \cdot H_2O_2$	infrared	2.60, (2.69)		
α-$SrO_2 \cdot 2\,H_2O_2$	cryst.	2.54, 2.67	88°, 103°, 107°, 107°	44°, 123°
β-$SrO_2 \cdot 2\,H_2O_2$	cryst.	2.56, 2.64	89°, 96°, 110°, 111°	47°, 128°
α-$BaO_2 \cdot 2\,H_2O_2$	cryst.	2.4, 2.8	90°, 100°, 115°, 115°	
α-$BaO_2 \cdot 2\,H_2O_2$	infrared	2.59, (2.70)		
β-$BaO_2 \cdot 2\,H_2O_2$	cryst.	2.5, 2.8	85°, 95°, 100°, 120°	
γ-$BaO_2 \cdot 2\,H_2O_2$	cryst.	2.3–2.9	70°–140°	
γ-$BaO_2 \cdot 2\,H_2O_2$	infrared	2.60, (2.71)		

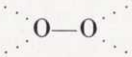
Table 10. The angles between the hydrogen bonds formed by one oxygen atom.

Compound	Angle between hydrogen bonds
α-$SrO_2 \cdot 2\,H_2O_2$	130°
β-$SrO_2 \cdot 2\,H_2O_2$	127°
α-$BaO_2 \cdot 2\,H_2O_2$	140°
β-$BaO_2 \cdot 2\,H_2O_2$	135°

Table 11. Hydrogen bond lengths and angles between bonds in $SrO_2 \cdot 8\,H_2O$.

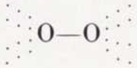
Species	Determination method	Bond length Å	Angle between hydrogen bond and peroxide axis or hydrogen bond	Azimuthal angle between hydrogen bond and hydrogen bond
$H_2O \cdots O_2^{2-}$	cryst.	2.66	106°3, 106°3 101°1, 86°4	38°
$H_2O \cdots H_2O$	cryst.	2.71	106°3, 90°	—
$H_2O \cdots H_2O$	cryst.	2.84	101°1, 90°	—
$H_2O \cdots O_2^{2-}$	infrared	2.67	—	—
$H_2O \cdots H_2O$	infrared			
$H_2O \cdots H_2O$	infrared	2.83	—	—

is found both in the monoperoxidates and in the diperoxidates. The arrangement



O—O

is found in solid hydrogen peroxide and in the diperoxidates. Finally, the arrangement



O—O

is found in the peroxide octahydrate.

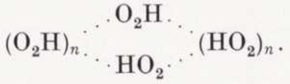
The first two arrangements would be expected to give the strongest bonds. The infrared and crystallographic data also support this view.

The idealized structures of the hydroperoxidates

In a series of publications in Acta Crystallographica (60–66), Wells has pointed out the dependence of the structure formed by the hydrogen bonds on the stoichiometric relation H/O. For the ion $(O_2 \cdot H_2O_2)^{2-}$ this relation is 1/2, for $(O_2 \cdot 2H_2O_2)^{2-}$ 2/3, and for H_2O_2 1/1.

A compound with the H/O relation 1/2 can form only two possible structures, a closed ring or an infinite chain

$$\cdots HO_2 \cdots HO_2 \cdots HO_2 \cdots$$



$$(O_2H)_n \begin{matrix} \cdot O_2H \cdot \\ \cdot HO_2 \cdot \end{matrix} (HO_2)_n.$$

In $BaO_2 \cdot H_2O_2$ a helical chain has been found. If it is now assumed that another hydrogen atom is attached to every second oxygen atom in the $\cdot HO_2 \cdot HO_2 \cdot HO_2 \cdot$ chain, this hydrogen atom can bond the helical chains into an infinite three dimensional lattice. The lattice now arrived at is the structure of hydrogen peroxide (65).

When the relation H/O is 2/3, there are many possible structures. However, this discussion will be limited to structures which contain the building units

$$H–O–O–H \cdots O–O \cdots H–O–O–H,$$

which can be written

$$H–R–O–O–R–H. \quad R = –O–OH \cdots$$

As it is an empirical rule, that the oxygen atoms denoted by R do not form any more hydrogen bonds, the ratio H/O is 1/1.

The building units can form a three-connected net in the following way

The simplest extended three-connected arrangement is the double chain.

The chain called (a) by Wells (63) is in fact the idealized α-structure which can be schematized as in Fig. 7. (N7, N8)

Fig. 7. The idealized structure of the anion in $\alpha\text{-}MeO_2 \cdot 2H_2O_2$.

The next arrangement in order of simplicity is the two-dimensional net; Net 1 according to Wells (60). This is the idealized structure of the β-compounds (N7, N8)

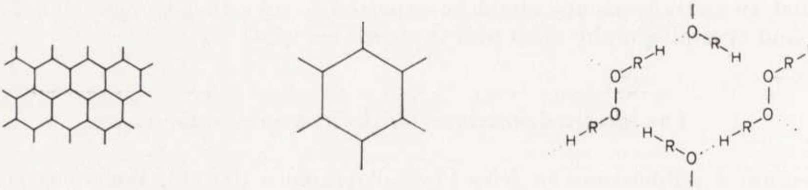


Fig. 8. The idealized structure of the anion in β-$MeO_2 \cdot 2H_2O_2$.

The idealized structure of γ-BaO_2 $2H_2O_2$, alternative I, (N8) contains a two-dimensional net which is denoted by Wells as Net 3 (60).

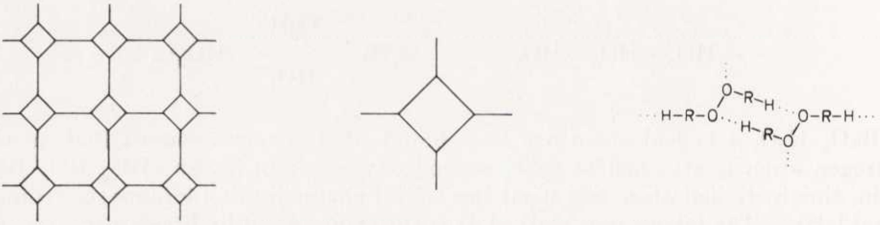


Fig. 9. The idealized structure of the anion in γ-$BaO_2 \cdot 2H \cdot O$ (Alternative I).

The alternative II is slightly curious, as it contains 10- and 2-gons in equal portions. The result is a hexagonal net, Net 1.

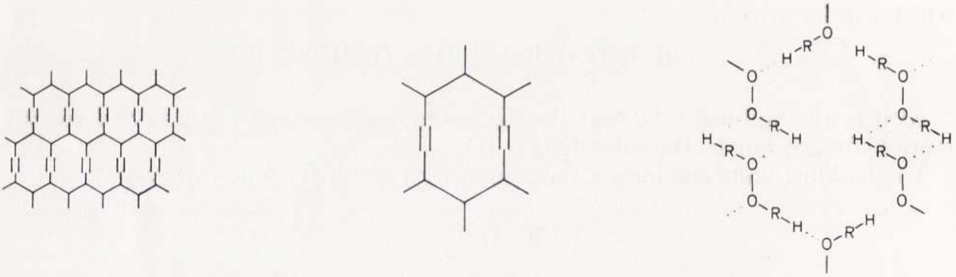
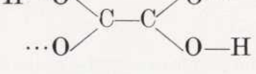


Fig. 10. The idealized structure of the anion in γ-$BaO_2 \cdot 2H_2O_2$ (Alternative II).

Although the treatment of Wells is very useful for the understanding of a hydrogen-bonded structure, in most cases it is impossible to predict a structure in this way. There are generally several structures to choose between.

Finally it will be pointed out that the repeating unit in oxalic acid is



This unit has great resemblance to the peroxide dihydroperoxidates. Anhydrous oxalic acid also crystallizes in two forms, one containing infinite chains, the other containing two-dimensional nets, the latter of the type Net 1 (Wells 50) (2).

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NILS-GÖSTA VANNERBERG

The formation and structure of magnesium peroxide

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1959

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The formation and structure of magnesium peroxide

By NILS-GÖSTA VANNERBERG

With 1 figure in the text

Introduction

According to literature, experiments to prepare magnesium peroxide have given a number of compounds with varying composition. The anhydrous peroxide has been prepared by Kleinberg and Schechter by adding solid potassium superoxide to a solution of magnesium nitrate in liquid ammonia (1). Oxidation of a metallic solution in liquid ammonia has also given small amounts of peroxide (2). It is also said to be produced when the oxide is heated in a quartz crucible in a stream of oxygen (3) or from the oxide when treated with oxygen in a discharge tube (4, 5). Some authors have prepared the peroxide from ether solutions of a magnesium compound and hydrogen peroxide (6, 7).

Makarov and Volnov (8) and Moles (9) have prepared magnesium peroxide hydrates by treating magnesium hydroxide with hydrogen peroxide of varying strength. On the other hand, peroxides do not seem to be formed when metallic magnesium is treated with hydrogen peroxide (10). If solutions of ammonia, a magnesium salt and hydrogen peroxide or sodium peroxide are mixed, compounds are obtained (11, 12) the formula of which can be written as

$$MgO_2 \cdot x Mg(OH)_2 \cdot y H_2O.$$

The maximum values of x and y are 3 and 2.

The decomposition of magneisum peroxide has been studied by several authors (12). According to Blumenthal (13) the dissociation pressure is 760 mm Hg at 88°C.

Hydrous magnesium peroxide is used as a stabilizing agent for alkaline peroxide solutions (14). This effect has been discussed by Pierron (15). Magnesium peroxide has also some medical use (12).

The behaviour of magnesium peroxide seems to be very similar to that of zink peroxide and cadmium peroxide (12). For the latter compound a structural investigation has been reported (16). According to this paper, only one crystalline cadmium peroxide phase was established, but the crystallite size of this phase varied strongly. When the crystallite size was small, and the overall surface correspondingly great, large amounts of water and hydroxide ions were adsorbed. At the minimum of crystallite size a compound with the formula $Cd(O_2)_{0.74}(OH)_{0.52}(H_2O)_{2.46}$ was obtained. With growing crystallite size the hydroxide and water content decreased. However, pure CdO_2 could not be prepared. The formula of the purest preparation was $Cd(O_2)_{0.88}(OH)_{0.24}$. It seemed probable that the same conditions would be valid in the magnesium system.

Experimental methods

Magnesium peroxide was prepared in the following manner. 1 g magnesium oxide was treated with 40 ml hydrogen peroxide solution of varying strength at 0 and 20°C. After some days the solid phase was filtered and washed with alcohol and ether. The percentage of magnesium was determined gravimetrically as pyrophosphate, while the peroxide proportion was determined by titration with permanganate. The water content was determined as rest of weight and the hydrogen peroxide or hydroxide ion percentage was calculated from the charge balance. (See Table 1.) X-ray powder photographs were taken of each sample in Guinier cameras.

Table 1. Composition of solid phases obtained by treating magnesium oxide with hydrogen peroxide solutions.

H_2O_2, % in liquid phase	Mg^{2+} %	O_2^{2-} %	OH^- %	H_2O_2 %	H_2O %	Solid phase
			I. 20°C			
1	41.0	—	57.4	—	1.6	$Mg(OH)_2$
5	40.5	0.6	56.0	—	2.9	$Mg(OH)_2$
10	35.2	23.6	24.2	—	17.0	$Mg(OH)_2 + MgO_2$
15	34.8	24.5	22.6	—	18.1	$Mg(OH)_2 + MgO_2$
30	34.1	40.3	4.9	—	20.7	MgO_2
85	33.1	43.6	—	9.5	13.8	MgO_2
			II. 0°C			
30	32.0	40.0	2.3	—	25.7	MgO_2

Experimental results

The X-ray investigation showed that only one crystalline phase exists besides magnesium hydroxide, but that the crystallite size of this phase was dependent upon the concentration of hydrogen peroxide used. Substances formed from weak hydrogen peroxide solutions showed small crystallite size. The solid phase is certainly pure magnesium peroxide. The crystallite size which was measured from the line broadening varies from about 30 Å to about 200 Å. As the overall surface increases with decreasing crystallite size, the amount of water adsorbed also increases (Table 1).

Those substances, which were prepared by treating magnesium oxide with concentrated hydrogen peroxide solutions, were brown coloured to some extent, indicating the presence of superoxide (17, 18). As the compounds are readily decomposed, a superoxide determination according to the usual volumetric or magnetic methods (19) is of doubtful value. However, a magnetic determination according to the Gouy method has given a qualitative evidence for the presence of superoxide ions. The percentage in the investigated preparations seemed not higher than two per cent $Mg(O_2)_2$.

The investigation of Makarov and Volnov

As mentioned above, Makarov and Volnov have also investigated the reaction between magnesium hydroxide and hydrogen peroxide (8). They have added magnesium hydroxide to hydrogen peroxide solutions and measured the percentage of magnesium ion in the liquid phase, plotting it against the hydrogen peroxide content in the same phase. At 0°C two peaks in the solubility curves appeared which, according to the authors, would explain the transitions $Mg(OH)_2 \rightarrow MgO_2 \cdot H_2O$ and $MgO_2 \cdot H_2O \rightarrow MgO_2 \cdot 0.5\,H_2O$. However, it must be very difficult in this system to separate the liquid and solid phase, because of the extremely small particle size in the latter. Thus the analyses cannot be considered as very accurate. Furthermore, a larger number of measuring points were desirable. Accounting to the error limits, which are easy to estimate from the data given by Makarov and Volnov, all but two of the measured points fall on a smooth curve.

As a consequence of the difficulty in separating the phases the method of Makorov and Volnov is not expected to give as reliable results in this system as for instance in the system Li_2O_2–H_2O–H_2O_2 (20).

In structure of magnesium peroxide

A peroxide compound suited for an X-ray investigation was obtained in the following way. A magnesium peroxide sample was treated for several days with 85% hydrogen peroxide in a water bath. The crystallite size after the treatment was about 200 Å. Its colour was white.

Analysis: $Mg^{2+} = 33.9\,\%$, $O_2^{2-} = 44.7\,\%$, $H_2O_2 = 6.1\,\%$, $H_2O = 15.3\,\%$.

This corresponds to the composition $MgO_2 \cdot 0.12\,H_2O_2 \cdot 0.61 H_2O$ and is the purest preparation of magnesium peroxide obtained by the author.

With the aid of this substance a structural investigation was performed. For the investigation a Debye Sherrer vacuum camera with LiF monochromator and a commercial Philips X-ray diffractometer were used. In the first case the intensity was recorded photometrically. Cu Kα radiation was used.

The X-ray powder pattern obtained could be indexed on the assumption of a cubic elementary cell with the edge length 4.839 ± 0.007 Å. Observed and calculated $\sin^2\theta$ values are tabulated in Table 2. No extra lines appeared. Systematic extinctions were found to be of the type $0kl$ absent when $k = 2n + 1$. This is characteristic for the space group No. 205 T_h^6–$Pa3$, which requires four formula units in the elementary cell. Four magnesium atoms can be placed in the positions $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; $0,\frac{1}{2},0$; $0,0,\frac{1}{2}$ or $0,0,0$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$ and eight oxygen atoms in $\pm(x,x,x;\ \frac{1}{2}+x,\ \frac{1}{2}-x,x;\ x,\frac{1}{2}+x,\frac{1}{2}-x;\ \frac{1}{2}-x,x,\frac{1}{2}+x)$. The structure factors and the intensity of the reflexions were then calculated for various values of x using ordinary formulae. (Table 3.) Best agreement between observed and calculated structure factors was found for the parameter value 0.089 (0.411).

According to the deduced structure, magnesium peroxide is isomorphous with cadmium peroxide and pyrite (FeS_2). The structures of these compounds contain discrete O_2 or S_2 groups. As is well known, these structures are geometrically closely related to that of rock salt, the centres of metalloid groups and the metallic atoms occupying the positions of sodium and chloride ions in the rock salt structure. The

Table 2. Observed and calculated $\sin^2\theta$ values for magnesium peroxide.

$h\,k\,l$	$10^4 \cdot \sin^2\theta_{obs}$	$10^4 \cdot \sin^2\theta_{calc}$
1 1 1	—	762
2 0 0	1018	1015
2 1 0. 1 2 0	1267	1269
2 1 1	1519	1523
2 2 0	2033	2030
2 2 1	2285	2284
3 1 1	2785	2792
2 2 2	3046	3046
2 3 0. 3 2 0	3298	3299
3 2 1. 1 2 3	3555	3553
4 0 0	4050	4060
4 1 0. 1 4 0 3 2 2	4320	4315
4 1 1	4564	4568
3 3 1	4816	4822
4 2 0	5069	5076
4 2 1. 1 2 4	5331	5330
3 3 2	—	5584
4 2 2	6107	6091
4 3 0. 3 4 0	6361	6345
4 3 1. 1 3 4	6611	6599
5 1 1 3 3 3	6833	6853

Table 3. Observed and calculated intensities and structure factors for magnesium peroxide.

$h\,k\,l$	I_{obs}[a] Photo.	I_{obs} G.M.	I_{calc} $x = 0.089$	F_{obs} G.M.	F_{calc} $x = 0.089$	
1 1 1	—	—	6.3	—	− 5.7	
2 0 0	240	294	291	53.6	53.3	
2 1 0. 1 2 0	63	58	60	19.1	−19.4	0.0
2 1 1	63	60	60	15.4	−15.3	
2 2 0	112	113	118	35.1	35.8	
2 2 1	7	8	6.1	7.2	− 6.3	
2 3 1	97	103	102	29.0	−28.9	
2 2 2	32	29	29	28.2	28.2	
2 3 0. 3 2 0	32	29	25	24.2	−22.4	0.0
3 2 1. 1 2 3	35	31	30	18.4	−18.2	1.2
4 0 0	—	2	1.7	9.2	8.4	
4 1 0. 1 4 0	7	6	3.0	7.3	− 9.0	0.0
3 2 2			5.3	7.3	− 8.4	
4 1 1	—	3	3.9	6.5	− 7.4	
3 3 1	26	27	31	19.7	−21.2	
4 2 0	14	9	8.1	16.3	15.6	
4 2 1. 1 2 4	—	3	3.0	6.7	5.7	−3.5
3 3 2	—	—	0.2	—	1.8	
4 2 2	17	26	19	16.9	16.7	
4 3 0. 3 4 0			6.4	14.4	−13.7	0.0
4 3 1. 1 3 4	64	67	9.1	11.5	−11.6	−0.8
5 1 1			62	27.6	−29.5	
3 3 3			7.4	17.2	−17.7	

[a] Corrected for the polarization in the monochromator crystal.

metallic atoms occupy the centres of octahedral groups of six metalloid atoms. Every metalloid atom has as neighbours three metallic and one metalloid atom forming a distorted tetrahedron (21).

In connection with the calculations, values of

$$\frac{\Sigma|I_c - I_o|}{\Sigma I_o} \quad \text{and} \quad \frac{\Sigma||F_c| - |F_o||}{\Sigma|F_o|}$$

were plotted as a function of x (Tables 4) (Fig. 1). The functions have minima at the same parameter value, which is $0.089\bar{4}$. As is clear from Fig. 1, it is possible to determine the oxygen–oxygen distance in a peroxide group very accurately. This is partly due to the fact that magnesium only contributes to the intensity of reflexions where $h + k = 2n$ and $k + l = 2n$. The value obtained, 1.498 Å, is in good agreement with published results. See Table 5.

Table 4. $\frac{\Sigma|I_c - I_o|}{\Sigma I_o}$, R and the oxygen–oxygen distance in a peroxide group calculated for different parameter values.

Parameter	$\frac{\Sigma\|I_c - I_o\|}{\Sigma I_o}$	$\frac{\Sigma\|\|F_o\| - \|F_c\|\|}{\Sigma\|F_o\|} = R$	O–O
0.088	0.063	0.046	1.475 Å
0.089	0.051	0.037	1.492
0.090	0.051	0.038	1.509
0.091	0.074	0.047	1.525

Table 5. The oxygen–oxygen distances in some peroxide compounds.

Compound	Bond length	Reference
H_2O_2	1.49 ± 0.02 Å	Abrahams *et al.* (22)
Na_2O_2	1.50 ± 0.03	Föppl (23)
BaO_2	1.49 ± 0.04	Abrahams *et al.* (24)
MgO_2	1.498 ± 0.014	This investigation
$SrO_2 \cdot 8H_2O$	1.48 ± 0.02	Vannerberg (25)
K_3CrO_8	1.49 ± 0.02	Stomberg (26)

The sample investigated contained a little amount of superoxide. As mentioned above, it is very difficult to get an accurate determination of the content, but magnetic measurements indicated that the percentage in this case did not exceed one per cent by weight. This implies that at most two per cent of the peroxide ions in the lattice might be replaced by superoxide ions. The distance between the oxygen atoms in the superoxide ions is 1.28 Å (28) while the same distance in a peroxide ion is 1.50 Å. An incorporation of two per cent superoxide ions in the lattice would alter the oxygen–oxygen distance by about 0.004 Å.

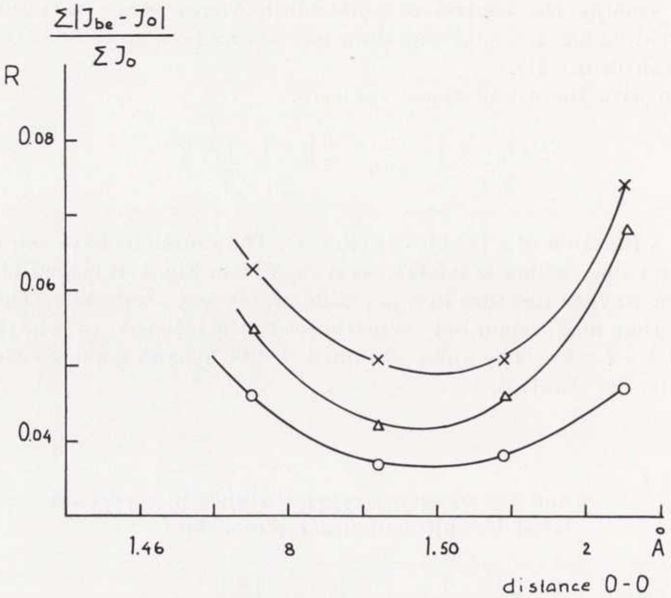

Fig. 1. $R\left(\frac{\Sigma\,||F_o|-|F_c||}{\Sigma\,|F_o|}\right)$ and $\frac{\Sigma\,|I_c - I_o|}{\Sigma\,I_o}$ as function of the distance between the oxygen atoms in magnesium peroxide.

× $\frac{\Sigma\,|I_c - I_o|}{\Sigma\,I_o}$ all reflexions included

△ $\frac{\Sigma\,|I_c - I_o|}{\Sigma\,I_o}$ only reflexion with $(\sin\theta)/\lambda < 0.5$ included

○ R all reflexions included

The parameter value obtained seems to be completely independent of the water content. A preparation which contained two water molecules per peroxide group gave, within the limits of error, the same relative integrated intensity as one which contained only half a molecule per peroxide group.

The standard deviation is calculated according to the least square method according to the formula.

$$\Delta x = \left(\frac{\Sigma\,(F_c - F_o)^2}{(m-n)\,\Sigma\left(\frac{\partial F_c}{\partial x}\right)^2}\right)^{\frac{1}{2}},$$

where Δx = the standard deviation
F_c = calculated structure factor
F_o = observed structure factor
m = number of different reflecting planes
n = number of independent variables (in this case = 1) (27).

This gives a standard deviation in the parameter value of 0.00085 and a deviation in the bond length of 0.014 Å.

The magnesium–oxygen distance is 2.08 Å, in good agreement with the corresponding distance in magnesium oxide, which is 2.10 Å.

SUMMARY

The system magnesium ion–hydrogen peroxide has been reinvestigated. Only one solid phase, namely magnesium peroxide, MgO_2, was found. It was isomorphours with pyrite, with $a = 4.839 \pm 0.007$ Å. The distance between the oxygen atoms in a peroxide group was found to be 1.498 ± 0.014 Å.

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Formation and structure of zinc peroxide

By NILS-GÖSTA VANNERBERG

Introduction

Experiments to prepare zinc peroxide have generally yielded hydrous compounds (1). An anhydrous zinc peroxide preparation has been obtained by Kleinberg *et al.* by adding potassium superoxide to a solution of zinc nitrate in liquid ammonia (2). A mixture of zinc and potassium peroxide, oxide and superoxide was obtained. Another attempt to prepare the anhydrous peroxide has been made by Ebler and Krause (3). They added an ether solution of diethylzinc to a dried solution of hydrogen peroxide in ether. However, the composition of the reaction product was $ZnO_2 \cdot 0.5H_2O$. An experiment by Nottebohm (4, 5) using solutions of zinc nitrate and hydrogen peroxide in concentrated ammonia yielded a product with the same composition.

Zinc oxide does not react with oxygen even at 300 atm (6), but small amounts of zinc peroxide are reported to have been prepared when oxygen reacted with zinc oxide in a discharge tube (7).

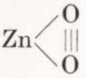
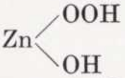
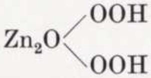
Preparations containing hydrous zinc peroxide have been obtained by several authors (1, 8, 9, 10, 11, 12) of which only the most important can be mentioned here. Two methods were usually employed. Either hydrogen peroxide was added to an alkaline zinc salt solution, or zinc oxide or hydroxide was treated with hydrogen peroxide solutions. The composition of the preparations varied from $3ZnO_2 \cdot 4Zn(OH)_2 \cdot 3H_2O$ (9) to $ZnO_2 \cdot 0.5H_2O$ (8). It does not seem to be possible to prepare anhydrous zinc peroxide by these methods. Addition compounds containing hydrogen peroxide have been reported (13).

On the basis of solubility measurements Makarov and Ladeinova (13, 14) claim to have proved the existence of the following peroxide compounds: $ZnO_2 \cdot 2H_2O$; $ZnO_2 \cdot 1.5H_2O$; $ZnO_2 \cdot H_2O$; $ZnO_2 \cdot 0.5H_2O$; ZnO_2; $ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$; $ZnO_2 \cdot H_2O_2$; $ZnO_2 \cdot 2H_2O_2$.

The investigation method of Makarov has lately been discussed by Vannerberg (15).

A large amount of technical preparation methods have been described and patented. A survey is given in Gmelin (16). Many of them can be found in pharmaceutical literature.

Zinc peroxide preparations are described as white (1) or yellow-white powder (8). According to Nottebohm (4) and Sjöström (12) they decompose already at 40°C but according to Foregget and Philip first at 170°C (17). The solubility in water at 20°C is very slight (17). On the other hand zinc peroxide is readily dissolved in strong acids, and under decomposition in strong bases (16).

Density determinations have given values between 1.5 and 3.0 g/cm³ (17, 18). A preparation with the formula $ZnO_2 \cdot H_2O$ is reported to give an X-ray powder photograph, which is different from that of ZnO (19). Older considerations about the constitution of zinc peroxide compounds assume formulae such as  $Zn\langle{}^{O}_{O}$ (4) and  $Zn\langle{}^{OOH}_{OH}$ or  $Zn_2O\langle{}^{OOH}_{OOH}$ (12, 20).

Zinc peroxide preparations have some pharmaceutical importance (16).

Methods of preparation and analysis

In the present investigation, zinc peroxide preparations have been obtained in two different ways, either by precipitating the compound from a solution of zinc nitrate in hydrogen peroxide with sodium hydroxide, or by treating zinc oxide with hydrogen peroxide. The zinc content in the preparations was determined gravimetrically as pyrophosphate while the peroxide content was determined by titration with potassium permanganate solution. The superoxide content was estimated magnetometrically

Table 1. The composition of the preparations obtained by precipitating a solution of $Zn(NO_3)_2$ in hydrogen peroxide by sodium hydroxide. The first column gives the hydrogen peroxide concentration in the liquid phase at equilibrium.

% H_2O_2 in the liquid phase	% Zn^{2+}	% O_2^{2-}	% OH^-	% H_2O	% H_2O_2	Solid phase
12.29	50.0	24.0	0.5	25.5	—	ZnO_2
4.39	51.4	21.3	4.1	23.2	—	,,
0.39	51.0	20.6	4.6	23.8	—	,,

Table 2. The composition of a precipitate dried at 120°C. The first column gives the concentration of hydrogen peroxide in the solution from which the precipitate was obtained. The magnetical susceptibility in the seventh column has been corrected for the diamagnetism of the Zn^{2+} (24), O_2^{2-} (25) and OH^- (24) ions and of the water molecules (21). The superoxide content has been calculated from the formula $\% O_2^- = \frac{100 \cdot \chi_{g\,cor}}{1300 \cdot 10^{-6}} \cdot 32$, where χ = magnetical susceptibility and $1300 \cdot 10^{-6}$ is the mol susceptibility at 20°C for a compound containing one single electron (21).

% H_2O_2 in the liquid phase	% Zn^{2+}	% O_2^{2-}	% OH^-	% H_2O	$\chi_g^{20°}$	$\chi_{g\,cor}^{20°}$	% O_2^-	Solid phase
0.39	59.1	16.3	12.0	10.0	$+0.75 \cdot 10^{-6}$	$+1.06 \cdot 10^{-6}$	2.6	ZnO_2

Table 3. The composition of the preparations obtained by treating zinc oxide by hydrogen peroxide solutions. The first column gives the hydrogen peroxide concentration at the start.

% H_2O_2 in the liquid phase	% Zn^{2+}	% O_2^{2-}	% OH^-	% H_2O	% H_2O_2	Solid phase
30.0	61.0	29.8	—	7.3	1.9	ZnO_2
6.0	62.1	29.0	1.5	7.4	—	,,
0.6	66.1	15.9	17.4	0.6	—	,,

according to the Gouy method (21). Only in heated preparations superoxide was encountered to measurable extent. The solid phases were identified with the aid of their X-ray powder photographs (Guinier method). After some preparatory work six syntheses were performed in manners given below.

Three solutions, each containing 1 g $Zn(NO_3)_2 \cdot 3H_2O$ in 50 ml of 1 %, 10 %, and 30 % hydrogen peroxide were precipitated with 50 ml 0.16 M NaOH each. The precipitates were allowed to stand for 24 hours and were then filtered, washed with the corresponding hydrogen peroxide solution, alcohol and ether and dried in a desiccator with phosphoric pentoxide at room temperature. Their compositions according to the analysis are given in Table 1. One of the precipitates was further dried at 120° in five hours and analyzed again. Besides, the magnetical susceptibility was measured to determine the superoxide content. The result can be found in Table 2.

Three samples of 1 g ZnO each were treated with 50 ml hydrogen peroxide solutions, containing 0.6 %, 6 %, and 30 %, respectively, for two weeks. The precipitates were then filtered off, washed with the corresponding hydrogen peroxide solution, alcohol and ether and dried in a desiccator with phosphoric pentoxide. The preparations were analyzed after a day. The results obtained are given in Table 3.

Experimental results

As can be shown from the tables, the best preparations of zinc peroxide are obtained if zinc oxide is treated with hydrogen peroxide. The preparation with the highest peroxide percentage corresponded to the formula $ZnO_2 \cdot 0.5H_2O$ reported by several authors (3, 4, 5, 8, 18). In the X-ray photographs of the preparations only one pattern appeared. The lines of this pattern were very broad, especially when the preparation contained large amounts of water and hydroxide ions. When the water content decreased, the lines narrowed.

The pattern belonged certainly to the phase ZnO_2. As the particle size of this phase varied, the surface area and the amount of adsorbed hydroxyl ions and water molecules also varied. The behaviour of zinc peroxide is accordingly the same as that of magnesium peroxide (15).

The structure of zinc peroxide

With the aid of the preparation which contained most ZnO_2 (from ZnO + 30 % H_2O_2) a structural investigation was performed. The powder pattern of the prepara-

Table 4. Observed an calculated $\sin^2\theta$ values for ZnO_2.

h k l	$10^4 \cdot \sin^2\theta_{obs.}$	$10^4 \cdot \sin^2\theta_{calc.}$
1 1 1	755	752
2 0 0	1007	1002
2 1 0.1 2 0	1255	1253
2 1 1	1508	1503
2 2 0	2005	2004
2 2 1	2255	2255
3 3 1	2754	2756
2 2 2	3014	3006
3 2 0.2 3 0	3257	3257
3 2 1.1 2 3	3505	3507
4 0 0	4004	4008
4 1 0.1 4 0	—	4259
3 2 2		
4 1 1	—	4509
3 3 1	4756	4760
4 2 0	5008	5010
4 2 1	—	5261
3 3 2	—	5511
4 2 2	6005	6012
4 3 0.3 4 0	—	6263
4 3 1	—	6513
5 1 1	6754	6764
3 3 3		

Table 5. Observed and calculated intensities for ZnO_2.

h k l	$I_{obs.}$	$I_{calc.}$
1 1 1	71	74
2 0 0	121	118
2 1 0.1 2 0	4.7	5.6
2 1 1	4.8	6.0
2 2 0	61	58
2 2 1	—	0.6
3 3 1	65	62
2 2 2	19	18
3 2 0.2 3 0	2.6	2.6
3 2 1.1 2 3	2.6	3.0
4 0 0	3.4	4.9
4 1 0.1 4 0	—	0.3
3 2 2		0.5
4 1 1	—	0.4
3 3 1	26	24
4 2 0	20	19
4 2 1	—	0.3
3 3 2	—	0.0
4 4 2	14	18
4 3 0.3 4 0	—	0.6
4 3 1	—	0.9
5 1 1	32	28.1
3 3 3		6.3

tion was recorded by a commercial Philips X-ray diffraction unit, using filtered Cu radiation. The pattern could be indexed on the assumption of a cubic elementary cell with $a = 4.871 \pm 0.006$ Å. (Table 4.) The only systematic extinction was found for reflexions of the type $0kl$ when $k = 2n + 1$, accordingly the space group is Pa3 No. 205. This space group requires four formula units in the elementary cell. The calculated density is 5.6 g/cm³. The highest reported density is 3.0 g/cm³ (18). As the particle size is very small, it is doubtful whether better agreement can be obtained.

From intensity calculations it was found that the four zinc atoms could be placed in the positions $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2}$ or $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$ while the eight oxygen atoms could be placed in $\pm(x, x, x; \frac{1}{2}+x, \frac{1}{2}-x, x; x, \frac{1}{2}+x, \frac{1}{2}-x; \frac{1}{2}-x, x, \frac{1}{2}+x)$. The x parameter was varied until the best agreement between calculated and observed intensities was obtained (see Table 5), which occurred at the parameter value of 0.088 (0.412).

According to the results here above zinc peroxide is isostructural with cadmium and magnesium peroxide and with pyrite (22, 15). A description of the structure can be found in Wells Structural Inorganic Chemistry (23). The distance between the oxygen atoms in the peroxide group is 1.48 Å. This is in good agreement with earlier determinations (15). The uncertainty may be ± 0.03 Å. The distance between the zinc and oxygen atoms is 2.10 ± 0.01 Å.

SUMMARY

The system zinc ion–hydrogen peroxide has been reinvestigated. Only one solid phase, namely zinc peroxide, ZnO_2, was found. This was isomorphous with purite with $a = 4.871 \pm 0.006$ Å. The distance between the oxygen atoms in a peroxide group was found to be 1.48 ± 0.03 Å.

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On the formation and structure of cadmium peroxides

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On the formation and structure of cadmium peroxides

By NILS-GÖSTA VANNERBERG

With 1 figure in the text

The system cadmium ion – hydrogen peroxide has been reinvestigated. Only one solid phase with variable composition was found. The limiting compositions were $Cd(O_2)_{0.74}\,(OH)_{0.52}\,(H_2O)_{2.46}$ and $Cd(O_2)_{0.88}\,(OH)_{0.24}$. The structure of the phase with the last-mentioned composition has been studied. It proved to be isomorphous with pyrite, with $a = 5.273 \pm 0.003$ Å. In this phase small amounts of superoxide were also detected.

Such experiments as have been reported in the literature regarding the production of pure cadmium peroxide have given rise to products which might possibly have been double salts consisting of peroxides and hydroxides. By treating cadmium hydroxide with weak solutions of hydrogen peroxide Kuriloff (1) obtained a product with the composition $CdO_2Cd(OH)_2$. In a similar manner, with 30 % hydrogen peroxide solution, Eijkmann (2) got a product with a composition corresponding to the formula $4CdO_2Cd(OH)_2$. By adding an excess of 30 % hydrogen peroxide to a weakly ammoniacal cadmium sulfate solution Teletow (3) arrived at a product which he supposed to be $5CdO_2CdO3H_2O$.

The purpose of the present investigation has been to find out which phases are formed by precipitating cadmium salt solutions with hydrogen peroxide. Besides, it was of interest to establish whether disproportionating to oxide and superoxide occurs as has been proved to be the case with calcium peroxide (4).

After a few preparatory syntheses the following one was found to be well adapted to its purpose.

Cadmium nitrate was dissolved in hydrogen peroxide solutions of varying strength and temperature. The concentration of cadmium was in all cases 0.130 *M*, while three concentrations of hydrogen peroxide (0.20, 2.5 and 9.9 *M*) were chosen.

To 50 ml of a cadmium nitrate–hydrogen peroxide solution, 15 ml 0.10 *M* sodium hydroxide solution were added. This was done at 20°C and at 80°C. In this way six samples were obtained. These were analysed with respect to cadmium (Cd^{2+}), peroxide (O_2^{2-}) and superoxide (O_2^-).

The proportion of peroxide was determined by titration with potassium permanganate and subsequent correction for the amount of superoxide. The proportion of superoxide was determined gasometrically according to Kleinberg (5). Cadmium was determined by electrolysis, whilst the hydroxide and water content were obtained from the charge balance and by difference of weight, respectively.

From the measured percentages, which can be found in Tables 1 and 2, the following conclusions may be drawn. When the precipitation of the peroxide is carried out in weak solutions of hydrogen peroxide, a phase is formed which consists of about

Table 1. 20°C.

		H_2O_2 concentration at equilibrium		
		0.15 *M*	1.9 *M*	7.6 *M*
CdO_2	w. %	58.2	75.2	81.4
	mol. %	21.4	47.4	65.4
$Cd(OH)_2$	w. %	16.7	16.4	13.2
	mol. %	7.5	10.2	10.4
H_2O	w. %	24.1	8.4	3.6
	mol. %	71.1	42.5	23.3
$Cd(O_2)_2$	w. %	—	—	1.6
	mol. %	—	—	1.0
Approx. formula		$Cd(O_2)_{0.74} \cdot (OH)_{0.52} \cdot (H_2O)_{2.46}$	$Cd(O_2)_{0.82} \cdot (OH)_{0.36} \cdot (H_2O)_{0.74}$	$Cd(O_2)_{0.85} \cdot (OH)_{0.28} \cdot (O_2^-)_{0.02} \cdot (H_2O)_{0.30}$
Colour		yellow	gray-yellow	gray

Table 2. 80°C.

		H_2O_2 concentration at equilibrium		
		0.15 *M*	1.9 *M*	7.6 *M*
CdO_2	w. %	73.9	85.7	85.4
	mol. %	62.7	71.4	86.0
$Cd(OH)_2$	w. %	23.5	10.4	12.5
	mol. %	19.7	8.6	12.3
H_2O	w. %	2.6	2.9	—
	mol. %	17.6	19.3	—
$Cd(O_2)_2$	w. %	—	1.0	2.1
	mol. %	—	0.7	1.7

two and a half times as much peroxide as hydroxide. The composition of this product is similar to the composition of those mentioned in the references (1) and (3). Besides, the precipitates contained considerable quantities of water, probably in the form of a gel. At higher concentrations of hydrogen peroxide and higher temperatures the precipitates approach the composition $Cd(O_2)_{0.88} \cdot (OH)_{0.24}$ that may be formulated as $7CdO_2 \cdot Cd(OH)_2$ (Tables 1 and 2). In the latter product there are also small impurities of superoxide, as could be shown at examination for magnetic properties according to the Gouy method.

The substance $Cd(O_2)_{0.88} \cdot (OH)_{0.24}$ decomposes violently when rapidly heated, but on slow heating to 100°C the peroxide disproportionates in the same way as has been shown in connection with calcium peroxide according to the formula

$$3CdO_2 + 2H_2O \rightarrow 2Cd(OH)_2 + Cd(O_2)_2.$$

More details of this work will be published at a later date.

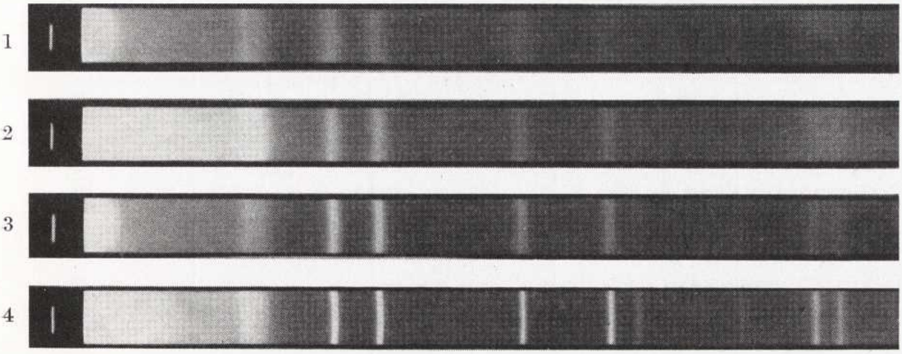

Fig. 1. Guinier photographs of products precipitated from solutions containing cadmium ions and hydrogen peroxide.

1. 20°C. 0.15 M H_2O_2
2. 20°C. 1.9 M H_2O_2
3. 20°C. 7.6 M H_2O_2
4. 80°C. 7.6 M H_2O_2

The products mentioned in Tables 1 and 2 were examined by the aid of powder photographs (Guinier method). In all cases the same pattern appeared. Only the diffraction breadths were different, so that samples containing much hydroxide and water have considerably wider lines than those rich in peroxide. No trace of cadmium hydroxide lines appeared. See Fig. 1. Consequently it seems that, although the compostition varies between $Cd(O_2)_{0.74} \cdot (OH)_{0.52} \cdot (H_2O)_{2.46}$ and $Cd(O_2)_{0.88} \cdot (OH)_{0.24}$, in the products formed by hydrogen peroxide and cadmium ions there is only one crystalline phase. The water is probably bound in the form of a gel, while, on the other hand, substitution of hydroxide ions in the peroxide lattice is not impossible. The varying diffraction breadths may be explained in terms of varying crystallite sizes.

In connection with the observation mentioned above it was of interest to investigate whether any intermediate phase, e.g. cadmium hydroxide, is formed by reaction of hydrogen peroxide with solid cadmium oxide. A sample of cadmium oxide was treated with 30 % hydrogen peroxide for a short time. On a powder photograph of the substance formed, there appeared, in addition to lines of cadmium oxide, lines from the above-mentioned phase.

A structural examination was undertaken by the aid of Guinier photographs of the precipitate obtained from a concentrated solution of hydrogen peroxide, i.e. $Cd(O_2)_{0.88} \cdot (OH)_{0.24}$. $\sin^2\theta$ for all the reflexions (Table 3) can be indexed on the assumption of a cubic elementary cell with an edge length of 5.273 Å. According to the experimentally determined density, 5,45 g/cm³, the number of formula units per elementary cell is only 3.3. Bearing in mind that density determinations generally give rather low values and that these compounds decompose yielding oxygen, it is probable that there are four formula units in the elementary cell. If four formula units are to be found in the elementary cell 41.4 % of the available space is occupied by atoms. In pyrite (FeS_2), which turned out to be isomorphous with the phase investigated, the same value is 40.6 %.

On the photographs no absence is observed for the reflections of the type *hkl*. But further it may be pointed out that those reflections which do not belong to a

Table 3.

hkl	$10^4 \mathrm{Sin}^2\,\theta_{\mathrm{obs}}$	$10^4 \mathrm{Sin}^2\,\theta_{\mathrm{calc}}$
111	640	641
200	856	855
210.120	1066	1068
112	1286	1282
220	1709	1710
221	~1910	1923
113	2353	2351
222	2568	2564
320.230	~2786	2778
321.123	2992	2992
400	3421	3419
410.140	~3628	3633
114	3846	3847
331	4060	4060
420.240	4273	4274
421.124	—	4488

$a = 5.273 \pm 0.003$ Å

face-centered lattice are very weak. The reflections $0kl$ are found only for $k = 2n$. This is characteristic for the space group No. 205 T_h^6–Pa3.

It was found that the four cadmium atoms could be placed in the positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}00$; $0\frac{1}{2}0$; $00\frac{1}{2}$ $(4b)$ and the eight oxygen atoms in

$$\pm(xxx;\ \tfrac{1}{2}+x\tfrac{1}{2}-xx;\ x\tfrac{1}{2}+x\tfrac{1}{2}-x;\ \tfrac{1}{2}-x,\,x,\,\tfrac{1}{2}+x) \qquad (8b)$$

The intensity calculations were made according to a method given by E. HELLNER (6).

The x-parameter was varied systematically. The best agreement between calculated and observed intensities was obtained with a parameter value of 0.082 (Table 4). This value was calculated on the assumption that the position $(8b)$ is occupied only by peroxide ions. However, as mentioned above, it is not improbable that some of the peroxide ions have been replaced by hydroxide ions. If this were taken in account, a slight change in the value of the parameter would probably result. But the dominance of the cadmium atoms is too great for the oxygen parameter value to be determined with certainty and accordingly nothing can here be said about the occurrence of hydroxide ions in this lattice. The parameter value mentioned corresponds to an oxygen–oxygen distance in the same peroxide group of 1.50 Å. The uncertainty may be of the order 0.1. The distance of oxygen to cadmium will then be 2.29 ± 0.02 Å. According to Pauling the calculated value for an ionic bond is 2.33 and for a covalent bond 2.23 Å. In spite of the fact that both the oxides and hydroxides of calcium and cadmium are isomorphous their peroxides are not. CaO_2 is isomorphous with calcium carbide, while CdO_2 crystallizes with the pyrite type structure. This indicates, in agreement with the greater electron negativity and the 18-electron structure of cadmium, a somewhat more covalent character of the bonds in the CdO_2 structure.

Finally it may be added that an investigation of peroxides and superoxides of

Table 4.

hkl	I_{obs}	I_{calc}		
		$x = 0.070$	$x = 0.082$	$x = 0.090$
111	65	61	65	68
002	70	75	71	67
210.120	1.0	0.7	1.1	1.5
112	1.2	0.9	1.2	1.5
220	45	48	45	43
221	0.1	0.3	0.3	0.3
113	50	46	50	52
222	14	17	16	15
320.230	0.5	0.6	0.8	0.8
321.123	0.7	0.8	0.9	1.1
004	7	7	6	5
410.140	0.3	0.1	0.1	0.1
114	0.4	0.2	0.2	0.2
331	21	24	24	24
420.240	19	21	22	22
421.124	0	0.0	0.0	0.0

magnesium, zinc and mercury is going on. It has been proved that ZnO_2 and one phase of HgO_2 are isomorphous with CdO_2 with edge lengths of the unit cells 4.87 and 5.32 Å respectively.

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Formation and structure of mercuric peroxides

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Formation and structure of mercuric peroxides

By NILS-GÖSTA VANNERBERG

With 2 figures in the text

Introduction

Mercurous peroxide, Hg_2O_2, is reported to have been prepared by von Antropoff (1). By treating metallic mercury with hydrogen peroxide solution, he obtained a black, easily decomposable compound, the colour of which changed to red in a couple of hours. Since no analysis is reported, however, it is doubtful, whether the compound obtained actually was mercurous peroxide.

The mercuric peroxide, HgO_2, was prepared by von Antropoff (2, 3) and Pellini (4) by treating mercuric oxide or mercuric oxynitrate with 30 % hydrogen peroxide solution. Pellini had also prepared the compound from a solution of mercuric chloride and hydrogen peroxide in alcohol (4). According to these authors, mercuric peroxide is a red instable compound, which detonates when struck or heated.

Generally, peroxides of such metals, which can easily change oxidation states, do not exist. The reason for this is that the peroxide group has both oxidizing and reducing properties, and can therefore oxidize the metallic ion from its lower to its higher oxidation state under evolution of oxygen and then reduce the metallic ion from a higher oxidation state to a lower.

The normal potential for the oxidation of metallic mercury to mercuric or mercurous ion are (5)

$$\begin{aligned} Hg &= Hg^{2+} + 2e^- \qquad E_0 = +0.854\ V \\ 2Hg &= Hg_2^{2+} + 2e^- \qquad E_0 = +0.799\ V \end{aligned}$$

The following oxidation-reduction couples involving the hydroperoxide ion have the potentials

$$\begin{aligned} OH^- + HO_2^- &= O_2 + H_2O + 2e^- \qquad E_0 = -0.08\ V \\ 3OH^- &= HO_2^- + H_2O + 2e^- \qquad E_0 = +0.87\ V \end{aligned}$$

The potential for the reaction

$$Hg^{2+} + OH^- + HO_2^- = Hg + O_2 + H_2O$$

is then $+0.93$ V and for the reaction

$$HO_2^- + H_2O + Hg = Hg^{2+} + 3OH^-$$

the potential becomes $+0.02$ V.

Similar values are obtained if it is assumed that Hg_2^{2+} takes part in the reactions. It is obvious that if we want to prepare mercuric peroxide from a solution, the concentration of mercuric ion and hydroxyl ion in this solution must be as low as possible; otherwise the mercuric ions will oxidize the hydroperoxide ions to oxygen. It is therefore impossible to precipitate mercuric peroxide from an alkaline solution of mercuric nitrate. In this case mercuric ions react violently with hydrogen peroxide ions to form oxygen and metallic mercury. If, on the other hand, mercuric oxide is treated with hydrogen peroxide solution at low temperatures, the concentration of mercuric ions will be low because of the low solubility of mercuric oxide and peroxide. The same reason will cause a low concentration of hydroxide and hydroperoxide ions. Accordingly, this can be a useful method to prepare mercuric peroxides.

Experimental

In all cases the peroxide samples were obtained by treating yellow mercuric oxide with hydrogen peroxide solutions of various strength and at various temperatures. To determine the peroxide content, a weighed sample was suspended in a cold sulphuric acid solution and titrated with potassium permanganate. The mercury content was determined as mercuric sulphide. The sample was dissolved in diluted hydrochloric acid, and the solution was boiled to decompose all hydrogen peroxide. Hydrogen sulphide was then passed through the solution and the mercuric sulphide formed was dried and weighed.

Table 1.

Compound	Colour	% Hg obs.	% Hg calc.	% O_2 obs.	% O_2 calc.
α-HgO_2	yellow	85.7	86.2	13.3	13.8
β-HgO_2	red-yellow	86.4	86.2	13.3	13.8

If yellow mercuric oxide is treated with 20 % hydrogen peroxide at the melting point of the solution, which is about $-15°C$, a yellow peroxide is formed. According to the analysis (Table 1) its formula is found to be HgO_2. This peroxide is here called α-mercuric peroxide; it explodes if heated or otherwise carelessly handled.

β-Mercuric peroxide can be prepared if yellow mercuric oxide is treated at the lowest possible temperature with a strong hydrogen peroxide solution. The strength of the solution must be higher than 30 % hydrogen peroxide. The analysis shows the same formula as for the α-compound (Table 1). β-Mercuric peroxide is a red-yellow instable compound. It seems, however, to be somewhat less sensitive to blow than the α-mercuric peroxide.

Crystallographical investigation

From all preparations X-ray photographs were taken with the aid of Guinier powder cameras using Cu $K\alpha$ radiation. The powder pattern of α-mercuric peroxide was very simple and of good quality. It could be indexed on the assumption of a cubic elementary cell with $a = 4.74$ Å. This indicates three formula units in the

Table 2.

$a = 4.736 \pm 0.005$, $\alpha = 90°$.

$h\,k\,l$	$\sin^2\theta_{\text{obs}} \cdot 10^4$	$\sin^2\theta_{\text{calc}} \cdot 10^4$	I
1 1 0	527	530	vst
1 1 1	795	795	st
2 1 0	1324	1325	st
2 2 0	2120	2120	st–
3 0 0. 2 2 1	2381	2385	w
3 1 1	2916	2915	w
2 2 2	3174	3180	m
3 2 1	3716	3710	vw
4 1 0. 3 2 2	4510	4505	w

elementary cell. However, an optical investigation showed a small birefringence; thus it is probable that this structure has rhombohedral symmetry with $a = 4.74$ Å and α very close to 90°. The structure is not yet completely solved.

The Guinier powder pattern of β-mercuric peroxide could be interpreted on the assumption of an orthorhombic elementary cell with

$$a = 6.080 \pm 0.010 \text{ Å}$$
$$b = 6.010 \pm 0.010 \text{ Å}$$
$$c = 4.800 \pm 0.010 \text{ Å}$$

The observed and calculated $\sin^2\theta$ values are given in Table 3.

Table 3.

$a = 6.080 \pm 0.005$, $b = 6.010 \pm 0.005$, $c = 4.800 \pm 0.005$.

$h\,k\,l$	$\sin^2\theta_{\text{obs}} \cdot 10^4$	$\sin^2\theta_{\text{calc}} \cdot 10^4$	I
1 1 1	586	584	vst
2 0 0	643	643	st
0 2 0	658	658	st
0 0 2	1033	1033	st
2 2 0	1302	1301	m
2 0 2	1674	1676	m
0 2 2	1690	1690	m
3 1 1	1869	1870	m
1 3 1	1900	1900	m
2 2 2	2336	2334	m
1 1 3	2647	2649	m
3 3 1	3181	3179	w
4 2 0	3254	3230	vw
2 4 0		3272	
4 0 2	3600	3605	vvw
0 4 2	3666	3666	vvw
3 1 3	3953	3935	w
1 3 3		3965	
0 0 4	4127	4130	vvw
4 2 2	4262	4263	w
2 4 2	4304	4309	w

Table 4.

$h\,k\,l$	I_0	I_c	F_0	F_c
1 1 1	113	140	210	236
2 0 0	50	49	300	292
0 2 0	50	49	300	291
0 0 2	22	22	260	255
2 2 0	24	29	220	239
2 0 2	16	17	210	216
0 2 2	16	17	210	215
3 1 1	25	25	200	195
1 3 1	25	25	200	195
2 2 2	17	17	190	186
4 0 0	23	3	170	170
0 4 0		3	170	169
1 1 3		13	200	174
3 3 1	14	8	150	160
4 2 0		4	150	152
2 4 0		4	150	151
4 0 2	4	2	130	142
0 4 2		2	130	141
3 1 3	10	5	130	135
1 3 3		5	130	135
0 0 4	1	1	110	121
4 2 2	6	4	110	127
2 4 2		4	110	127
5 1 1	7	4	120	131
1 5 1		4	120	131
2 0 4	4	2	130	113
0 2 4		2	130	113
4 4 0	3	1	100	110
3 3 3		2	100	109

As mercuric peroxide is a very unstable compound, it is very difficult to determine its density, but the number of formula units in the elementary cell can be calculated in another way.

The volume of the elementary cell is 144 Å³. The corresponding value for strontium peroxide SrO_2 is 165 Å³ (6). This cell holds four formula units. As the ions Sr^{2+} and Hg^{2+} have nearly the same radii it is probable that there are four formula units in the elementary cell of β-HgO_2, too.

Besides Guinier photographs, the powder pattern was recorded with a Philips X-ray diffraction unit. From the intensities it seemed probable that the structure was pseudotetragonal. Pairs of reflexions of the type hkl and khl have the same intensities. Sometimes such pairs of reflexions were not resolved. In these cases it was assumed that the total intensity could be shared equally between the two reflexions. The intensities were corrected for Lorentz and polarization factors. The calculated structure factors were multiplied by $e^{-B(\sin^2\theta/\lambda)^2}$ where B is 2.6 Å².

All reflexions with mixed indices are absent, which points to a face-centered cell. However, it is plausible that only the mercury atoms form a face-centered lattice, since it is impossible to record reflexions dependent upon the oxygen atoms only. The possible space groups are then *Fmmm*, *F*222, *Fmm*2 and *Pccn* or *Pbca*.

From the intensity calculations it is obvious that the mercury atoms occupy the positions 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$. Accordingly, space group *Fmm*2 can be ruled out.

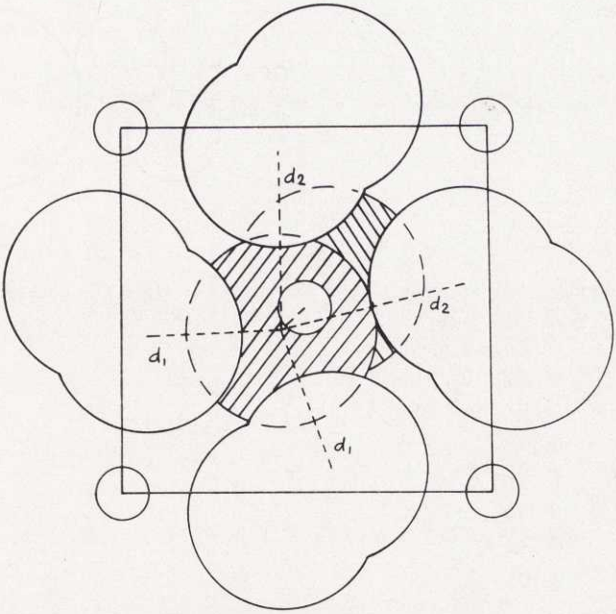

Fig. 1. Small circles indicate mercury atoms; large circles oxygen atoms. The shaded oxygen atoms are placed symmetrically around the position $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the other around the positions $\frac{1}{2}00$ and $0\frac{1}{2}0$. The van der Waals radii are drawn for the oxygen atoms, while the mercury atoms are not up to scale.

The space group *Fmmm* and *F*222 requires the oxygen atoms to be placed in $\pm x00$, $\pm y00$ or $\pm z00$. The distance between the oxygen atoms in a peroxide group is 1.49 Å (8). If the oxygen atoms are placed in the positions $\pm z00$, this parameter would be 0.155. The distance mercury–oxygen is then $(0.500\text{–}0.155) \cdot 4.80 = 1.66$ Å, which is far too short. The reported distance in mercuric oxide is 2.03 Å (7). If the positions $\pm x00$ or $\pm y00$ are assumed, the distance between the oxygens in two peroxide ions would be $\sqrt{(3.04\text{–}1.49)^2 + 2.40^2} = 2.86$ Å, which cannot be accepted as a packing distance between oxygen atoms. The corresponding distance in mercuric oxide is 3.37 Å (7). The space groups *Fmmm* and *F*222 may accordingly be ruled out. Then there are only the groups *Pccn* No. 56 and *Pbca* No. 61 left. Of those, the last was chosen as a trial because this space group seems to give the most probable distribution of the peroxide ions.

The oxygen parameters were now determined by "trial and error". A good fit between calculated and observed structure factors and intensities was found for $x = y = 0.07$, $z = 0.41$; see Table 4. Of course these oxygen parameters are rather uncertain, but they are verified by the fact that the same result can be obtained in another way, given below.

The distance between the oxygen atoms in a peroxide group is 1.49 Å (8) as mentioned above. The distance between two oxygen atoms in different groups is about 3.20 Å (9). In mercuric oxide the shortest distance between the oxygen atoms is 3.37 Å (7). In Fig. 1 the nearest neighbours of an oxygen atom can be seen. It has been assumed that the two distances d_1 are equal for symmetrical reasons and amount to 3.30 Å. This gives

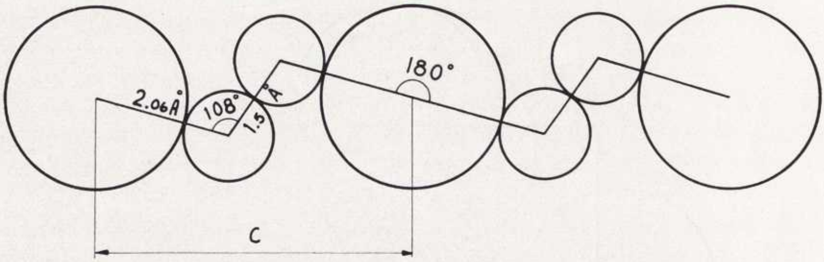

Fig. 2. Diagram showing the infinite zigzag chain –Hg–O–O–Hg–. The covalent radii are drawn for both the mercury and the oxygen atoms.

$$
\begin{aligned}
d_1^2 &= (\tfrac{1}{2}-2y)^2\cdot b^2 + (\tfrac{1}{2}c)^2\\
d_1^2 &= (\tfrac{1}{2}-2x)^2\cdot a^2 + 4y^2\cdot b^2 + (\tfrac{1}{2}c)^2\\
d_1^2 &= 3.30^2\\
1.49^2 &= 4x^2\cdot a^2 + 4y^2\cdot b^2 + 4(\tfrac{1}{2}-z)^2\cdot c^2\\
x &= 0.075\\
y &= 0.062\\
z &= 0.405
\end{aligned}
$$

The values are, as can be seen, in very good agreement with those found from the observed intensities.

Discussion of the structure

In the structure proposed, a mercury atom is surrounded by two oxygen atoms at a short bonding distance and four at considerably longer distances. The six oxygen atoms form a distorted octahedron. The short bonding distance is 2.0_6 Å. The longer weak-bonding distances are 2.6_6 and 2.6_8 Å. The angle between the two bonds which a mercury atom forms is 180°. The angle between the peroxide axis and the direction of the oxygen–mercury bond is 108°. The distance between the oxygen atoms in a peroxide group is 1.5 Å. The oxygen atoms too are surrounded by six neighbours in some kind of octahedral symmetry. Of these neighbours, one mercury and one oxygen atom are bonded to the oxygen atom with covalent bonds. The other four are all mercury atoms at 2.6_6 and 2.6_8 Å. Then there are four oxygen atoms at distances which indicate only weak van der Waals bonds. The last-mentioned distances are 3.2, 3.4, 3.4 and 3.5 Å.

Table 5.

	β-HgO_2	HgO
Hg-coordination	2	2
Hg–O distance	2.06 Å	2.03 Å
O–O packing distance	3.2–3.5 Å	3.39 Å
Hg–O packing distance	2.66–2.68 Å	2.82 Å
Λ O–Hg–O	180°	179°
Λ Hg–O–O	108°	—
Λ Hg–O–Hg	—	109°

The mercury atoms and the peroxide groups form infinite zigzag chains extended along the c-axis (see Fig. 2). The similarity of this structure and that of mercuric oxide is striking. A comparison between the structure reported here and that of mercuric oxide as proposed by K. Aurivillius (7) is made in Table 5.

According to the structure described here, the coordination number of mercury in mercuric peroxide and the angle between the bonds indicates sp-hybridization for the mercury atom while the angle between the peroxide axis and the direction of the oxygen–mercury bond may indicate sp^3 hybridization for the oxygen atoms.

SUMMARY

The α- and β-mercuric peroxides have been prepared and their crystal structures investigated. α-HgO_2 may have rhombohedral symmetry with $a = 4.74$ and α very close to 90°. β-HgO_2 has rhombic symmetry with $a = 6.080$ Å, $b = 6.010$ Å, $c = 4.800$ Å and crystallizes according to the space group *Pbca* No. 61. The mercury atoms and the peroxide groups form infinite chains extended along the c-axis.

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On the system SrO_2-H_2O-H_2O_2

2. The crystal structure of strontium peroxide octahydrate

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Communicated 28 January 1959 by ARNE WESTGREN and GUNNAR HÄGG

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By NILS-GÖSTA VANNERBERG

With 11 figures in the text

Introduction

Calcium, strontium and barium peroxide form hydrates with eight molecules of water (1, 2, 3, 4). No other hydrate has been satisfactorily identified, even if hydrates with 12, 10, 9, 7, 6, 2, and 1 molecules of water have been reported (1, 3, 5, 6). On the other hand sodium peroxide forms octa-, hexa-, and dihydrates (7). These are identified from their X-ray powder pattern. Of the hydrates, the octahydrate seems to have the greatest existence range (7).

Strontium peroxide octahydrate ($SrO_2 \cdot 8H_2O$) was prepared by Schöne (2) and Conroy (3) in 1876 and by Nottebohm (4, 8) in 1914. de Focrand (5) has reported a hydrate with nine water molecules; this compound, however, is certainly identical with insufficiently dried octahydrate (9). Schöne and Conroy precipitated the octahydrate from a strontium hydroxide solution with hydrogen peroxide. Nottebohm prepared the compound by dissolving strontium chloride in 3 % hydrogen peroxide solution. When a solution of 1 % ammonia was added, the peroxide octahydrate was precipitated.

Some other preparation methods of less interest have also been reported. The compound can be precipitated from a strontium salt solution with a solution of sodium peroxide (8). It can also be prepared electrolytically (10, 11, 12).

Since sodium and the heavier earth alkaline metals form a peroxide octahydrate, it is possible that the water molecules and the peroxide ions build up a certain group and the metal ions are introduced in the lattice solely to compensate the charge. However, the only complete investigation in this field up to now seems to be the present work.

The elementary cell and the possible space groups of sodium peroxide octahydrate was determined by Kotov (13). The symmetry was proved to be monoclinic, space group either Cc or $C\,2/c$. The a-axis is 13.5 Å, the b-axis 6.5 Å, and the c-axis 11.5 Å. The monoclinic angle β is 100.5°. There are four formula units in the elementary cell. The complete structure has never been determined. The earth alkaline peroxide octahydrates have earlier been investigated by Natta (14), Miller and King (15). Here powder photographs were used, which unfortunately were wrongly indexed, so that the wrong space group was chosen. This mistake caused a distorted view of the structure. Later King (15) has corrected this mistake on the basis of a single crystal investigation and in a private communication (16) presented a structural proposal for $CaO_2 \cdot 8H_2O$, which, in the main features, agrees with that described in this paper (see Table 5).

Preparation method

Crystals of strontium peroxide octahydrate were easily obtained when a solution of strontium nitrate in hydrogen peroxide was carefully mixed with diluted ammonia. 10 g $Sr(NO_3)_2$ was dissolved in 60 ml 3 % hydrogen peroxide. The solution was cooled to 0° and 100 ml 0.5 *M* ammonia was added. After an hour beautiful crystals separated. They were filtered off and washed with cold water, alcohol and ether. The strontium content was determined gravimetrically as oxide. The peroxide content was analyzed by titration with permanganate solution. The following values were obtained:

Sr^{2+}	obs. 39.4 %	calc. 39.3 %
O_2^{2-}	obs. 12.1 %	calc. 12.1 %

X-ray methods

The structural investigation was based on single-crystal methods. The single crystals were rotated around suitable crystal axes and Weissenberg photographs were taken for all zones detectable with Cu $K\alpha$ radiation. Multiple film technique was used. The reflexion intensities were estimated by visual comparison with known scales and corrected for Lorentz and polarization factors. As all crystals used in this investigation were very small (cross-section $< 0.01 \times 0.01$ cm), no allowance was made for absorption. The unit cell dimensions were obtained from Guinier photographs.

Determination of the structure

The single crystals of strontium peroxide octahydrate appear as small, rather thick, square plates. In contrast to the dihydroperoxidates the octahydrate is stable for months at atmospheric conditions and does not seem to suffer decomposition by the X-rays. The compound is tetragonal. The unit cell dimensions are: $a = 6.340 \pm 0.002$ Å, $c = 11.188 \pm 0.004$ Å. Observed and calculated values of $\sin^2\theta$ are given in Table 1. The measured density was 1.95 g/cm³. This value corresponds to two formula units in the elementary cell, as the calculated density is 1.947 g/cm³.

In all photographs only reflexions from planes of the following types were observed.

hkl	all orders (Most reflexions with $l = 2n + 1$ were very week.)
$hk0$	all orders
$h0l$ $0kl$	with $l = 2n$
hhl	with $l = 2n$

The space group is accordingly either D_{4h}^2–$P4/mcc$ no. 124 or C_{4v}^5–$P4/cc$ no. 103. As King and Shinemann (15) remark, the latter is very improbable, since there are no equivalent positions available for two formula units of strontium peroxide octahydrate.

Table 1. X-ray powder diffraction data for $SrO_2 \cdot 8H_2O$.

$h\ k\ l$	$10^4 \cdot \sin^2 \theta_{obs}$	$10^4 \cdot \sin^2 \theta_{calc}$	I
1 0 0	148	148	m
0 0 2	190	190	m
1 1 0	296	296	m
1 0 2	338	338	m
1 1 2	485	486	s
2 0 0	592	592	w
2 0 2	782	782	m
2 1 1	788	787	m
1 0 4	908	906	w
2 1 2	929	930	m
1 1 4	1056	1054	m
2 1 3	1163	1167	w
2 2 0	1180	1183	m
3 0 0	1327	1330	w
2 0 4	1351	1350	m
3 1 0	1476	1479	s
3 1 2	1665	1669	m
0 1 6	1855	1854	w
3 2 0 3 1 5	1920	1923 1925	m
1 1 6	2007	2002	vw
3 0 4	2088	2089	m
3 2 2	2113	2113	m
2 0 6	2297	2298	vw
2 1 6	2448	2446	w
4 1 0	2516	2514	w
4 0 2	2553	2556	m
4 1 2	2704	2704	vw
4 2 0	2956	2958	w
3 1 6	3189	3185	w
3 3 4	3421	3420	vw
3 2 6	3634	3629	vw
5 1 2	4031	4035	w
4 1 6	4220	4220	w
4 3 4	4459	4456	m
5 1 4	4606	4603	w

In space group $P4/mcc$ there are two sets of equivalent twofold positions where the strontium ions can be placed: $000\ 00\frac{1}{2}$ or $00\frac{1}{4}\ 00\frac{3}{4}$. The latter was recommended by King and Shinemann and was chosen as a trial. This will later on be shown to be the correct position. On the basis of the positions of the Sr^{2+} ions, the signs of all structure factors of the type $hk0$ and $h0l$ could be estimated. Two electron density projections could then be made, one along the c-axis and the other along the b-axis. From these projections, the positions of all atoms except the hydrogens could be fixed (Figs. 1 and 2) and the signs of all structure factors could be calculated. The structure was refined with the aid of a complete three-dimensional calculation. This was very important, as it also includes reflexions of the type hkl with $l = 2n + 1$, the strontium contribution to this kind of reflexions being zero.

An attempt was then made to determine the positions of the hydrogen atoms. This was tried on the basis of difference projections. From the observed structure factors,

Table 2. Observed and calculated structure factors for $SrO_2 \cdot 8H_2O$.

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
1 0 0	45	+52	2 1 2	48	−44	7 2 4	41	+41
2 0 0	45	+50	3 1 2	60	−42	3 3 4	75	+83
3 0 0	43	+40	4 1 2	40	−32	4 3 4	55	+57
4 0 0	29	+26	5 1 2	49	−49	5 3 4	32	+32
5 0 0	<12	+1	6 1 2	32	−31	6 3 4	42	+41
6 0 0	68	+74	7 1 2	38	−40	7 3 4	17	+18
7 0 0	41	+41	2 2 2	62	−66	4 4 4	33	+28
8 0 0	33	+37	3 2 2	40	−38	5 4 4	23	+22
1 1 0	65	+64	4 2 2	52	−52	6 4 4	45	+47
2 1 0	22	+27	5 2 2	34	−32	5 5 4	27	+23
3 1 0	119	+110	6 2 2	41	−43	2 1 5	31	+39
4 1 0	42	+40	7 2 2	28	−27	3 1 5	14	+15
5 1 0	52	+46	3 3 2	55	−57	4 1 5	14	−19
6 1 0	39	+36	4 3 2	36	−31	5 1 5	<15	−5
7 1 0	35	+35	5 3 2	44	−44	6 1 5	<21	−7
2 2 0	84	+83	6 3 2	29	−35	3 2 5	<12	−5
3 2 0	51	+47	7 3 2	41	−36	4 2 5	14	−13
4 2 0	82	+76	4 4 2	44	−43	5 2 5	17	+20
5 2 0	39	+38	5 4 2	33	−29	6 2 5	<22	+13
6 2 0	37	+39	6 4 2	44	−39	4 3 5	<15	−8
7 2 0	18	+17	5 5 2	48	−39	5 3 5	<18	+8
3 3 0	20	+14	6 5 2	39	−27	5 4 5	<22	−13
4 3 0	19	+12	2 1 3	44	+39	0 0 6	34	−27
5 3 0	52	+54	3 1 3	13	+14	0 1 6	56	−65
6 3 0	24	+21	4 1 3	19	+18	0 2 6	35	−32
7 3 0	56	+53	5 1 3	<14	−4	0 3 6	55	−56
4 4 0	55	+60	6 1 3	<18	−6	0 4 6	36	−27
5 4 0	45	+43	3 2 3	<12	−4	0 5 6	40	−42
6 4 0	27	+27	4 2 3	14	−12	0 6 6	27	−31
7 4 0	29	+22	5 2 3	21	+19	0 7 6	34	−40
5 5 0	46	+53	6 2 3	<18	+11	1 1 6	34	−33
6 5 0	16	+15	4 3 3	<14	−7	1 2 6	54	−59
2 1 1	52	−49	5 3 3	<17	+7	1 3 6	36	−37
3 1 1	17	−17	5 4 3	<19	−12	1 4 6	47	−50
4 1 1	23	+21	0 0 4	32	+33	1 5 6	31	−29
5 1 1	<14	+5	1 0 4	50	+51	1 6 6	44	−42
6 1 1	<16	+7	2 0 4	73	+81	1 7 6	29	−25
3 2 1	<11	+5	3 0 4	45	+46	2 2 6	38	−34
4 2 1	15	+15	4 0 4	72	+74	2 3 6	51	−53
5 2 1	17	−21	5 0 4	64	+67	2 4 6	34	−33
6 2 1	<17	−13	6 0 4	18	+12	2 5 6	42	−45
4 3 1	<14	+8	7 0 4	19	+20	2 6 6	30	−27
5 3 1	<15	−8	1 1 4	69	+78	2 7 6	32	−36
5 4 1	<18	+14	2 1 4	63	+63	3 3 6	35	−26
0 0 2	72	−83	3 1 4	20	+15	3 4 6	44	−43
1 0 2	43	−47	4 1 4	42	+38	3 5 6	31	−29
2 0 2	68	−77	5 1 4	45	+45	3 6 6	41	−38
3 0 2	44	−40	6 1 4	30	+30	4 4 6	30	−30
4 0 2	54	−58	7 1 4	41	+39	4 5 6	45	−42
5 0 2	40	−35	2 2 4	41	+42	4 6 6	29	−24
6 0 2	41	−43	3 2 4	41	+36	5 5 6	32	−28
7 0 2	28	−28	4 2 4	29	+27	2 1 7	28	−23
8 0 2	25	−27	5 2 4	32	+33	5 2 7	15	−13
1 1 2	68	−83	6 2 4	38	+41	0 0 8	74	+84

Table 2 (*continued*)

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
1 0 8	59	+ 62	6 3 8	33	+ 33	4 3 10	39	− 39
2 0 8	17	+ 13	2 1 9	20	− 27	5 3 10	27	− 26
3 0 8	52	+ 54	0 0 10	40	− 24	2 1 11	17	+ 13
5 0 8	24	+ 24	1 0 10	42	− 43	1 0 12	31	+ 29
6 0 8	52	+ 45	2 0 10	37	− 37	2 0 12	45	+ 48
0 1 8	57	+ 62	3 0 10	40	− 40	3 0 12	33	+ 29
1 1 8	19	+ 17	4 0 10	28	− 36	4 0 12	48	+ 50
2 1 8	44	+ 48	5 0 10	41	− 41	0 1 12	27	+ 29
3 1 8	43	+ 51	0 1 10	42	− 43	1 1 12	40	+ 46
4 1 8	43	+ 52	1 1 10	33	− 37	2 1 12	33	+ 35
5 1 8	26	+ 22	2 1 10	39	− 43	3 1 12	23	+ 21
6 1 8	51	+ 45	3 1 10	35	− 27	4 1 12	28	+ 26
0 2 8	17	+ 13	4 1 10	35	− 32	0 2 12	44	+ 48
1 2 8	48	+ 48	5 1 10	33	− 35	1 2 12	36	+ 35
2 2 8	37	+ 33	0 2 10	37	− 37	2 2 12	32	+ 33
3 2 8	50	+ 56	1 2 10	37	− 43	3 2 12	23	+ 25
4 2 8	38	+ 39	2 2 10	35	− 31	0 3 12	33	+ 29
5 2 8	44	+ 48	3 2 10	35	− 38	1 3 12	26	+ 21
6 2 8	19	+ 20	4 2 10	31	− 28	2 3 12	28	+ 25
0 3 8	53	+ 54	5 2 10	38	− 34	3 3 12	50	+ 55
1 3 8	49	+ 50	0 3 10	41	− 40	0 0 14	42	− 47
2 3 8	52	+ 56	1 3 10	37	− 27	0 1 14	32	− 26
4 3 8	30	+ 31	2 3 10	42	− 38	1 1 14	38	− 35
5 3 8	31	+ 29	3 3 10	26	− 27			

the contributions of the strontium and oxygen atoms were subtracted. Some peaks really appeared in probable positions, but too much significance is not to be put on these (see Figs. 3, 4). Anyhow the difference maps gave some information about the temperature factors of the atoms and the accuracy of the investigation. The R factor $= \Sigma ||F_c| - |F_o|| / \Sigma |F_o|$ was, after the three-dimensional refinement, 0.08. The hydrogens are not included in F_c. $||F_c| - |F_o||$, in those cases, where no reflexion was observed, was assumed to be $||F_c| - |F_{\text{min}}|/2||$, F_{min} being the smallest structure factor observed for the diffraction angle in question. The temperature factor was calculated in the usual way. Log F_o/F_c was plotted against $(\sin^2\theta)/\lambda^2$ and a straight line was drawn through the points. From the slope of the line the temperature factor was calculated. This was done for every zone perpendicular to $\vec{c}$. The values are tabulated in Table 3. The calculated temperature factor increases with increasing l. This can be due to absorption but it can also be a real thermal effect. As will be shown later on, there are more hydrogen bonds in the xy directions than in the z direction. However, the total effect must be rather small and therefore it may be assumed that the reason for the $\vec{c}$ dependence of the "temperature factor" is to the greatest extent due to absorption.

The established positions for the different atoms can be found in Table 4.

Fig. 1. Electron density projection on [001]. Contours at intervals about 4 e.Å^{-2}; the zero contour is not drawn. Every second equidensity line is drawn for the strontium atoms.

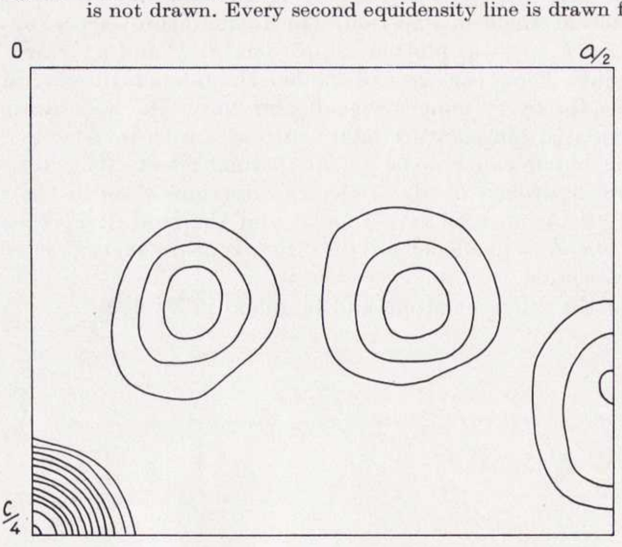

Fig. 2. Electron density projection on [010]. Contours at intervals about 3 e.Å^{-2}; the zero contour is not drawn. Every second equidensity line is drawn for the strontium atoms.

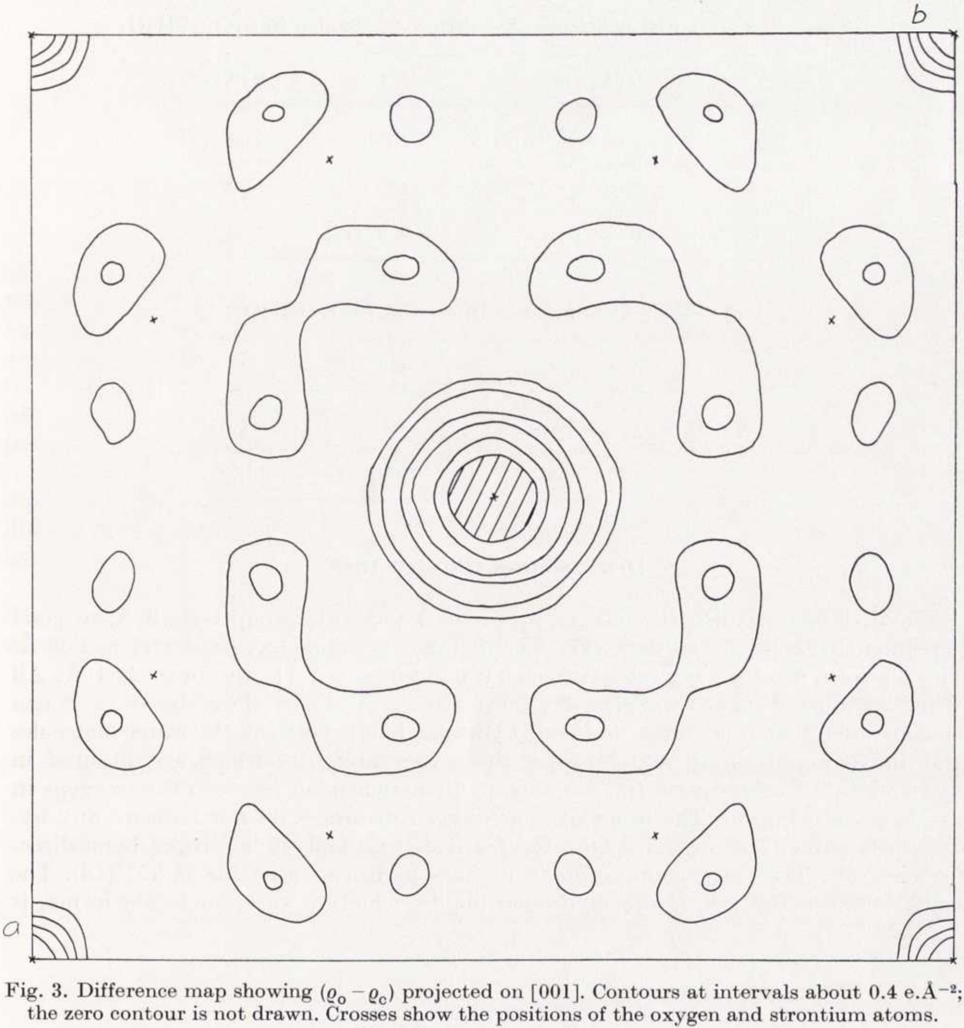

Fig. 3. Difference map showing $(\varrho_o - \varrho_c)$ projected on [001]. Contours at intervals about 0.4 e.Å^{-2}; the zero contour is not drawn. Crosses show the positions of the oxygen and strontium atoms. Shaded area is negative.

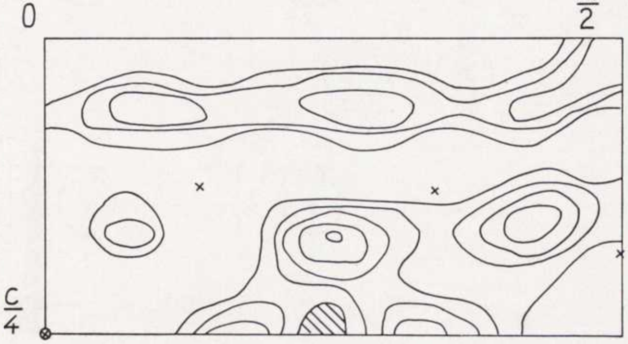

Fig. 4. Difference map showing $(\varrho_o - \varrho_c)$ projected on [010]. The a- and c-axes are not drawn to the same scale. Contours at intervals about 0.3 e.Å^{-2}; the zero contour is not drawn. Crosses show the positions of the oxygen and strontium atoms. Shaded area is negative.

Table 3. Temperature factors for different *l*-zones in $SrO_2 \cdot 8H_2O$.

l	*B* (Å)	*l*	*B* (Å)
0	0.61	10	0.92
2	0.64	12	0.94
4	0.68	14	1.09
6	0.82	1, 3, 5,	
8	0.87	7, 9, 11	1.00

Table 4. Atomic co-ordinates in $SrO_2 \cdot 8H_2O$.

			x	*y*	*z*
2	Sr	*a*)	0	0	$\frac{1}{4}$
4	O	*h*)	$\frac{1}{2}$	$\frac{1}{2}$	0.184
16	O	*n*)	0.322	0.136	0.121

Discussion of the structure

The distance between the oxygen atoms in a peroxide group is 1.48 Å, in good agreement with published data (17). The distance peroxide oxygen–water is 2.66 Å. The shortest distance between two water molecules is 2.71, the next 2.84 Å. All other distances between oxygens are more than 3 Å. From these distances it can be concluded that there must be strong hydrogen bonds between the water molecules and the peroxide group and between the water molecules which are situated in xyz and $xy\bar{z}$. Furthermore, there is a weak hydrogen bond between the oxygens in xyz, $\bar{x}\bar{y}z$ (see Fig. 6). The other oxygen–oxygen distances do not indicate any hydrogen bonding. The angle between the peroxide axis and the hydrogen bond direction is 106°. The corresponding angle in pure hydrogen peroxide is 97° (18). The angle between the two strong hydrogen bonds, which a water molecule forms, is

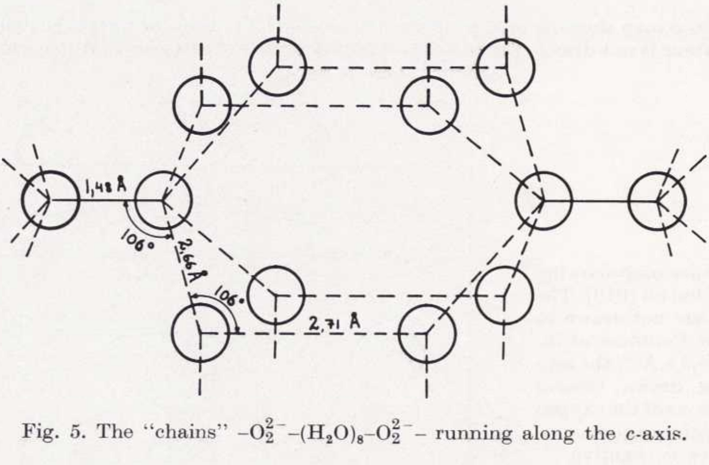

Fig. 5. The "chains" $-O_2^{2-}-(H_2O)_8-O_2^{2-}-$ running along the *c*-axis.

Table 5. Atomic co-ordinates in $CaO_2 \cdot 8H_2O$ according to King.

			x	y	z
2	Ca	a)	0	0	$\frac{1}{4}$
4	O	h)	$\frac{1}{2}$	$\frac{1}{2}$	0.182
16	O	n)	0.309	0.129	0.128

also 106°. The angles between the weak and the two strong bonds are 101° and 90° which is in good agreement with published data (19, 23). The angle between the hydrogen bonds formed by an oxygen atom in a peroxide group is 86°. The azimuthal angle between planes containing the peroxide axis and two hydrogen bonds is found to be 90°, if the hydrogen bonds are formed by the same oxygen atom, while it is 38° or 52° if the bonds are formed by the two different oxygen atoms in the same peroxide group (see Fig. 7). The corresponding angle in hydrogen peroxide is 94° (18).

The structure can be described as long chains of peroxide and water molecules linked together by strong hydrogen bonds. The chains O_2^{2-}–$(H_2O)_8$–O_2^{2-}–$(H_2O)_8$ are linked together to a three-dimensional network by the strontium ions and weak hydrogen bonds. A part of the chain can be seen in Fig. 5.

The strontium ions are surrounded by eight water molecules which form a square Archimedean antiprism with edge length 3.13, 3.33 and 3.36 Å and a rotatory angle of 44.3°. This configuration is also found in $SrCl_2 \cdot 2H_2O$ (20) and certainly in $Sr(OH)_2$-

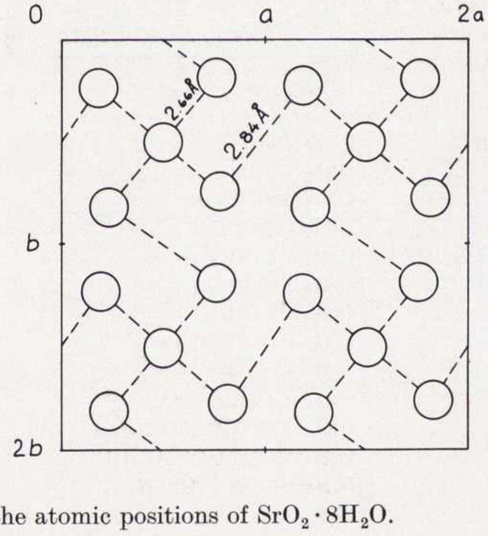

Fig. 6. A section through $z \approx 1/8$, showing the hydrogen bonding in this plane.

Table 6. Standard deviations in the atomic positions of $SrO_2 \cdot 8H_2O$.

	x (Å)	y (Å)	z (Å)
Sr	0	0	0
$O(O_2^{2-})$	0	0	0.012
$O(H_2O)$	0.014	0.014	0.021

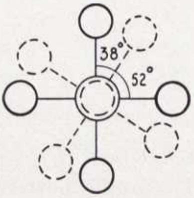

Fig. 7. A peroxide group and its neighbours projected along the *c*-axis. Full-drawn circles represent oxygen atoms with $z \approx 1/8$, dotted circle oxygen atoms with $z \approx 3/8$.

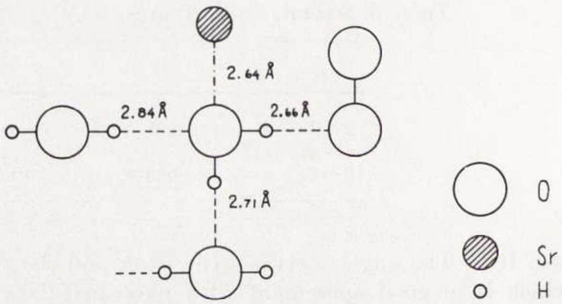

Fig. 8. An idealized picture of a water molecule and its four neighbours.

$8H_2O$ (21), too. The distance between the strontium ion and the water molecules found in the present investigation is 2.64 Å. The same distance in $Sr(OH)_2 \cdot 8H_2O$ is 2.60 Å and in $SrCl_2 \cdot 2H_2O$ 2.71–2.83 Å. The water molecules have four nearest neighbours, one strontium ion at 2.64 Å, one peroxide oxygen atom at 2.66 Å, and two water molecules at 2.71 and 2.84 Å. The configuration is that of a distorted tetrahedron (see Fig. 8).

Bond lengths and angles between bonds can be found in Table 7. The standard deviations (Table 6) are calculated according to the method given by Cruickshank (25).

Table 7. Bond lengths and angles in $SrO_2 \cdot 8H_2O$.

Sr^1–Sr^2	6.34 ± 0.00 Å
Sr^2–Sr^3	5.59 ± 0.00
Sr–O (H_2O)	2.64 ± 0.02
O(O_2^{2-}–O(O_2^{2-})	1.48 ± 0.02
O(O_2^{2-})–O(H_2O)	2.66 ± 0.03
O(H_2O^1)–O(H_2O^2)	2.71 ± 0.04
O(H_2O^1)–O(H_2O^3)	2.84 ± 0.04
O(H_2O^1)–O(H_2O^4)	3.13 ± 0.01
O(H_2O^1)–O(H_2O^5)	3.33 ± 0.04
O(H_2O^1)–O(H_2O^6)	3.36 ± 0.04
O(H_2O)–O(O_2^{2-})–O(O_2^{2-})	106°.3 ± 0°.5
O(O_2^{2-})–O(H_2O^1)–O(H_2O^2)	106°.3 ± 0°.5
O(O_2^{2-})–O(H_2O^1)–O(H_2O^3)	101°.1 ± 1°.0
O(H_2O^2)–O(H_2O^1)–O(H_2O^3)	90°.0 ± 0°.0
O(H_2O^1)–O(O_2^{2-})–O(H_2O^4)	86°.4 ± 0°.5
The plane O(H_2O^1) O(O_2^{2-}) O(O_2^{2-})– the plane O(H_2O^5) O(O_2^{2-}) O(O_2^{2-})	38°.0 ± 1°.0
The plane O(H_2O^1) O(O_2^{2-}) O(O_2^{2-})– the plane O(H_2O^4) O(O_2^{2-}) O(O_2^{2-})	90°.0 ± 0°.0

H_2O^1	$x\,y\,z$	H_2O^4	$\bar{y}\,x\,z$
H_2O^2	$x\,y\,\bar{z}$	H_2O^5	$y\,x\,\frac{1}{2}-z$
H_2O^3	$\bar{x}\,\bar{y}\,\bar{z}$	H_2O^6	$x\,\bar{y}\,\frac{1}{2}-z$

The hydrogen bonds

In one formula unit of strontium peroxide octahydrate there are 16 hydrogen bonds. Accordingly all hydrogen atoms are involved in bond formation. The hydrogen bonds are in many respects peculiar. The peroxide group is bonded to eight water molecules. This is more than one would expect. From the oxygen–oxygen distances it can be concluded that the bonds are fairly strong. Strong bonds are only formed in the direction of a free, directed electron pair (22). If one assumes that the oxygens in the peroxide groups are sp^3 hybridized, this accounts well for the angle betewen the hydrogen bond and the peroxide axis, but not for the angle between two hydrogen bond directions. The last-mentioned angle is 86°. This can of course be explained if the peroxide ion is assumed to rotate about its axis. It is, however, an improbable assumption. If, on the other hand, it is assumed that the s electrons do not take part in the bond formation between the oxygens, but the free electron pairs and the bonding electrons are of pure *p*-character, the last-mentioned angle is somewhat easier to explain. However, the angle between the peroxide axis and the hydrogen bond would be 90°. As mentioned above, it is 106°, but this is certainly due to the contact between the water molecules. If the angle were 90°, the packing distance would be about 2.0 Å, which is far too short. The distance which appeared in this structure is 3.33 Å. The orbital directions of the two oxygen atoms in the peroxide group seem to be rotated 38° in relation to each other. This is similar to the case in C_2H_6 or $N_2H_6^{2+}$ (23) where there are sp^3 bonds, but it is certainly also the case

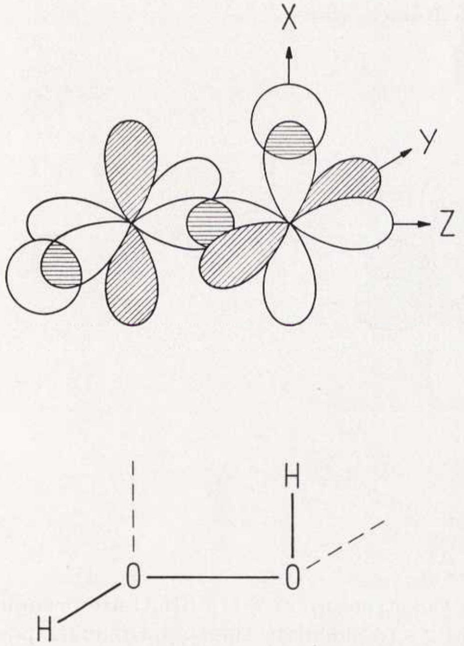

Fig. 9 a.

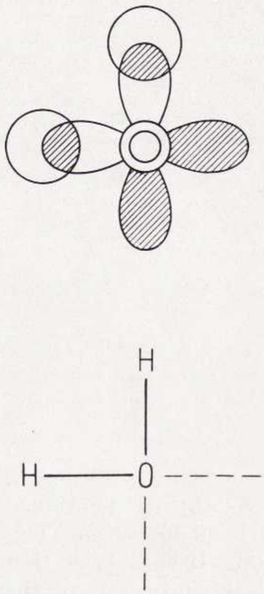

Fig. 9 b.

Fig. 10.

in O_2^{2-} even if a pure *p*-bond is assumed. In H_2O_2 the orbital directions in the two oxygen atoms are rotated about 90° as a consequence of the strong repulsion of the free electron pairs when these are situated in parallel orbitals (24). (See Fig. 9.)

The least repulsion between free electron pairs in O_2^{2-} would be expected if the oxygens with their orbitals are rotated 45° in relation to each other (See Fig. 10.) If this model is accepted, it explains well the hydrogen bonding of the peroxide group. Morerover the very successful quantum mechanical treatment of the hydrogen peroxide molecule also neglected the influence of the 2*s* electrons (24, 26).

Strontium hydroxide octahydrate has a structure which is very similar to the peroxide structure just described (21). In this structure the hydroxide ions are octahedrally surrounded by four water molecules and two hydroxide ions. All the groups are at distances which indicate hydrogen bonding. If here, too, it is assumed that the 2*s* electrons are not used for the bond formation in OH^-, a model can be obtained which is very similar to that mentioned above.

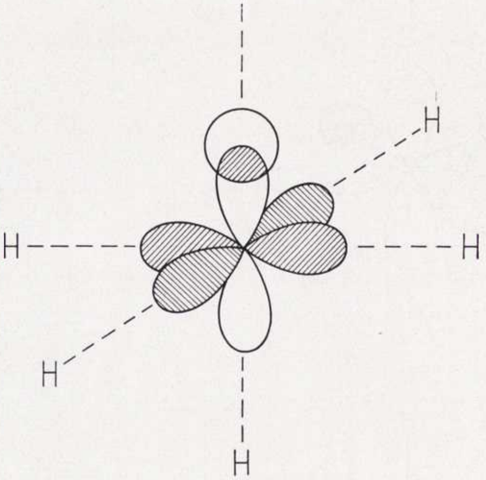

Fig. 11.

As already mentioned, all hydrogens in the structure of $SrO_2 \cdot 8H_2O$ are occupied in bond formation. This gives us a possibility to calculate their approximate positions. If we assume that the hydrogen–oxygen bond is 1.0 Å and that the atoms lie in the direction of the hydrogen bonds, the parameter values given in Table 8 are obtained. The corresponding parameter values from the difference projections

Table 8. Calculated and observed coordinates of hydrogen atoms in $SrO_2 \cdot 8H_2O$.

	x	*y*	*z*
a) 16 H *n*)	0.39 (0.41)	0.27 (0.26)	0.15 (0.15)
b) 16 ½H *n*)	0.32 (0.26)	0.14 (0.08)	0.04 (0.06)
c) 16 ½H *n*)	0.45 (0.41)	0.10 (0.09)	0.12 (0.15)

are given in parentheses. The hydrogens in the positions denoted *b* and *c* are thought to be distributed, respectively, over the positions 0.32, 0.14, 0.04 and 0.32, 0.14, −0.04 on the one hand, and 0.45, 0.10, 0.12 and −0.45, −0.10, 0.12 on the other. From the values in Table 8 it seems possible that the peaks observed in the difference maps may indicate the hydrogen atom positions.

SUMMARY

The crystal structure of $SrO_2 \cdot 8H_2O$ have been determined by the use of three-dimensional Fourier methods. The following crystallographic data were evaluated.

Space group *P*4/*mcc* No. 124, $a = 6.340 \pm 0.002$ Å, $c = 11.188 \pm 0.004$ Å.

2 Sr (*a*)	0	0	¼
4 O (*h*)	½	½	0.184
16 O (*n*)	0.322	0.136	0.121

In this structure there are "chains" $-O_2^{2-}-(H_2O)_8-O_2^{2-}-$ held together by strong hydrogen bonds. These chains are linked into a three-dimensional network by the strontium ions and by weak hydrogen bonds.

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Department of Inorganic Chemistry, Chalmers University of Technology, Göteborg, Sweden, January 1959.

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NILS-GÖSTA VANNERBERG

On the system BaO_2-H_2O-H_2O_2

1. Investigation of the existing phases and their preparation

2. The structure of $BaO_2 \cdot H_2O_2$

ALMQVIST & WIKSELL / STOCKHOLM

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Communicated 11 March 1959 by ARNE WESTGREN and GUNNAR HÄGG

On the system BaO_2–H_2O–H_2O_2

1. Investigation of the existing phases and their preparation
2. The structure of $BaO_2 \cdot H_2O_2$

By NILS-GÖSTA VANNERBERG

With 7 figures in the text

Introduction

The best known compounds containing barium and peroxide ions are barium peroxide and barium peroxide octahydrate. The first compound, barium peroxide, BaO_2, has been known for a long time. It was first prepared by A. von Humboldt in 1799 (1, 2) by heating barium oxide in air. Barium peroxide octahydrate, $BaO_2 \cdot 8\,H_2O$, was prepared by Thénard in 1817 (3) and Schöne in 1873 (4). The latter dissolved solid barium peroxide in a hydrogen chloride solution and got in this way a solution which contained about two per cent hydrogen peroxide. To this solution a saturated barium hydroxide solution was added. Very fine satiny crystals of barium peroxide octahydrate were obtained. Still more preparation methods of barium peroxide and barium peroxide octahydrate can be found in works such as Machu "Wasserstoffperoxyd" (2). The existence of other hydrates of barium peroxide described in literature (2), seems to be somewhat questionable (5).

The compound barium monohydroperoxidate, $BaO_2 \cdot H_2O_2$, was first prepared by Schöne (4). He obtained it when treating barium peroxide octahydrate with excess of hydrogen peroxide. According to another description in "Annalen der Chemie" he dissolved barium peroxide in diluted hydrochloric acid as to obtain a solution with about two per cent hydrogen peroxide. To this solution 10 % ammonia was added. A white compound with the formula $BaO_2 \cdot H_2O_2$ was formed. Nottebohm (6) obtained the compound by dissolving barium chloride in water and adding to it a solution of ammonia in 3 % hydrogen peroxide at 50°C. Yellow-white crystals were obtained.

The barium dihydroperoxidate, $BaO_2 \cdot 2\,H_2O_2$, was first prepared by Nottebohm (6). The preparation method was the same as that of the monohydroperoxidate, except for the reaction temperature, which was changed to -2°C. The crystals were described as being small and white.

The existence of a compound $BaO_2 \cdot H_2O_2 \cdot H_2O$ has been predicted by de Focrand (7) on the basis of thermochemical measurements. Askenasy and Rose (8) obtained preparations with the formula $BaO_2 \cdot mH_2O_2 \cdot nH_2O$ $(m+n=8)$ by precipitating a hydrogen peroxide solution with saturated barium hydroxide solution. The preparations are probably mixtures of the compounds mentioned above.

The peroxidates are described as rather instable compounds which decompose to peroxide, water and oxygen. At the same time small amounts of the brown superoxide are formed (9).

The structure of BaO_2 has been determined by Bernal and co-workers (10), Butuzov (11), and Abrahams and Kalnajs (12). They have all found a tetragonal face centered elementary cell. According to Abrahams et al., the bond lengths in this compound are the following: oxygen–oxygen in the peroxide group 1.49 Å, and barium–oxygen 2.68 Å (two distances) and 2.79 Å (eight distances). The structures of the other compounds have not yet been investigated although the space group and the elementary cell of barium peroxide octahydrate were determined by King and Shineman (13). The compound is isomorphous with strontium peroxide octahydrate. The structure of the latter compound has been determined by Vannerberg (14), who also determined the structures of α- and β-strontium dihydroperoxidates (15).

1. Investigation of the existing phases and their preparation

Ammonia was added to solutions of a barium salt and hydrogen peroxide. The precipitates formed were filtered, dried with alcohol and ether and analysed. The peroxide content was determined by titration with permanganate. The barium content was determined as sulphate. The phase determination was performed with the aid of X-ray powder photographs (Guinier method). The total concentration of barium, hydrogen peroxide and ammonia in the system, as well as the temperature was varied systematically within the limits

Ba^{2+} 0.02 – 0.4 *M* temp. 0°C – 15°C
H_2O_2 0.1 – 8 *M*
NH_3 0.02 – 0.5 *M*

As a result, the existence of the following compounds could be established in the system $BaO_2-H_2O-H_2O_2$:

Barium peroxide BaO_2
Barium peroxide octahydrate $BaO_2 \cdot 8H_2O$
Barium peroxide monohydroperoxidate $BaO_2 \cdot H_2O_2$
(Barium peroxide monohydroperoxidate dihydrate $BaO_2 \cdot H_2O_2 \cdot 2H_2O$)
α-Barium peroxide dihydroperoxidate α-$BaO_2 \cdot 2H_2O_2$
β-Barium peroxide dihydroperoxidate β-$BaO_2 \cdot 2H_2O_2$
γ-Barium peroxide dihydroperoxidate γ-$BaO_2 \cdot 2H_2O_2$

As already mentioned above, good preparation methods of the compounds BaO_2 and $BaO_2 \cdot 8H_2O$ can be found in literature (2). The preparation methods for the other compounds are given below. These are developed in the present investigation. They yield rather pure and large crystals, well suited for single crystal work.

Preparation and analysis of the compound $BaO_2 \cdot H_2O_2$

1 g $BaCl_2 \cdot 2H_2O$ and 4 ml 25 % ammonia were separately dissolved each in 10 ml 1.5 % H_2O_2. The solutions obtained were cooled to 10°C and mixed cautiously. After

a short time crystals were formed. They were filtered off and dried with alcohol and ether.

Analysis: Found Ba^{2+} 66.4 % O_2^{2-} 30.4 %
Calc. Ba^{2+} 67.5 % O_2^{2-} 31.5 %.

Preparation and analysis of the compound $BaO_2 \cdot H_2O_2 \cdot 2H_2O$

One preparation of α-$BaO_2 \cdot 2H_2O_2$ according to Nottebohm (see above), yielded white tiny crystalline plates. About five mg were obtained. However, it has not succeeded so far to reproduce this preparation and the sample obtained was too small for an accurate analysis. On the other hand, a crystallographic investigation could be performed. The data obtained indicate that the formula is $BaO_2 \cdot H_2O_2 \cdot 2H_2O$. Further details on this compound will be published in another paper.

Preparation and analysis of the compound α-$BaO_2 \cdot 2H_2O_2$

2 g $BaCl_2 \cdot 2H_2O$ and 1 ml 25 % ammonia were separately dissolved each in 10 ml 30 % H_2O_2. The solutions were cooled to 0°C, mixed and allowed to stand for an hour. The crystals formed were filtered and dried with alcohol and ether.

Analysis: Found Ba^{2+} 57.2 % O_2^{2-} 40.4 %.
Calc. Ba^{2+} 57.9 % O_2^{2-} 40.4 %.

Preparation and analysis of the compound β-$BaO_2 \cdot 2H_2O_2$

β-$BaO_2 \cdot 2H_2O_2$ was obtained in a similar way. In this case 1 g $BaCl_2 \cdot 2H_2O$ and 0.10 ml ammonia were dissolved in two portions of 10 ml 20 % hydrogen peroxide. The solutions were cooled to 0°C, mixed and filtered after an hour.

Analysis: Found Ba^{2+} 57.5 % O_2^{2-} 40.1 %.
Calc. Ba^{2+} 57.9 % O_2^{2-} 40.4 %.

Preparation and analysis of the compound γ-$BaO_2 \cdot 2H_2O_2$

γ-$BaO_2 \cdot 2H_2O_2$ could also be prepared in a similar way. The only difference from the preparation method of the β-compound is that 30 % hydrogen peroxide and 0.25 ml ammonia were used and that the crystals were allowed to stand at 0°C for twenty-four hours. Very often crystals of β-$BaO_2 \cdot 2H_2O_2$ were first precipitated, but these crystals turn into the γ-compound after some hours.

Analysis: Found Ba^{2+} 57.5 % O_2^{2-} 39.7 %
Calc. Ba^{2+} 57.9 % O_2^{2-} 40.4 %.

2. The stucture of barium peroxide monohydroperoxidate

Experimental

Single crystals of barium monohydroperoxidate were obtained as described above. The crystals were small, short rods. The crystallographic a-axis (see below) coincides with the length of the rod. The compound appeared to be rather stable. Decomposi-

Table 1. X-ray powder diffraction data for $BaO_2 \cdot H_2O_2$.

$h\ k\ l$	$10^4 \cdot \sin^2 \theta_{obs}$	$10^4 \cdot \sin^2 \theta_{calc}$	I
0 1 1	152	154	m
0 2 0	263	265	vs
0 0 2 0 2 1 1 0 0	352	352 353 355	s
1 1 0	416	419	vs
1 0 2	604	604	m
1 2 0	620	621	w
$\bar{1}$ 1 2	667	670	m
0 3 1	686	685	w
1 2 1	760	762	m
1 0 2	811	812	m
1 1 2 $\bar{1}$ 2 2	868	868 869	s
1 3 0	951	953	w
$\bar{1}$ 3 1	988	989	s
0 4 0	1059	1062	w
1 2 2	1077	1077	w
0 4 1	1153	1150	w
$\bar{1}$ 2 3	1261	1258	w
0 3 3	1387	1389	w
0 0 4	1407	1408	w
2 1 0	1492	1489	m
1 2 3 $\bar{2}$ 0 2	1564	1567 1568	m
$\bar{1}$ 1 4 $\bar{2}$ 1 2	1626	1622 1634	w
$\bar{1}$ 4 2	1663	1665	w
0 5 1	1750	1747	w
$\bar{2}$ 2 2	1838	1833	w
0 4 3	1860	1855	w
1 3 3	1904	1899	w
2 0 2	1978	1979	w
2 3 0	2023	2020	vw
$\bar{1}$ 4 3	2060	2054	m
2 3 1	2215	2212	w
0 6 1	2479	2479	w
$\bar{2}$ 2 4	2680	2682	w
0 3 5	2797	2797	w
$\bar{1}$ 3 5	2889	2884	w
$\bar{2}$ 4 3	2973	2966	w
2 5 0	3082	3083	vw
3 0 0	3199	3202	vw
$\bar{1}$ 1 6	3281	3279	w
2 1 4	3319	3311	vw
$\bar{3}$ 2 1	3404	3399	w
3 2 0 $\bar{2}$ 4 4	3473	3466 3479	w
$\bar{2}$ 5 3	3567	3564	vw
1 4 5	3880	3877	w
$\bar{2}$ 0 6	3979	3983	w
3 1 4 $\bar{1}$ 7 2	4057	4052 4063	w

tion was only just noticeable after twelve hours. Rotation and Weissenberg photographs were taken with rotation about the length axis of the crystal and about one direction perpendicular to this. In the former case copper radiation was used since the cross-section of the crystal was small and approximately square and therefore absorption could be neglected. In the other direction of rotation the absorption of copper radiation could not be neglected. In that case zirconium filtered molybdenum radiation was used. The reflexions from the single crystals were recorded using multiple film technique. When molybdenum radiation was used the films were interleaved by tin foils. The intensities were measured visually by comparison with known scales. Correction was made for Lorentz and polarization factors but not for absorption effects.

The elementary cell dimensions were determined from Guinier powder photographs using Cu $K\alpha$ radiation and potassium chloride as internal standard.

The crystal symmetry was found to be monoclinic with

$$a = 4.132 \pm 0.004 \text{ Å} \qquad c = 8.308 \pm 0.008 \text{ Å}$$
$$b = 9.464 \pm 0.009 \text{ Å} \qquad \beta = 98°35' \pm 5'$$

Observed and calculated $\sin^2 \theta$-values are given in Table 1.

The only systematic extinctions were found for reflexions of the type $h0l$ with $l = 2n+1$ and $0k0$ with $k = 2n+1$. The space group is accordingly P 2_1/c No. 14.

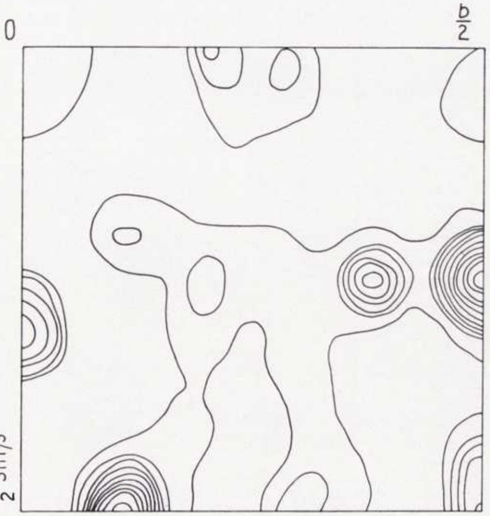

Fig. 1. Patterson projection along the *a*-axis in $BaO_2 \cdot H_2O_2$. Contours are at arbitrary intervals.

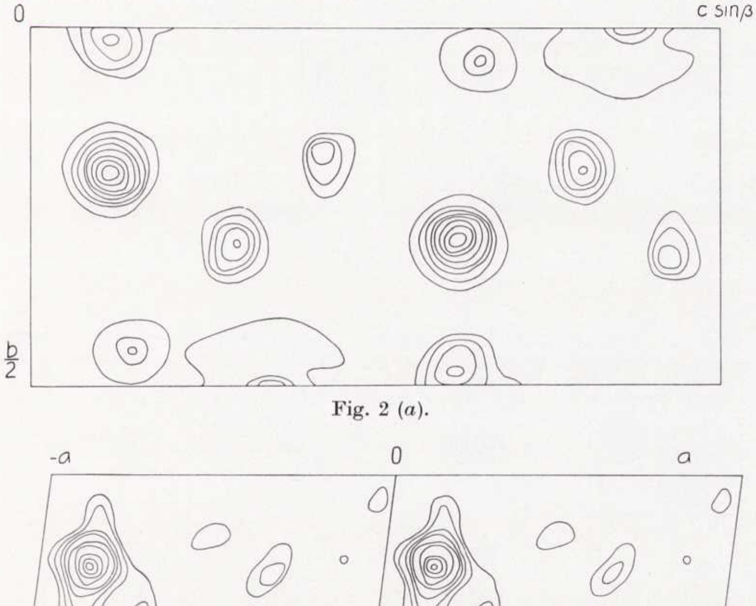

Fig. 2 (*a*).

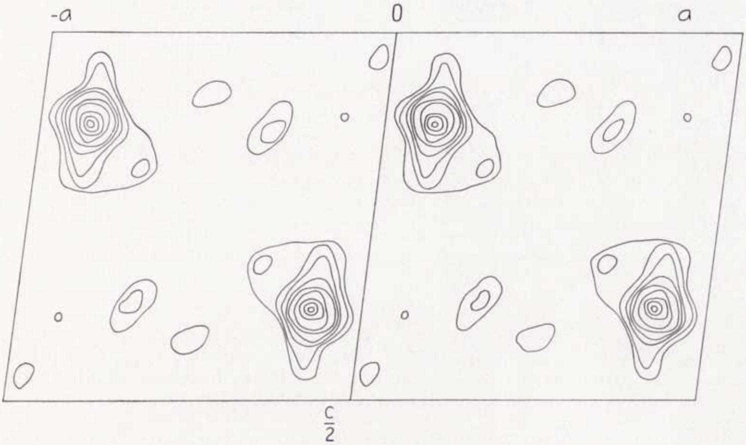

Fig. 2 (*b*).

Fig. 2. Electron density projection of $BaO_2 \cdot H_2O_2$. (*a*) on the plane (001); (*b*) on the plane (010). The contours are at equal but arbitrary intervals. Every fourth contour is drawn for the barium atoms.

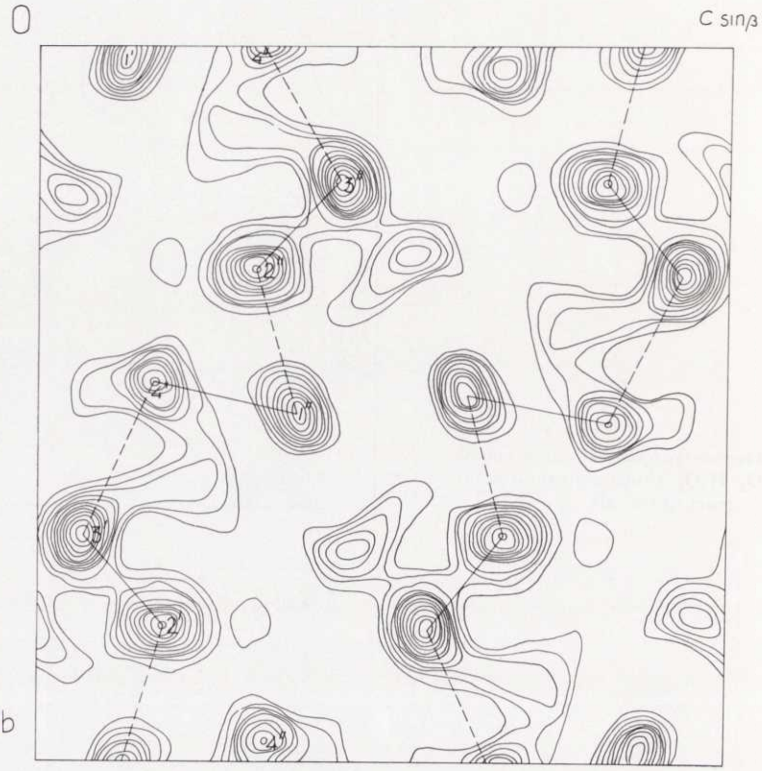

Fig. 3 (*a*).

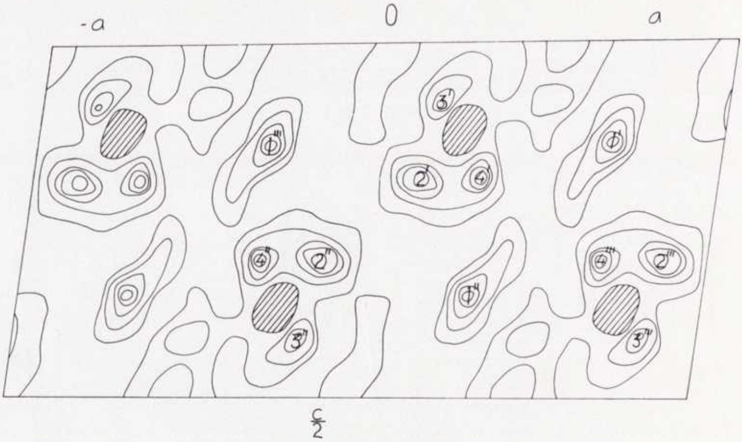

Fig. 3 (*b*).

Fig. 3. Difference electron density projection of $BaO_2 \cdot H_2O_2$, showing $\varrho_{obs} - \varrho_{Ba}$. (*a*) on the plane (001); (*b*) on the plane (010). Contours are at equal but arbitrary intervals. Shaded area represents negative field inside a positive field.

Table 2. Observed and calculated structure factors for $h0l$ and $0kl$ planes of $BaO_2 \cdot H_2O_2$.

$h\ k\ l$	F_{obs}	F_{calc}
1 0 0	107	+ 146
2 0 0	55	− 56
3 0 0	129	− 118
4 0 0	129	− 134
5 0 0	56	− 55
6 0 0	68	+ 56
7 0 0	104	+ 91
$\bar{1}$ 0 2	196	+ 175
$\bar{2}$ 0 2	273	+ 205
$\bar{3}$ 0 2	59	+ 69
$\bar{4}$ 0 2	56	− 42
$\bar{5}$ 0 2	88	− 95
$\bar{6}$ 0 2	85	− 90
0 0 2	15	− 19
1 0 2	218	− 175
2 0 2	175	− 176
3 0 2	73	− 62
4 0 2	68	+ 41
5 0 2	99	+ 102
6 0 2	75	+ 91
$\bar{1}$ 0 4	97	− 109
$\bar{2}$ 0 4	42	+ 46
$\bar{3}$ 0 4	101	+ 103
$\bar{4}$ 0 4	91	+ 106
$\bar{5}$ 0 4	65	+ 40
$\bar{6}$ 0 4	71	− 47
$\bar{7}$ 0 4	92	− 81
0 0 4	231	− 199
1 0 4	80	− 80
2 0 4	69	+ 30
3 0 4	98	+ 89
4 0 4	155	+ 113
5 0 4	90	+ 40
6 0 4	76	− 56
$\bar{1}$ 0 6	64	− 92
2 0 6	127	− 134
$\bar{3}$ 0 6	43	− 40
$\bar{4}$ 0 6	48	+ 47
$\bar{5}$ 0 6	67	+ 73
$\bar{6}$ 0 6	77	+ 72
0 0 6	—	+ 18
1 0 6	74	+ 74
2 0 6	95	+ 107
3 0 6	106	+ 58
4 0 6	73	− 37
$\bar{1}$ 0 8	63	+ 64
$\bar{2}$ 0 8	27	− 26
$\bar{3}$ 0 8	84	− 86
$\bar{4}$ 0 8	79	− 82
$\bar{6}$ 0 8	85	+ 50
$\bar{7}$ 0 8	63	+ 64
0 0 8	110	+ 105
1 0 8	76	+ 57
3 0 8	52	− 67
4 0 8	63	− 82
$\bar{1}$ 0 10	66	+ 65
$\bar{2}$ 0 10	69	+ 144
$\bar{4}$ 0 10	41	− 44
$\bar{5}$ 0 10	74	− 68
0 0 10	—	− 9
1 0 10	57	− 54
2 0 10	79	− 91
$\bar{1}$ 0 12	62	− 55
$\bar{3}$ 0 12	66	+ 79
$\bar{4}$ 0 12	76	+ 85
0 0 12	68	− 90
1 0 12	71	− 58
$\bar{1}$ 0 14	88	− 57
$\bar{2}$ 0 14	82	− 93
0 0 2	22	− 19
0 0 4	188	− 199
0 0 6	—	+ 18
0 0 8	122	+ 105
0 0 10	—	− 9
0 1 1	48	+ 50
0 1 2	121	− 153
0 1 3	47	− 50
0 1 4	—	+ 3
0 1 5	47	− 47
0 1 6	139	+ 156
0 1 7	53	+ 39
0 1 8	—	+ 1
0 1 9	54	+ 40
0 1 10	88	− 114
0 2 0	149	− 147
0 2 1	79	− 75
0 2 2	28	− 15
0 2 3	89	− 100
0 2 4	102	+ 106
0 2 5	48	+ 51
0 2 6	—	+ 13
0 2 7	73	+ 67
0 2 8	80	− 77
0 2 9	59	− 53
0 2 10	—	− 8
0 3 1	114	− 96
0 3 2	84	+ 65
0 3 3	125	+ 130
0 3 4	—	+ 8
0 3 5	58	+ 59
0 3 6	77	− 75
0 3 7	74	− 82
0 3 8	—	− 6
0 3 9	67	− 57
0 3 10	57	+ 63
0 4 0	111	+ 82
0 4 1	129	+ 117
0 4 2	—	− 10

Table 2 (*cont.*)

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
0 4 3	143	+129	0 7 1	68	−63
0 4 4	54	−54	0 7 2	91	−100
0 4 5	80	−83	0 7 3	81	+72
0 4 6	—	+12	0 7 4	—	+10
0 4 7	86	−86	0 7 5	58	+47
0 4 8	40	+28	0 7 6	94	+98
0 4 9	71	+75	0 7 7	62	−56
0 4 10	—	−5	0 7 8	—	−5
0 5 1	126	+111	0 8 0	130	−130
0 5 2	—	−4	0 8 1	48	+40
0 5 3	131	−128	0 8 2	—	−3
0 5 4	—	+8	0 8 3	49	+35
0 5 5	93	−92	0 8 4	111	+104
0 5 6	—	−15	0 8 5	37	−35
0 5 7	102	+94	0 8 6	—	+3
0 5 8	—	−7	0 8 7	36	−24
0 5 9	76	+89	0 9 1	—	+14
0 6 0	124	+110	0 9 2	112	+91
0 6 1	84	−83	0 9 3	—	−10
0 6 2	—	−4	0 9 4	—	+8
0 6 3	117	−105	0 10 0	156	+134
0 6 4	77	−77	0 10 1	—	+22
0 6 5	77	−64	0 10 2	—	−1
0 6 6	—	−7	0 10 3	—	+21
0 6 7	88	+87	0 10 4	104	−114
0 6 8	61	+45	0 11 1	49	+44
0 6 9	57	−71	0 11 2	67	−83

Assuming four formula units in the elementary cell, the calculated density is 4.19 g/cm^3. The observed density is 4.04 g/cm^3. The discrepancy is due to experimental difficulties. The density could not be determined by the flotation method, nor could the method of Schrewelius (16) be applied, using finely grained samples, because of the instability of the crystals. Instead a sample consisting of rather large crystals was weighed in a bulb and benzene was introduced into it without evacuation. Then the pressure in the bulb was reduced until the benzene boiled gently. After a minute the boiling was stopped and the density determination proceeded after usual lines.

With the described method, decomposition was partly avoided but some still remained. Other sources of error are the unsufficient removal of adsorbed air and the enclosing of mother liquid in the large crystals.

Patterson projections were made along the *a*-axis (Fig. 1) and *b*-axis. From these, the positions of the barium ions could be determined. The signs of most structure factors of the type 0*kl* and *h*0*l* could now be fixed. The electron density projections along the *a* and *b* axis were then evaluated (see Fig. 2). As could be expected, the positions of the oxygen atoms were rather uncertain. To determine the oxygen positions more sharply, differential syntheses were made. From the observed structure factors the calculated contributions of the barium ions were drawn. The rest, which contained the oxygen contribution and the error in the observed structure factor, were used as coefficients in two Fourier syntheses. (See Fig. 3.) From these, rather

Table 3. Observed interatomic distances in $\mathrm{BaO_2 \cdot H_2O_2}$.

Ba'—Ba'''	4.32 Å	O_1''—O_4'	1.6 Å
Ba'—Ba''	4.42	O_3'—O_4'	2.3
Ba''—O_3''	2.2	O_2'—O_1'''	2.7
Ba'—O_2''	2.3	O_4'—O_2''	2.8
Ba'—O_1'	2.7	O_2''—O_4''	3.2
Ba'—O_4'	2.8	O_3'—O_1''	3.1
Ba''—O_2''	2.7	O_2'—O_3''	3.6
Ba'—O_3''	2.8	O_2'—O_1''	3.3
Ba'—O_1'''	2.8	O_2'—O_1'	3.2
Ba''—O_1''	3.1	O_3'—O_1''	3.1
Ba''—O_2''''	3.4	O_1''—O_3''	3.7
Ba''—O_4''''	3.4	O_3'—O_1'	3.4
O_2'—O_3'	1.5		

The deviation of the O—O distances is about ±0.3 Å.

Table 4. Angles between different bonds real or assumed in $\mathrm{BaO_2 \cdot H_2O_2}$.

$\wedge$ O_2''—O_4'—O_1''	70°
$\wedge$ O_4'—O_3'—O_2'	116°
$\wedge$ O_1''—O_2''—O_3''	120°
$\wedge$ O_2''—O_1''—O_4'	73°
$\wedge$ O_3'—O_4'—O_1''	101°
$\wedge$ O_4''—O_2'—O_3'	142°
$\wedge$ O_3''—O_4''—O_2'	117°
$\wedge$ the plane $\mathrm{O}_1'''\mathrm{O}_2'\mathrm{O}_3'$ – the plane $\mathrm{O}_4'\mathrm{O}_2'\mathrm{O}_3'$	110°
$\wedge$ the plane $\mathrm{O}_3'\mathrm{O}_4'\mathrm{O}_1''$ – the plane $\mathrm{O}_2''\mathrm{O}_1''\mathrm{O}_4'$	118°
$\wedge$ the plane $\mathrm{O}_4'\mathrm{O}_3'\mathrm{O}_2'$ – the plane $\mathrm{O}_4''\mathrm{O}_2'\mathrm{O}_3'$	108°

accurate oxygen positions could be calculated. The barium atoms appeared to be in a fourfold position set and the sixteen oxygen atoms in four different fourfold position sets.

The structure was refined until $R(0kl) = 0.11$, $R(h0l) = 0.17$, where $R = \dfrac{\Sigma\,||F_0| - |F_c||}{\Sigma |F_0|}$. Reflexions, which were not observed, are not included. Observed structure factors have been corrected for thermal vibration by the factor exp. $B(\sin\theta/\lambda)^2$ with $B(0kl) = 1.5 \cdot 10^{-16}$ cm², $B(h0l) = 1.0 \cdot 10^{-16}$ cm².

The result arrived at is the following:

Space group $P2_1/c$ No. 14

	x	y	z
4 Ba in (e)	0.139	0.196	0.125
4 O_1 in (e)	0.663	0.013	0.131
4 O_2 in (e)	0.125	0.807	0.190
4 O_3 in (e)	0.133	0.690	0.070
4 O_4 in (e)	0.300	0.475	0.180

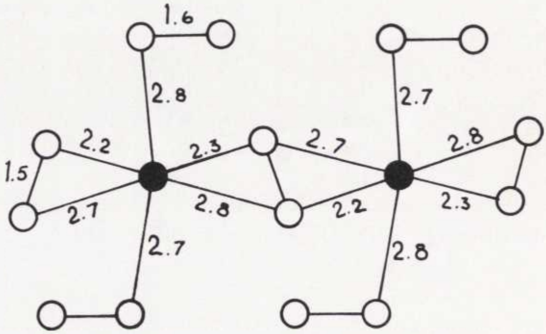

Fig. 4. The surroundings of the barium atoms in $BaO_2 \cdot H_2O_2$. Small black circles represent barium atoms; large unfilled circles oxygen atoms.

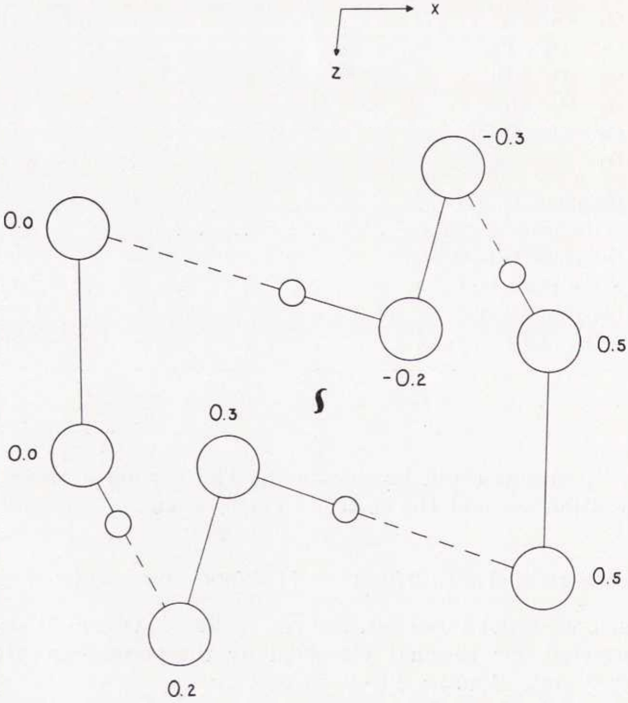

Fig 5.

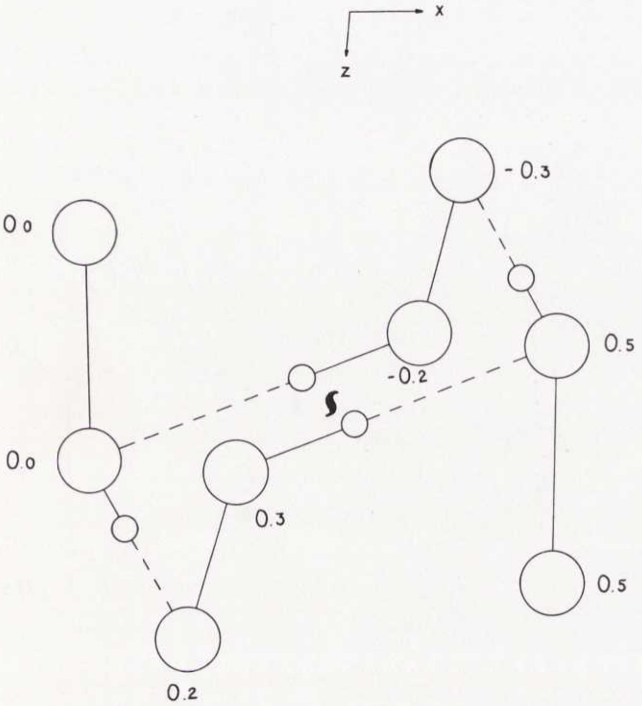

Fig. 6.

A comparison between observed an calculated structure factors can be found in Table 2, and the calculated distances between the atoms in Table 3. The angles between different bonds real or assumed are tabulated in Table 4.

Discussion of the structure

The structure of barium peroxide monoperoxidate appears to be built up of barium ions and infinite helical chains of peroxide groups, held together by strong hydrogen bonds.

The barium ions are surrounded by six oxygen atoms in a distorted octahedral arrangement. The distances are 2.2, 2.3, 2.7, 2.7, 2.8, and 2.8 Å. The arrangement can be seen in Fig. 4. At 2.8, 3.1, 3.4 and 3.4 Å there are four more oxygen atoms.

The distances between the oxygen atoms in the peroxide groups are 1.5 and 1.6 Å.

As the hydrogen atoms in this structure cannot be localized by X-ray methods, the hydrogen bonding is only indicated by a short oxygen–oxygen distance. There are three such short distances in the asymmetric unit but only two hydrogen atoms. The distances are 2.3, 2.7 and 2.8 Å. The first distance indicates certainly a hydrogen bond, but then a choice must be made between the next two. Three different structural proposals can be suggested, which can be seen in figures 5, 6 and 7. In these figures, small circles denote hydrogen atoms, large circles oxygen atoms, broken lines hydrogen bonds, fulldrawn lines covalent bonds. The structures are projected on the xz-plane. The figures give the y-coordinate of every oxygen atom.

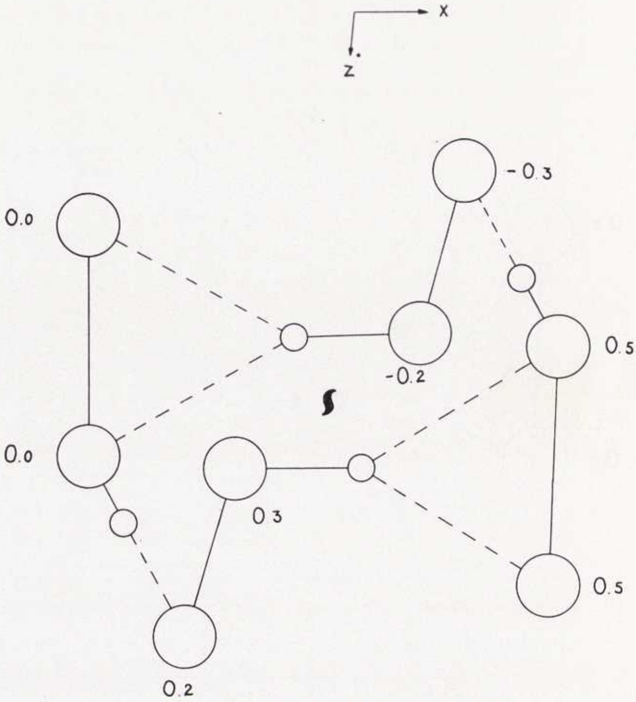

Fig. 7.

An idealized picture of a projection along the helix direction of the first proposal can be seen in Fig. 5. (Structure I.) In this structure, every oxygen atom in a peroxide group is bonded by a hydrogen bond to only one other oxygen atom, in such a way that a helical arrangement is formed.

However, as mentioned above, the distances between the oxygen atoms alone do not exclude another helix structure (Structure II) (Fig. 6). In this structure, half of the oxygens form one hydrogen bond, one part in four forms two, while the remaining part forms no hydrogen bonds at all.

Although the distance between the oxygen atoms does not exclude the latter proposal, the angles between the bonds make it improbable. (See below.) A third possibility is a combination of the structures I and II. (Fig. 7.) Such a structure implies a bifurcated hydrogen bond, which, in this case, does not seem to be very probable. Moreover in solid hydrogen peroxide there is a distance between two oxygen atoms which is 2.90 Å, although there is no hydrogen bond between these oxygen atoms (17).

By comparison of the alternatives mentioned above the following can be concluded. Structure III is rather improbable. Of the other two, structure I (Fig. 5) has the most probable bond distribution. This is supported by the following calculations of angles and bond distances.

In structure I, the angles between the peroxide axes and the hydrogen bond directions will be 116°, 120°, 73°, 101°. In structure II the corresponding angles are

116°, 101°, 142°, and 70°. These values should be compared with the mean value of 100° found in β-$SrO_2 \cdot 2H_2O_2$ (15). The distance between the hydrogen bonded atoms are for structure I 2.3 and 2.7 Å and for structure II 2.3 and 2.8 Å. The corresponding distances in β-$SrO_2 \cdot 2H_2O_2$ are 2.64 Å and 2.56 Å. The angles between the two planes containing the peroxide axis and the hydrogen bonds attached to a peroxide group are 118° and 110° for structure I and 108° for structure II.

An investigation of the other three peroxidates is in progress and will soon be published. The α- and β-dihydroperoxidate seems to be isostructural with the corresponding strontium compounds, while the γ-dihydroperoxidate has a structure strongly related to the α-compound.

SUMMARY

The system BaO_2–H_2O_2–H_2O has been investigated and preparation methods for the existing solid phases are described.

The structure of $BaO_2 \cdot H_2O_2$ has been determined. The following crystallographic data were obtained:

Space group $P2_1/c$ No. 14

$a = 4.132 \pm 0.004$ $c = 8.308 \pm 0.008$
$b = 9.464 \pm 0.009$ $\beta = 98°35' \pm 5'$

	x	y	z
4 Ba (e)	0.139	0.196	0.125
4 O (e)	0.663	0.013	0.131
4 O (e)	0.125	0.807	0.190
4 O (e)	0.133	0.690	0.070
4 O (e)	0.300	0.475	0.180

The structure consists of Ba^{2+} ions and infinite helical chains of peroxide groups, held together by hydrogen bonds.

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NILS-GÖSTA VANNERBERG

On the system SrO_2-H_2O-H_2O_2

1. The crystal structure of α- and β-$SrO_2 \cdot 2H_2O_2$

ALMQVIST & WIKSELL / STOCKHOLM
1958

ARKIV FÖR KEMI Band 13 nr 3

Communicated 26 February 1958 by Arne Westgren and Gunnar Hägg

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By Nils-Gösta Vannerberg

With 5 figures in the text

Introduction

Earlier work

In connexion with investigations concerning the formation, structure, and reactions of inorganic peroxides and superoxides, the system SrO_2–H_2O–H_2O_2 has been investigated. Among the compounds which have been proved to exist in this system, the dihydroperoxidates with the formula $SrO_2 \cdot 2H_2O_2$ have been studied with single crystal methods. Previously both these compounds as well as the corresponding barium and calcium compounds have been investigated with chemical methods by Riesenfeld and Nottebohm (1, 2). They have obtained the barium compound from a water solution of barium chloride and hydrogen peroxide by adding to it diluted ammonia. The calcium and strontium compounds were obtained when the corresponding peroxide octahydrates were treated with 30 % hydrogen peroxide solution at low temperature. The barium and calcium compounds were fairly pure, but the strontium compound could only be prepared as a 50 % mixture with the peroxide octahydrate. According to Riesenfeld and Nottebohm (1, 2) this was due to the extreme instability of the strontium compound.

General methods of preparation

After some trial syntheses the following procedure was found to be suitable for preparation of strontium and also of barium peroxide dihydroperoxidates. A certain amount of the metal nitrate was dissolved in a hydrogen peroxide solution. This solution was cooled to 0°C and a dilute ammonia solution was cautiously added. In this manner a solution supersaturated with the respective peroxide compound was obtained. Crystallization occured very slowly. After about one hour the first crystals were visible. When they had reached a suitable size, they were filtered off and were washed with alcohol and ether. In this way rather good crystals suitable for X-ray single crystal investigations could be obtained. As will be mentioned later their properties were strongly dependent of the concentration of the metal ions, hydrogen peroxide, and ammonia.

X-ray methods

For the sake of phase identification powder photographs of Guinier type were taken of all preparations. The structural investigation was based on single crystal methods. The single crystals were rotated about suitable crystal axes and Weissenberg photographs were taken of the zero and first layer lines. Multiple film technique was used. The reflection intensities were estimated by visual comparison with known scales, and corrected with Lorentz and polarization factors. Since all crystals used in this investigation were very small no allowance was made for the absorption factor. The unit cell dimensions were obtained from Guinier photographs. CuK_α radiation was used in all cases.

The system SrO_2–H_2O–H_2O_2

Established phases

In the system SrO_2–H_2O–H_2O_2 the existence of the following five compounds has been established.

Strontium peroxide, SrO_2
Strontium peroxide octahydrate, $SrO_2 \cdot 8H_2O$
Strontium peroxide monohydroperoxidate, $SrO_2 \cdot H_2O_2$
α-Strontium peroxide dihydroperoxidate, α-$SrO_2 \cdot 2H_2O_2$
β-Strontium peroxide dihydroperoxidate, β-$SrO_2 \cdot 2H_2O_2$.

Strontium peroxide has been prepared by dehydration of the peroxide octahydrate (1, 2) or from direct reaction between strontium oxide and oxygen (3). The peroxide octahydrate is precipitated when a diluted ammonia solution is added to a strontium nitrate solution in 3 % hydrogen peroxide. The other three compounds have not earlier been prepared in pure form. The crystal structure of strontium peroxide have been investigated by Bernal and co-workers (4). A preliminary examination of the octahydrate structure has been performed by King (5, 6).

Preparation and analysis of the compound α-$SrO_2 \cdot 2H_2O_2$

0.5 g $Sr(NO_3)_2$ and 0.5 ml 25 % ammonia was dissolved in two flasks containing 20 ml 30 % H_2O_2 each. The solutions were cooled to 0°C and mixed cautiously. The supersaturated solution obtained was allowed to stand at 0°C for 20 hours. The crystals formed were filtered off and dried with alcohol and ether. The peroxide content was determined by titration with permanganate. The metal content was determined as oxide after ignition to 1000°C.

Analysis: Found: Sr^{2+} 46.2 %, O_2^{2-} 51.2 %. Calc.: Sr^{2+} 46.7 %, O_2^{2-} 50.6 %.

Preparation and analysis of the compound β-$SrO_2 \cdot 2H_2O_2$

β-$SrO_2 \cdot 2H_2O_2$ was obtained in a similar way. This time 1 g $Sr(NO_3)_2$ and 2 ml 25 % ammonia were dissolved in two portions of 20 ml 30 % hydrogen peroxide.

Analysis: Found: Sr^{2+} 46.2 %, O_2^{2-} 51.2 %. Calc.: Sr^{2+} 46.7 %, O_2^{2-} 50.6 %.

As the compounds could not be sufficiently dried, the Sr^{2+} analyses gave somewhat low values.

The structure of the α-strontium peroxide dihydroperoxidate

The single crystals of α-$SrO_2 \cdot 2H_2O_2$ consist of rather thick plates, where the crystallographic a and b axes coincide with the plate diagonals, while the *c* axis forms an angle of about 90° with the plate surface. The crystals are well developed, but twin formation is common. The α-compound is not stable at room temperature. The decomposition was usually total after about four hours. As the crystals could easily be adjusted, however, the time available was sufficient for the exposures.

The compound is monoclinic with the following dimensions of the unit cell

$$a = 8.262 \pm 0.006 \text{ Å} \qquad c = 8.050 \pm 0.005 \text{ Å}$$
$$b = 6.024 \pm 0.004 \text{ Å} \qquad \beta = 79^\circ\ 28' \pm 8'.$$

Calculated and observed $\sin^2\theta$ are tabulated in Table 1.

In all photographs only reflections from planes of the following types were observed:

$$hkl \text{ with } h + k = 2n$$
$$h0l \text{ with } h = 2n,\ l = 2n.$$

Accordingly, possible space groups are C 2/*c* no. 15 and C*c* no. 9.

Table 1. X-ray powder diffraction data for α-$SrO_2 \cdot 2H_2O_2$.

$h\,k\,l$	$10^4 \cdot \sin^2\theta_{obs}$	$10^4 \cdot \sin^2\theta_{calc}$	$h\,k\,l$	$10^4 \cdot \sin^2\theta_{obs}$	$10^4 \cdot \sin^2\theta_{calc}$
1 1 0	253	254	3 3 0	2285	2284
1 1 1	314	315	$\bar{4}$ 2 1	2321	2326
2 0 0	360	360	1 1 5	2450	2457
0 0 2	381	380	5 1 2		2457
$\bar{1}$ 1 1		382	$\bar{5}$ 1 1	2673	2679
$\bar{1}$ 1 2	700	701	0 4 1	2721	2715
0 2 1	748	748	$\bar{4}$ 2 2	2741	2746
$\bar{2}$ 0 2	874	875	$\bar{1}$ 1 5	2799	2795
3 1 1	968	968	2 2 4		2804
1 1 3	1005	1006	4 2 4	3076	3073
0 2 2	1034	1034	$\bar{5}$ 1 2	3137	3133
2 2 1	1042	1042	$\bar{1}$ 3 4	3211	3216
3 1 2	1152	1151	6 0 0	3237	3242
$\bar{3}$ 1 1	1171	1171	$\bar{4}$ 2 3	3359	3359
$\bar{2}$ 2 1	1179	1178	2 0 6	3376	3383
$\bar{1}$ 1 3	1208	1208	1 1 6	3465	3467
2 2 2	1259	1260	$\bar{2}$ 4 3	3631	3631
4 0 0	1442	1441	5 3 2	3763	3767
0 0 4	1519	1518	$\bar{3}$ 1 5	3846	3853
4 0 2	1549	1550	4 4 1	4020	4021
3 1 2	1560	1557	$\bar{6}$ 0 2		4027
1 3 0		1564	$\bar{4}$ 2 4	4163	4155
2 2 3	1667	1666	2 0 6	4180	4181
1 3 2	1876	1876	1 5 0		4184
$\bar{1}$ 1 4	1910	1907	4 4 1	4289	4291
$\bar{1}$ 3 2	2008	2011	7 1 1	4434	4435
4 2 1	2058	2056	1 1 7	4665	4665
$\bar{3}$ 1 3	2131	2132	3 5 1	4899	4898

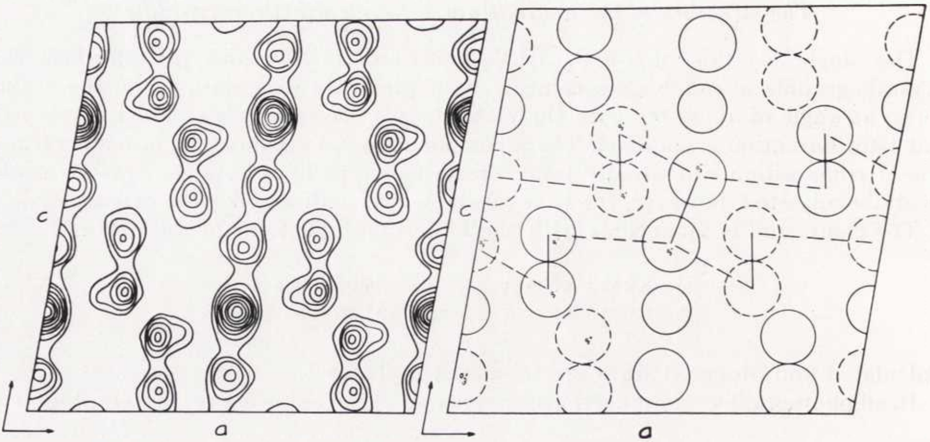

Fig. 1. (*a*) Electron density projection of $\alpha\text{-}SrO_2 \cdot 2H_2O_2$ on the plane [010]. Electron density in arbitrary units. Every third equidensity line is drawn for the strontium atoms. (*b*) Schematic representation of the structure. Large full-drawn circles represent oxygen atoms with $y \approx 0$, dotted circles oxygen atoms with $y \approx \frac{1}{2}$.

As a consequence of the great instability of this compound, no determination of the specific gravity could be performed. However, if there were four formula units in the elementary cell, 70 % of the available space were filled up by ions. As the corresponding percentage for SrO_2 is 69 % and for $H_2O_2(s)$ 61 % the above assumption is probably correct. Moreover, the space groups calls for $4 \cdot n$ formula units. The only reasonable value of n is 1.

The Patterson projection of $\frac{1}{8}$ of the unit cell content on the [001] plane gave a half Sr–Sr vector and 3 Sr–O vectors. No other vectors were observed. This is only consistent with the space group C $2/c$. This space group has five fourfold position sets. According to the Patterson projection the four strontium ions must be placed in (*e*) $0z\frac{1}{4}$; $0\bar{z}\frac{3}{4}$, where the parameter z was estimated to be 0.179. The evaluation of the positions of the strontium ions made it possible to determine most of the signs of the structure amplitudes. Using structure factors of the reflections $hk0$ and $h0l$ and $0kl$, three Fourier projections were made. From these (Fig. 1) was established that the 24 oxygens were located in three general (eightfold) positions and their approximate parameters could be evaluated.

The structure was refined until $R(h0l) = 0.18$, $R(hk0) = 0.21$, $R(0kl) = 0.21$, where $R = \sum \| F_{\text{calc}} | - | F_{\text{obs}} \| / \sum | F_{\text{obs}} |$. Observed structure factors have been corrected for thermal vibration by the factor $\exp[-B(\sin\theta/\lambda)^2]$ with $B = 2.3 \times 10^{-16}\ \text{cm}^2$. The result arrived at is the following.

Atomic coordinates of $\alpha\text{-}SrO_2 \cdot 2H_2O_2$.

	x	y	z
4 Sr in (*e*)	0	0.179	$\frac{1}{4}$
8 O_1 in (*f*)	0.173	0.010	0.450
8 O_2 in (*f*)	0.196	−0.150	0.308
8 O_3 in (*f*)	0.015	0.520	0.088

Table 2. Observed and calculated structure factors for the *hk*0, *h*0*l*, and 0*kl* planes of α-$SrO_2 \cdot 2H_2O_2$.

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
2 0 0	100	+ 113	10 0 4	39	+ 42
4 0 0	109	+ 137	0 0 6	86	− 101
6 0 0	127	+ 147	2 0 6	78	− 83
8 0 0	50	+ 57	4 0 6	121	− 133
10 0 0	77	+ 84	6 0 6	52	− 74
1 1 0	35	+ 39	8 0 6	61	− 61
3 1 0	39	− 56	0 0 8	27	+ 35
5 1 0	41	+ 52	2 0 8	81	+ 96
7 1 0	20	+ 14	4 0 8	40	+ 76
9 1 0	14	+ 5	6 0 8	31	+ 48
0 2 0	11	+ 3	8 0 8	51	+ 95
2 2 0	63	− 44	0 0 10	36	− 53
4 2 0	44	− 46	2 0 10	30	− 60
6 2 0	28	− 14	$\bar{2}$ 0 2	119	− 124
8 2 0	46	− 41	$\bar{4}$ 0 2	45	− 51
10 2 0	46	− 37	$\bar{6}$ 0 2	82	− 70
1 3 0	132	− 133	$\bar{8}$ 0 2	86	− 54
3 3 0	159	− 125	$\bar{2}$ 0 4	88	+ 69
5 3 0	120	− 110	$\bar{4}$ 0 4	85	+ 77
7 3 0	65	− 69	6 0 4	123	+ 92
9 3 0	75	− 83	$\bar{8}$ 0 4	90	+ 47
0 4 0	6	+ 10	$\bar{2}$ 0 6	146	− 135
2 4 0	9	+ 8	$\bar{4}$ 0 6	57	− 56
4 4 0	13	− 10	$\bar{6}$ 0 6	115	− 101
6 4 0	12	+ 7	$\bar{2}$ 0 8	60	+ 81
8 4 0	14	− 3	$\bar{4}$ 0 8	65	+ 57
1 5 0	81	+ 54	0 2 0	17	+ 3
3 5 0	56	+ 32	0 2 1	71	− 60
5 5 0	92	+ 54	0 2 2	165	+ 135
7 5 0	69	+ 46	0 2 3	42	+ 53
0 6 0	97	+ 112	0 2 4	57	− 71
2 6 0	37	+ 59	0 2 5	97	− 82
4 6 0	59	+ 71	0 2 6	35	+ 18
6 6 0	85	+ 81	0 2 7	86	+ 77
1 7 0	16	− 2	0 2 8	49	− 59
3 7 0	23	− 29	0 2 9	55	− 62
2 0 0	118	+ 113	0 4 0	6	+ 10
4 0 0	136	+ 138	0 4 1	72	+ 65
6 0 0	164	+ 147	0 4 2	60	+ 67
8 0 0	68	+ 57	0 4 3	121	− 94
10 0 0	117	+ 84	0 4 4	16	− 24
0 0 2	95	− 84	0 4 5	94	+ 71
2 0 2	39	− 59	0 4 6	—	− 14
4 0 2	144	− 128	0 4 7	88	− 74
6 0 2	71	− 72	0 4 8	—	− 16
8 0 2	83	− 75	0 6 0	120	+ 112
10 0 2	140	− 94	0 6 1	76	− 51
0 0 4	115	+ 100	0 6 2	87	− 57
2 0 4	56	+ 74	0 6 3	39	+ 20
4 0 4	54	+ 69	0 6 4	86	+ 61
6 0 4	54	+ 53	0 6 5	64	− 37
8 0 4	50	+ 67	0 6 6	68	− 65

Table 3. Standard deviations in the atomic positions of α-$SrO_2 \cdot 2H_2O_2$.

	x (Å)	y (Å)	z (Å)
Sr	0	0.01	0
O_1	0.06	0.03	0.06
O_2	0.07	0.10	0.10
O_3	0.08	0.03	0.09

Table 4. Bond lengths and angles in α-$SrO_2 \cdot 2H_2O_2$.

	Sr'—Sr''	4.57 ± 0.01 Å
	Sr'—Sr'''	5.11 ± 0.00
	Sr—O_2	2.65 ± 0.14
	Sr—O_3	2.44 ± 0.08
	O_1'—O_2'	1.50 ± 0.13
	O_3''—O_3'''	1.48 ± 0.18
	O_1'—O_3''	2.54 ± 0.10
	O_2''—O_3''	2.67 ± 0.19
	O_2'—O_2'''	3.23 ± 0.15
	O_1''—O_3'''	3.21 ± 0.13
$\wedge$	O_1'—O_3''—O_3'''	103° ± 7°
$\wedge$	O_3''—O_1'—O_2'	88° ± 8°
$\wedge$	O_3'''—O_2''—O_1''	107° ± 9°
$\wedge$	O_2''—O_3''—O_3'''	107° ± 9°
$\wedge$	the plane $O_1'O_3''O_3'''$ —the plane $O_3''O_3'''O_2'''$	44°
$\wedge$	the plane $O_3''''O_2'O_1'$ —the plane $O_2'O_1'O_3''$	123°
$\wedge$	O_2'—the plane $O_1'O_3''O_3'''$	40°
$\wedge$	O_1''—the plane $O_2''O_3''O_3'''$	39°

The deviation of the last four angles is about 10°.

The comparison between the observed and calculated F-values is given in Table 2. There is considerable overlap between oxygen atoms in the projections along the a and c axes, while the resolution is very good in the projection along the b axis. The standard deviations were calculated with Cruickshank's method (7) (Table 3). Distances and angles between the various atoms are tabulated in Table 4.

According to the crystallographic data obtained the α-$SrO_2 \cdot 2H_2O_2$ is built up of Sr^{2+} ions in a double chain consisting of peroxide ions held together by strong hydrogen bonds. The distances between 2 oxygen atoms in the same peroxide group are 1.48 Å and 1.50 Å respectively. This is in good agreement with published data (8). The distances between oxygen atoms, held together by hydrogen bonds are 2.67 Å and 2.54 Å respectively. It is not impossible that this difference in the bond distance is real. The former value refers back to a part of the chain, where the peroxide ions are in

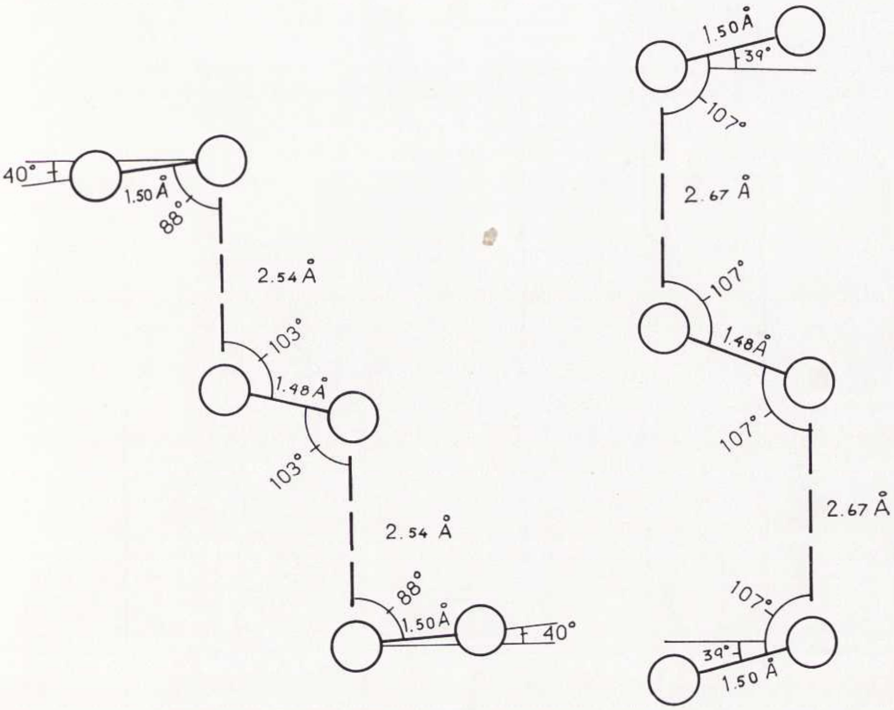

Fig. 2. A section of the peroxide double chain in α-$SrO_2 \cdot 2H_2O_2$. (*a*) The "trans" chain. (*b*) The "cis" chain.

a *cis*-position to the hydrogen bond, the later to a part, where the peroxide groups are in a *trans*-position to the hydrogen bond. See Fig. 2. The angle between the peroxide axis and the hydrogen bond direction is somewhat larger than the same angle in hydrogen peroxide, but this may be a consequence of the strong coulomb forces occurring in this structure. All the hydrogen atoms are involved in bond formation.

The angles between the two planes, containing the hydrogen bonds attached to a peroxide group, are 44° and 123°. The great similarity in the building units in the solid hydrogen peroxide lattice and in this structure can be seen in Fig. 3. The strontium ions are coordinated by four oxygen atoms arranged in a slightly deformed tetrahedron. The distances between oxygen and strontium are 2.44 Å and 2.65 Å respectively.

The structure of β-strontium dihydroperoxidate

Single crystals of β-strontium peroxide diperhydrate were obtained as previously described. The crystal needles are shaped in the form of lancets. None of the crystallographic axes coincide with the needle axis, so that the crystals had to be adjusted by the aid of Laue and oscillating photographs. As for the α-compound the crystals are not stable at room temperature, but the decomposition started not until after

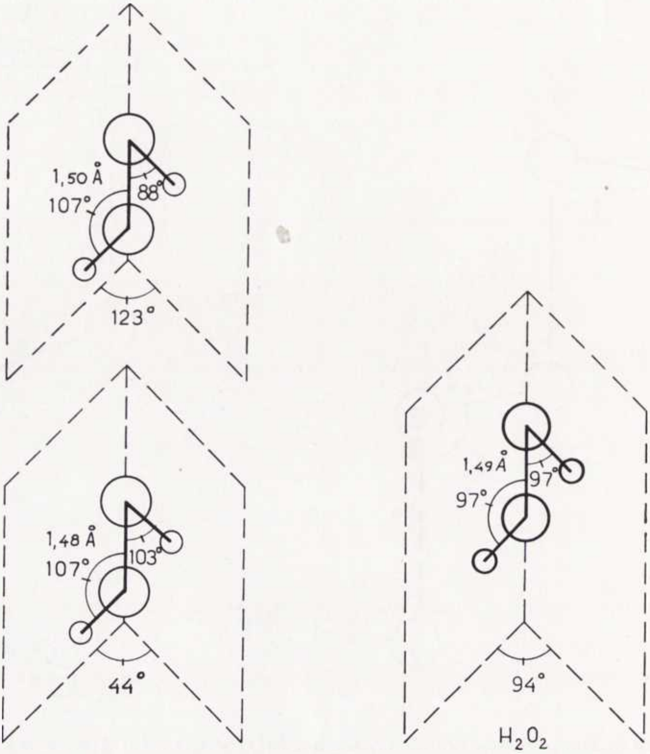

Fig. 3. (*a*) The peroxide units in α-$SrO_2 \cdot 2H_2O_2$; (*b*) the peroxide unit in H_2O_2. The hydrogen atom positions in these figures are assumed to lie on the hydrogen bond directions.

seven hours. However, once started it was very rapid. The time available was mostly sufficient for the mounting, adjusting, and the exposure.

The compound was found to be monoclinic with following dimensions of the unit cell:

$$a = 7.715 \pm 0.004 \text{ Å} \qquad c = 6.015 \pm 0.003 \text{ Å}$$
$$b = 8.754 \pm 0.005 \text{ Å} \qquad \beta = 86^\circ\, 20' \pm 2'$$

The observed and calculated $\sin^2\theta$ are tabulated in Table 5.

The pattern obeys the same extinction rules as the pattern of the α-compound; accordingly, the space group must be C $2/c$, or Cc. Also in this case the Patterson projections gave a verdict for the former space group, which requires four formula units in the elementary cell.

A Patterson projection on [001] showed that the four strontium atoms must lie in $(e)0z\frac{1}{4};\ 0\bar{z}\frac{3}{4}$. Probably by coincidence the parameter value was 0.179 also in this structure. When the positions of the strontium ions had been determined the signs of all the structure amplitudes could be obtained. Using the *hk*0 and *hhl* structure factors two Fourier projections were made (Fig. 4). From these projections it could be seen that the 24 oxygen atoms were located in three general (eightfold) positions.

Table 5. X-ray powder diffraction data for β-$SrO_2 \cdot 2H_2O_2$.

h k l	$10^4 \cdot \sin^2\theta_{obs}$	$10^4 \cdot \sin^2\theta_{calc}$	*h k l*	$10^4 \cdot \sin^2\theta_{obs}$	$10^4 \cdot \sin^2\theta_{calc}$
1 1 0	178	178	0 2 3	1793	1794
0 2 0	310	310	$\bar{2}$ 4 1	1840	1839
1 1 1	327	326	4 2 0	1914	1914
$\bar{1}$ 1 1	360	359	4 2 1	2014	2014
0 2 1	474	475	2 2 3	2098	2097
0 0 2	657	659	3 3 2	2164	2162
2 2 0	710	711	$\bar{3}$ 3 2	2361	2359
1 3 0	799	798	1 5 2	2667	2665
2 2 1	842	843	$\bar{5}$ 1 1	2833	2831
$\bar{1}$ 1 2	870	870	0 2 4	2946	2947
$\bar{2}$ 2 1	909	909	2 4 3	3031	3027
1 3 1	945	947	$\bar{4}$ 4 1	3076	3076
0 2 2	969	969	$\bar{2}$ 0 4	3168	3170
3 1 0	982	980	4 2 3	3202	3201
2 0 2	997	994	$\bar{2}$ 4 3	3226	3224
3 1 1	1094	1095	4 4 2	3371	3373
$\bar{2}$ 0 2	1123	1125	3 5 2	3401	3402
$\bar{3}$ 1 1	1191	1193	$\bar{5}$ 3 1	3453	3451
2 2 2	1305	1304	3 5 2	3601	3599
0 4 1	1405	1405	4 0 4	3979	3979
1 3 2	1425	1424	$\bar{5}$ 1 3	4307	4314
4 0 0	1604	1604	0 2 5	4434	4431
1 1 3	1612	1612	$\bar{3}$ 3 4		4435
$\bar{1}$ 1 3	1713	1711	2 6 3	4584	4579
2 4 1	1774	1773	4 6 4	4924	4924

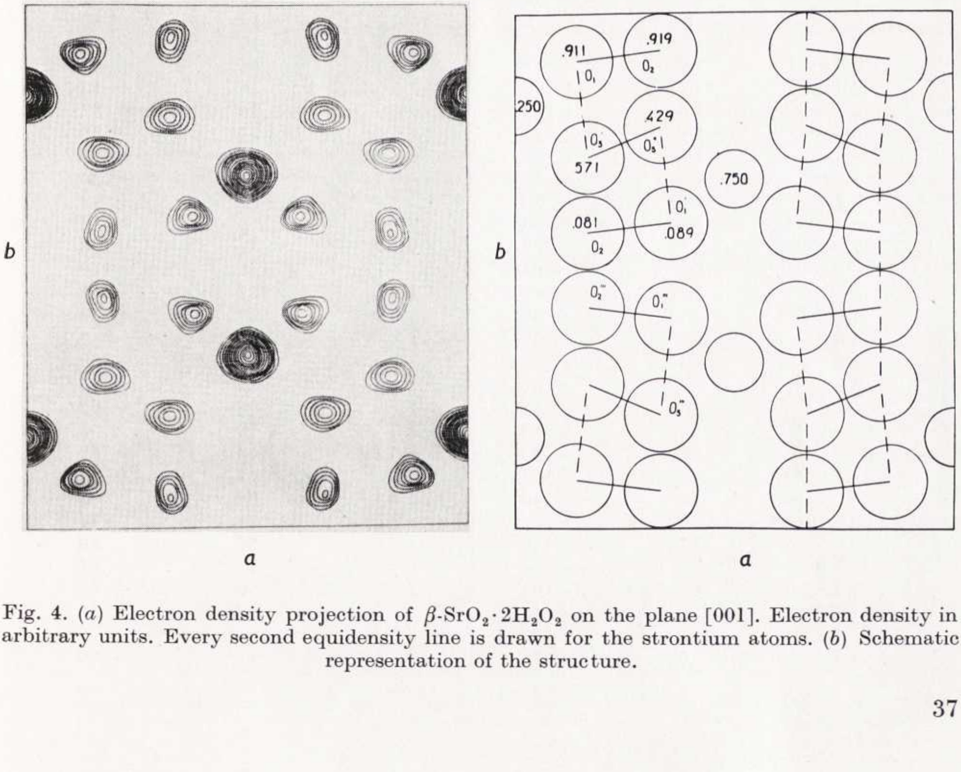

Fig. 4. (*a*) Electron density projection of β-$SrO_2 \cdot 2H_2O_2$ on the plane [001]. Electron density in arbitrary units. Every second equidensity line is drawn for the strontium atoms. (*b*) Schematic representation of the structure.

Table 6. Observed and calculated structure factors for *hk*0 and *hhl* planes of β-$SrO_2 \cdot 2H_2O_2$.

k h l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
2 0 0	50	+ 71	1 1 5	93	− 61
4 0 0	38	+ 41	1 1 6	35	− 33
6 0 0	149	+ 164	1 1 7	39	+ 55
8 0 0	70	+ 59	2 2 0	50	− 70
1 1 0	56	+ 64	2 2 1	91	− 121
3 1 0	56	+ 65	2 2 2	100	+ 97
5 1 0	—	+ 13	2 2 3	97	+ 68
7 1 0	35	+ 41	2 2 4	52	− 35
9 1 0	35	+ 48	2 2 5	55	− 57
0 2 0	83	− 82	2 2 6	38	+ 47
2 2 0	70	− 70	2 2 7	47	+ 59
4 2 0	86	− 71	3 3 0	83	− 110
6 2 0	57	− 52	3 3 1	16	+ 8
8 2 0	39	− 39	3 3 2	75	+ 87
1 3 0	133	− 118	3 3 3	—	+ 12
3 3 0	123	− 110	3 3 4	74	− 82
5 3 0	84	− 81	3 3 5	57	+ 45
7 3 0	75	− 73	3 3 6	69	+ 70
9 3 0	41	− 67	4 4 0	—	− 12
0 4 0	29	− 31	4 4 1	29	+ 40
2 4 0	24	− 31	4 4 2	20	+ 31
4 4 0	—	− 12	4 4 3	86	− 117
6 4 0	—	− 13	4 4 4	22	− 14
8 4 0	—	− 29	4 4 5	75	+ 71
1 5 0	64	+ 57	5 5 0	52	+ 72
3 5 0	115	+ 92	5 5 1	45	+ 52
5 5 0	78	+ 72	5 5 2	45	− 40
7 5 0	41	+ 39	5 5 3	49	− 69
0 6 0	26	+ 12	5 5 4	53	+ 37
2 6 0	135	+ 106	5 5 5	18	+ 17
4 6 0	114	+ 113	6 6 0	38	+ 32
6 6 0	38	+ 32	6 6 1	57	− 38
8 6 0	38	+ 58	6 6 2	71	− 68
1 7 0	—	+ 13	6 6 3	18	+ 20
3 7 0	35	− 26	6 6 4	92	+ 82
5 7 0	—	+ 25	7 7 0	—	+ 2
7 7 0	—	− 2	7 7 1	87	− 78
0 8 0	100	− 84	1 1 $\bar{1}$	114	− 110
2 8 0	75	− 62	1 1 $\bar{2}$	157	− 115
4 8 0	56	− 57	1 1 $\bar{3}$	127	+ 108
6 8 0	58	− 67	1 1 $\bar{4}$	—	− 0.2
1 9 0	70	− 58	1 1 $\bar{5}$	83	− 69
3 9 0	47	− 52	1 1 $\bar{6}$	31	− 33
5 9 0	49	− 58	1 1 $\bar{7}$	68	+ 60
0 10 0	51	+ 43	2 2 $\bar{1}$	76	− 84
2 10 0	21	+ 30	2 2 $\bar{2}$	42	+ 49
1 11 0	72	+ 67	2 2 $\bar{3}$	41	+ 62
0 0 2	55	− 46	2 2 $\bar{4}$	58	− 99
0 0 4	62	+ 56	2 2 $\bar{5}$	74	− 74
0 0 6	133	− 129	2 2 $\bar{6}$	34	+ 39
1 1 0	39	+ 64	2 2 $\bar{7}$	70	+ 51
1 1 1	82	− 101	3 3 $\bar{1}$	26	+ 26
1 1 2	—	+ 13	3 3 $\bar{2}$	58	+ 92
1 1 3	140	+ 126	3 3 $\bar{3}$	—	+ 8
1 1 4	56	+ 75	3 3 $\bar{4}$	47	− 79

Table 6 (*continued*)

$h\,k\,l$	F_{obs}	F_{calc}	$h\,k\,l$	F_{obs}	F_{calc}
$3\,3\,\bar{5}$	43	+ 25	$5\,5\,\bar{2}$	94	− 72
$3\,3\,\bar{6}$	47	+ 69	$5\,5\,\bar{3}$	44	− 45
$4\,4\,\bar{1}$	94	+ 95	$5\,5\,\bar{4}$	53	+ 37
$4\,4\,\bar{2}$	—	+ 11	$6\,6\,\bar{1}$	44	− 30
$4\,4\,\bar{3}$	86	− 107	$6\,6\,\bar{2}$	95	− 65
$4\,4\,\bar{4}$	—	− 35	$6\,6\,\bar{3}$	—	− 7
$4\,4\,\bar{5}$	75	+ 43	$6\,6\,\bar{4}$	48	+ 58
$5\,5\,\bar{1}$	44	+ 45	$7\,7\,\bar{1}$	36	− 64

The structure was then refined by the aid of the "least square" method, until $R_{hk0} = 0.14$ and $R_{hhl} = 0.19$. Calculated amplitudes have been corrected for thermal vibration $B = 2.9 \times 10^{-16}$ cm². The result is given below. See also Table 6.

Atomic coordinates for β-$SrO_2 \cdot 2H_2O_2$

	x	y	z
4Sr in (*e*)	0	0.179	$\frac{1}{4}$
$8\,O_1$ in (*f*)	0.143	0.093	0.911
$8\,O_2$ in (*f*)	0.332	0.073	0.919
$8\,O_3$ in (*f*)	0.331	0.220	0.429

Also here the standard deviations were calculated according to Cruickshank's method (7). Table 7.

The structure of β-$SrO_2 \cdot 2H_2O_2$ as determined here consists of Sr^{2+} ions and double chains of peroxide groups. Distances and angles between the various atoms are tabulated in Table 8. The peroxide groups are held together by strong hydrogen

Table 7. Standard deviations in the atomic positions of β-$SrO_2 \cdot 2H_2O_2$.

	x (Å)	y (Å)	z (Å)
Sr	0	0.008	0
O_1	0.04	0.04	0.09
O_2	0.03	0.05	0.11
O_3	0.07	0.03	0.08

Table 8. Bond lengths and angles in β-$SrO_2 \cdot 2H_2O_2$.

$Sr'—Sr''$	4.34 ± 0.01 Å	$\wedge\ O_3''—O_1—O_2$	89° ± 5°
$Sr'—Sr'''$	4.90 ± 0.01	$\wedge\ O_1—O_3''—O_3'$	111° ± 6°
$Sr—O_1$	2.38 ± 0.11	$\wedge\ O_2'''—O_3'—O_3''$	110° ± 4°
$Sr—O_3$	2.56 ± 0.10	$\wedge\ O_3'—O_2'''—O_3'''$	96° ± 4°
$O_1—O_2$	1.47 ± 0.06	$\wedge$ the plane $O_2'''\,O_3'\,O_3''$ —the plane $O_3'\,O_3''\,O_1'$	47°
$O_3'—O_3''$	1.55 ± 0.15	$\wedge$ the plane $O_3'\,O_2'''\,O_1'''$—the plane $O_2'''\,O_1'''\,O_3'''$	128°
$O_1—O_3''$	2.64 ± 0.12	$\wedge$ O_1'''—the plane $O_2'''\,O_3'\,O_3''$	34°
$O_2'''—O_3'$	2.56 ± 0.08	$\wedge\ O_2$—the plane $O_1O_3'O_3''$	40° ± 6°
$O_2'—O_2'''$	3.26 ± 0.17		
$O_2'—O_3'$	3.22 ± 0.15		

the deviation of the last three angels is about 8°

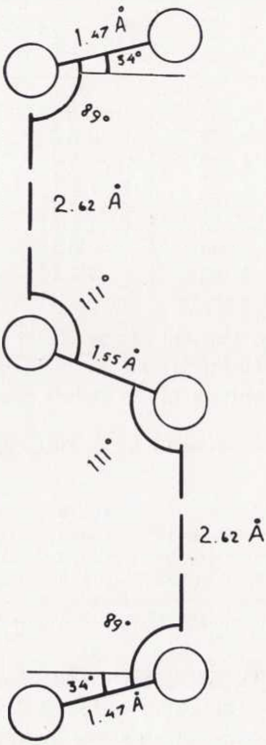

Fig. 5. Part of the chain in β-$SrO_2 \cdot 2H_2O_2$.

bonds. The distances between 2 oxygen atoms in a peroxide group are 1.47 Å and 1.55 Å. These differences are not significant. The corresponding distance for hydrogen peroxide is 1.49 Å (8). The distance between two oxygen atoms involved in the first hydrogen bond is 2.64 ± 0.10 Å. See Figs. 4 and 5. A hydrogen atom must be placed somewhere in the region between these oxygen atoms. This accounts for two of the four hydrogen atoms in β-$SrO_2 \cdot 2H_2O_2$. The other two must be bonded to the oxygen atoms in $x = 0.332$, $y = 0.073$, $z = 0.919$ and can form another hydrogen bond. The distance between this oxygen atom and the bonded atom in the next group is 2.56 Å. The angle between the peroxide axis and the hydrogen bond direction are 89°, 96°, 110° and 111°. The corresponding angle for hydrogen peroxide is 97°. The discrepancy, if real, is certainly due to the interaction of the strong electrostatic forces in this structure.

The angle between the two planes which contain the hydrogen bonds attached to a peroxide group, are 47° and 128°, in good agreement with the value for the α-compound.

The strontium ion is tetrahedrally coordinated to four oxygen atoms. However, the tetrahedron is not regular. The distances between oxygen and strontium are 2.38 Å and 2.56 Å respectively.

From Figs. 2 and 5 it is clear that the "cis chain" in α-$SrO_2 \cdot 2H_2O_2$ is very similar to one of the chains in β-$SrO_2 \cdot 2H_2O_2$. Furthermore it is interesting to note that these two groups are very similarly placed in the lattice. This is readily seen if the axes are interchanged in the following way: The a axes in the α-compound correspond to the b axes in the β-compound, the b axes in α to the c axes in β, and the c axes in α to the a axes in β.

SUMMARY

α- and β-$SrO_2 \cdot 2H_2O_2$ have been prepared and their crystal structures have been investigated. The following crystallographic data were evaluated

α	α-$SrO_2 \cdot 2H_2O_2$	β-$SrO_2 \cdot 2H_2O_2$
Space group	C 2/c No. 15	C 2/c No. 15
a	8.262 ± 0.006 Å	7.715 ± 0.004 Å
b	6.024 ± 0.004 Å	8.754 ± 0.005 Å
c	8.050 ± 0.005 Å	6.015 ± 0.003 Å
β	79° 28′ ± 8′	86° 20′ ± 2′

4Sr (e)	0	0.179	$\frac{1}{4}$	0	0.179	$\frac{1}{4}$
8O (f)	0.173	0.010	0.450	0.143	0.093	0.911
8O (f)	0.196	−0.150	0.308	0.332	0.073	0.919
8O (f)	0.015	0.520	0.088	0.331	0.220	0.429

The α- and β-compound contains infinite double chains of peroxide groups extended in the [110] and [011] plane.

ACKNOWLEDGEMENTS

My thanks are due to Professor C. Brosset for interesting and valuable discussions, and to Mrs. M. Biéth for technical assistance. This investigation was financially supported by Research Institute of National Defence.

Department of Inorganic Chemistry, Chalmers University of Technology, Göteborg, Sweden. February, 1958.

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Tryckt den 6 augusti 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB

ERRATA

Nils-Gösta Vannerberg, On the system SrO_2-H_2O-H_2O_2. 1. The crystal structure of α- and β-$SrO_2 \cdot 2H_2O_2$ (this volume, pp. 29—41).

In this paper the right coordination of Sr atoms has been missed. According to the structures of the compounds α- and β-$SrO_2 \cdot 2H_2O_2$ arrived at, the strontium ions are surrounded by one more oxygen tetrahedron than mentioned in the paper. The eight oxygen atoms then form a distorted dodecahedron.

The peroxide chains in the β-compound are linked into nets parallel with (100), which does not, either, follow clearly from the paper.

Corrections to be inserted

Page 34 Table 4 *add* Sr-O_1 2.55 ± 0.05 Å
Sr-O_2''' 2.67 ± 0.08

Page 35 line 9 *for* four *read* eight
» 10 *for* tetrahedron *read* dodecahedron
» 10 *for* 2.44 and 2.65 Å *read* 2.44, 2.55, 2.65 and 2.67 Å

Page 39 line 7 *for* double chains *read* nets
Table 8 *add* Sr-O_2' 2.69 ± 0.07 Å
Sr-O_1'''' 2.79 ± 0.06

Page 40 line 16 *for* tetrahedrally *read* dodecahedrally
line 18 *for* 2.38 and 2.56 Å *read* 2.38, 2.56, 2.69 and 2.79 Å

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Band 14 nr 14

Nils-Gösta Vannerberg

On the system BaO_2-H_2O-H_2O_2

3. The crystal structure of α-, β-, and γ-$BaO_2 \cdot 2H_2O_2$ and $BaO_2 \cdot H_2O_2 \cdot 2H_2O$

ALMQVIST & WIKSELL / STOCKHOLM

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By NILS-GÖSTA VANNERBERG

With 10 figures in the text

Introduction

In a preceding paper (1) dealing with the existing phases in the system BaO_2–H_2O–H_2O_2 and with the crystal structure of the compound $BaO_2 \cdot H_2O_2$, the chemical literature in this field, including the compounds α-, β-, γ-$BaO_2 \cdot 2H_2O_2$ and $BaO_2 \cdot H_2O_2 \cdot 2H_2O$, has been reviewed. The methods of preparation for these compounds have also been described. The present paper deals with their structure as established by X-ray methods.

X-ray methods

The phase identification was performed with Guinier powder photographs. The structural investigations were based on single crystal methods. The single crystals were rotated about suitable crystal axes and Weissenberg photographs were taken generally of the zero and first layer lines, sometimes of all the layer lines. Multiple film technique was used. The reflexion intensities were estimated by visual comparison with known scales and corrected by Lorentz and polarization factors. With some exceptions, no allowance was made for the absorption factor. Cu $K\alpha$ radiation was used in all cases.

The structure of α-$BaO_2 \cdot 2H_2O_2$

The single crystals of α-$BaO_2 \cdot 2H_2O_2$ show several different crystal habits. They can develop as monoclinic tablets or prismas or long needles. In weak solutions the prismas or tablets are dominant, in strong solutions the needles.

The compound is not stable at room temperature but the decomposition is not noticeable before six hours.

α–$BaO_2 \cdot 2H_2O_2$ appeared to be monoclinic. The following cell dimensions were found from Guinier photographs

$$a = 8.454 \pm 0.006 \text{ Å} \qquad c = 8.084 \pm 0.005 \text{ Å}$$
$$b = 6.398 \pm 0.004 \text{ Å} \qquad \beta = 96°32' \pm 4'$$
$$v = 434.4 \text{ Å}^3$$

Table 1. Powder diffraction data for α–$BaO_2 \cdot 2H_2O_2$.

$h\ k\ l$	$10^4 \sin^2 \theta_{obs}$	$10^4 \sin^2 \theta_{calc}$	I	$h\ k\ l$	$10^4 \sin^2 \theta_{obs}$	$10^4 \sin \theta_{calc}$	I
1 1 0	230	230	w	2 2 3	1926	1925	w
$\bar{1}$ 1 1	302	302	vs	2 0 4	1965	1969	vw
2 0 0	338	337	vs	0 2 4	2053	2054	w
0 0 2	368	369	m	$\bar{3}$ 3 1	2095	2096	w
0 2 0	581	580	w	4 2 2	2134	2135	vw
$\bar{2}$ 0 2	626	626	w	$\bar{1}$ 3 3	2156	2159	vw
1 1 2	637	639	m	1 3 3	2279	2279	vw
0 2 1	671	672	w	3 3 2	2316	2312	vw
2 0 2	784	786	m	$\bar{5}$ 1 2	2416	2419	w
2 2 0	918	917	m	$\bar{1}$ 1 5	2439	2433	vw
$\bar{3}$ 1 1	936	938	s	$\bar{4}$ 0 4	2501	2501	vw
0 2 2	948	949	m	$\bar{2}$ 2 4	2545	2549	w
$\bar{1}$ 1 3	999	1000	s	$\bar{3}$ 3 3	2709	2713	vw
3 1 1	1054	1056	m	5 1 3	2786	2783	w
1 1 3	1117	1120	vw	1 3 4	2942	2943	vw
$\bar{3}$ 1 2	1153	1153	vw	$\bar{2}$ 4 2		2945	
2 2 2	1209	1206	m	6 0 0	3029	3033	vw
4 0 0	1349	1348	m	3 3 3	3080	3074	vw
2 2 2	1367	1365	w	4 0 4	3148	3142	vw
3 1 2	1392	1393	m	2 4 3	3369	3368	vw
$\bar{1}$ 3 1	1465	1463	w	$\bar{2}$ 0 6	3410	3413	vw
0 0 4	1474	1474	w	3 1 5	3505	3508	vw
$\bar{3}$ 1 3	1553	1553	s	$\bar{1}$ 3 5	3600	3595	vw
4 0 2		1556		0 4 2	3791	3796	vw
$\bar{1}$ 1 4	1627	1626	vw	4 4 1	3844	3842	vw
$\bar{2}$ 2 3		1627		0 2 6	3892	3897	vw
2 0 4	1650	1653	vw	5 3 2	3984	3982	vw
$\bar{1}$ 3 2	1720	1720	w	6 2 2	4228	4222	vw
1 3 2	1801	1800	w	3 5 0	4394	4389	vw
3 1 3	1907	1912	w	$\bar{1}$ 1 7	4609	4606	vw

Calculated and observed $\sin^2\theta$ values are given in Table 1. The observed density is 3.57 g/cm³, the calculated 3.63 g/cm³ if four formula units in the elementary cell are assumed. The density determination was performed as described earlier (1).

In all photographs, reflexions from planes of the following types only were observed

$$hkl \text{ with } h + k = 2n$$
$$h0l \text{ with } h = 2n,\ l = 2n.$$

Accordingly, possible space groups are C2/c No. 15 and Cc No. 9.

Since the unit cell dimensions in Å of α-$SrO_2 \cdot 2H_2O_2$ are $a = 8.262$, $b = 6.024$, $c = 8.050$ and $\beta = 100°32'$ $(79°28')$, it seemed probable that α-$BaO_2 \cdot 2H_2O_2$ is isomorphous with this compound (2). In such case the space group might be C2/c No. 15. The present investigation showed this to be the case.

The barium atom parameters were determined from Patterson projections on the (100) and (010) planes; using these parameter values, the signs of the structure factors could be calculated. Then it was attempted to determine the oxygen atom positions from electron density projections. However, especially in the projection on the (010) plane, the oxygen peaks were very small. For this reason a difference projection on

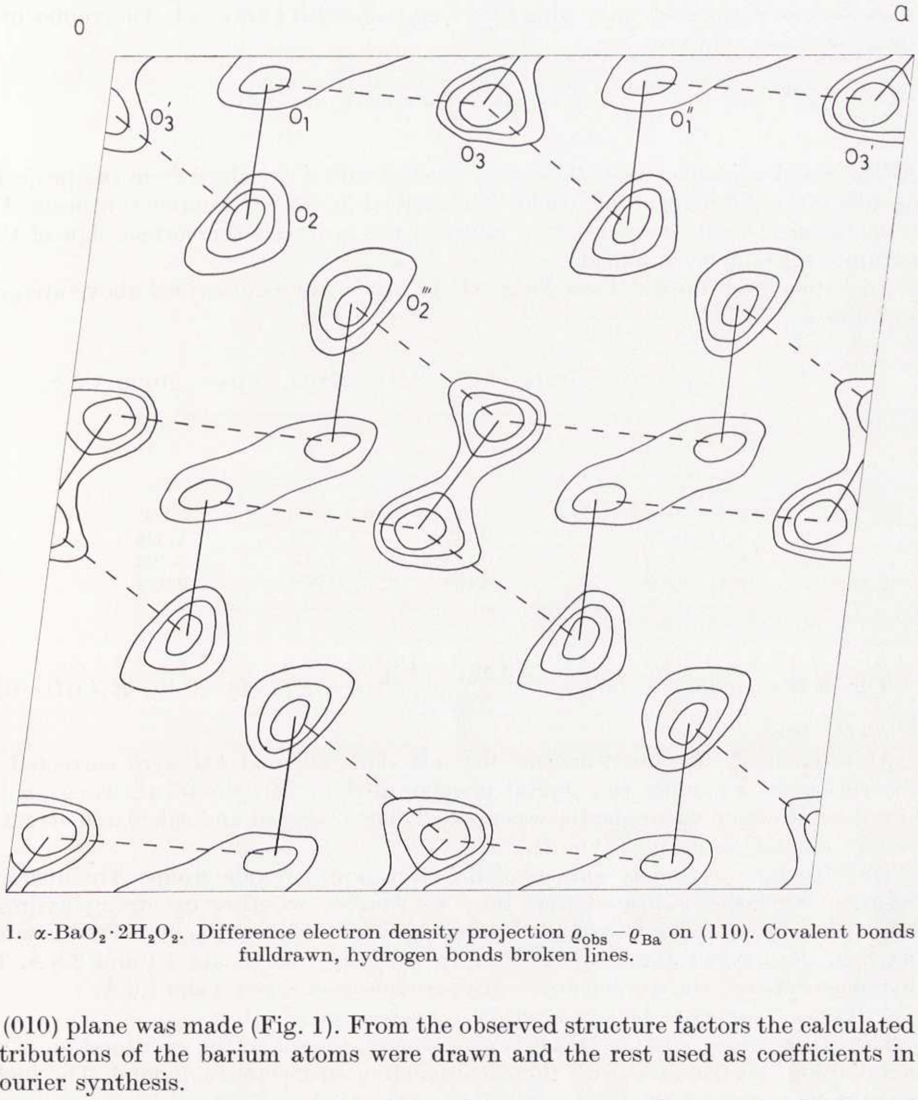


Fig. 1. α-$BaO_2 \cdot 2H_2O_2$. Difference electron density projection $\varrho_{\text{obs}} - \varrho_{\text{Ba}}$ on (110). Covalent bonds fulldrawn, hydrogen bonds broken lines.

the (010) plane was made (Fig. 1). From the observed structure factors the calculated contributions of the barium atoms were drawn and the rest used as coefficients in a Fourier synthesis.

However, the y parameters being deduced from structure factors of reflexions of the type $hk0$, the signs are undetermined. This follows from the expression for A, the phase part of the structure factor. For such reflexions this is

$$A_n = N_n \cdot \cos 2\pi h x_n \cdot \cos 2\pi k y_n$$

where x_n and y_n are the x and y parameters of the n:th atom and N_n the number of equal positions of the n:th atom. It is obvious that for a given x parameter the y parameters can have two values $\pm y_n$. The proper x, y combinations could be obtained from a Fourier synthesis based on the reflexions $h1l$. Two such difference syntheses were performed, one with $l = 2n$ and one with $l = 2n + 1$. The values of the latter Fourier synthesis are

$$\sum_h \sum_l F(h\,1\,l) \sin 2\pi(hx + lz) \cdot \sin 2\pi ky.$$

As the x and z parameters of the atoms were already determined from the projection on (010), the different atoms could be identified in the $h1l$ Fourier synthesis. Thus from the sign of the corresponding peaks in the synthesis the correct sign of the y parameter could be obtained.

The atomic parameters for α-$BaO_2 \cdot 2H_2O_2$ arrived at as described above are given in Table 2.

Table 2. Atomic coordinates for α-$BaO_2 \cdot 2H_2O_2$. Space group C2/c.

	x	y	z
4 Ba in (e)	0	0.206	1/4
8 O_1 in (f)	0.179	0.975	0.026
8 O_2 in (f)	0.173	0.865	0.202
8 O_3 in (f)	0.458	0.060	0.059

The corresponding R factors $\frac{\Sigma \| F_0 | - | F_c \|}{\Sigma | F_0 |}$ are $R(hk0) = 0.15$, $R(h0l) = 0.13$, $R(h1l) = 0.18$.

At refinement, the intensities of the reflexions $h0l$ and $h1l$ were corrected for absorption by assuming the crystal prismas used to be cylindrical, using general formulas. No temperature factor was applied. The observed and calculated structure factors are tabulated in Table 3.

The structure arrived at consists of Ba^{2+} ions and peroxide groups. The distances between the latter indicated that they are bonded together by strong hydrogen bonds into infinite chains extended parallel with [110] (see Fig. 1). The distances between the oxygen atoms which form the hydrogen bonds are 2.4 and 2.8 Å. The distances between the oxygen atoms in a peroxide group are 1.4 and 1.6 Å.

A Ba^{2+} ion seems to be surrounded by twelve oxygen atoms.

The structure of α $BaO_2 \cdot 2H_2O_2$ is accordingly, except in the coordination of the metallic ion, isostructural with the corresponding strontium-compound. The higher coordination number of the barium ions in the former is caused by a small twist of one of the peroxide groups.

In Table 4 some interatomic distances and bond angles can be found.

The structure of β-$BaO_2 \cdot 2H_2O_2$

The single crystals of this compound consist of short prismas, very often showing skeletal growths. Similar to all other hydroperoxidates so far investigated, β-barium peroxide dihydroperoxidate is not stable at room temperature. The decomposition was total after four hours.

Table 3. Observed and calculated structure factors for α-$BaO_2 \cdot 2H_2O_2$.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
2	0	0	202	+186	6	0	4	143	+161	3	1	3	159	+164
4	0	0	206	+164	8	0	4	129	+111	3	1	4	—	−8
6	0	0	228	+189	0	0	6	182	−132	3	1	5	133	−126
8	0	0	105	+78	2	0	6	187	−177	3	1	6	50	−46
10	0	0	111	+94	4	0	6	101	−83	3	1	7	105	+110
1	1	0	29	+48	6	0	6	110	−94	3	1	8	38	+46
3	1	0	54	−55	8	0	6	88	−92	3	1	9	67	−88
5	1	0	77	+72	0	0	8	95	+90	$\bar{3}$	1	1	107	−182
7	1	0	60	+44	2	0	8	98	+101	$\bar{3}$	1	2	66	−64
9	1	0	—	+18	4	0	8	119	+109	$\bar{3}$	1	3	171	+169
0	2	0	111	−84	0	0	10	92	−102	$\bar{3}$	1	4	35	+26
2	2	0	145	−148	$\bar{2}$	0	2	131	−141	$\bar{3}$	1	5	98	−124
4	2	0	126	−125	$\bar{4}$	0	2	183	−185	$\bar{3}$	1	6	54	−34
6	2	0	126	−96	$\bar{6}$	0	2	166	−140	$\bar{3}$	1	7	120	+100
8	2	0	143	−122	$\bar{8}$	0	2	112	−129	$\bar{3}$	1	8	67	+44
10	2	0	99	−94	$\overline{10}$	0	2	121	−124	$\bar{3}$	1	9	62	+94
1	3	0	124	−139	$\bar{2}$	0	4	131	+106	5	1	10	62	+72
3	3	0	116	−124	$\bar{4}$	0	4	128	+114	5	1	1	175	−142
5	3	0	97	−99	$\bar{6}$	0	4	109	+123	5	1	2	43	−36
7	3	0	95	−92	$\bar{8}$	0	4	66	+71	5	1	3	149	+129
9	3	0	70	−73	$\overline{10}$	0	4	71	+80	5	1	4	39	+30
0	4	0	78	+64	$\bar{2}$	0	6	166	−129	5	1	5	123	−122
2	4	0	82	+67	$\bar{4}$	0	6	166	−178	5	1	6	—	−14
4	4	0	71	+65	$\bar{6}$	0	6	77	−100	5	1	7	111	+122
6	4	0	68	+50	$\bar{8}$	0	6	72	−109	5	1	8	35	+30
8	4	0	61	+48	$\bar{2}$	0	8	133	+105	$\bar{5}$	1	1	115	−106
1	5	0	158	+140	$\bar{4}$	0	8	89	+94	$\bar{5}$	1	2	43	−29
3	5	0	131	+125	$\bar{6}$	0	8	62	+102	$\bar{5}$	1	3	113	+119
5	5	0	116	+124	2	0	10	95	−104	$\bar{5}$	1	4	51	+73
7	5	0	105	+104	1	1	0	30	+48	$\bar{5}$	1	5	76	−102
0	6	0	—	+16	1	1	1	129	−156	$\bar{5}$	1	6	—	−24
2	6	0	—	−12	1	1	2	103	−116	$\bar{5}$	1	7	105	+98
4	6	0	—	−0.4	1	1	3	179	−153	$\bar{5}$	1	8	47	+28
6	6	0	—	+24	1	1	4	51	+47	7	1	0	47	+44
1	7	0	75	−79	1	1	5	145	−103	7	1	1	139	−188
3	7	0	82	−114	1	1	6	69	−52	7	1	2	60	−59
5	7	0	75	−78	1	1	7	145	+119	7	1	3	98	+99
0	8	0	43	−58	1	1	8	—	+36	7	1	4	—	+16
2	8	0	31	−83	1	1	9	104	−103	7	1	5	100	−90
2	0	0	179	+186	1	1	10	24	−24	7	1	6	70	−63
4	0	0	195	+164	$\bar{1}$	1	1	122	−183	$\bar{7}$	1	1	130	−119
6	0	0	205	+189	$\bar{1}$	1	2	18	−38	$\bar{7}$	1	2	—	−6
8	0	0	100	+78	$\bar{1}$	1	3	155	+190	$\bar{7}$	1	3	152	+121
10	0	0	97	+94	$\bar{1}$	1	4	75	+64	$\bar{7}$	1	4	50	+48
0	0	2	160	−155	$\bar{1}$	1	5	185	−148	$\bar{7}$	1	5	96	−121
2	0	2	173	−176	$\bar{1}$	1	6	—	+20	$\bar{7}$	1	6	—	+3
4	0	2	87	−90	$\bar{1}$	1	7	182	−137	9	1	0	—	+18
6	0	2	133	−121	$\bar{1}$	1	8	65	+55	9	1	1	104	−127
8	0	2	116	−126	$\bar{1}$	1	9	96	−116	9	1	2	30	−26
10	0	2	73	−88	$\bar{1}$	1	10	—	+0.4	9	1	3	99	+103
0	0	4	294	+212	3	1	0	70	−55	$\bar{9}$	1	1	105	−113
2	0	4	168	+157	3	1	1	216	−208	$\bar{9}$	1	2	—	−23
4	0	4	147	+144	3	1	2	39	−90	$\bar{9}$	1	3	106	+102

Table 4. Interatomic distances and bond angles in α-$BaO_2 \cdot 2H_2O_2$.

$Ba - Ba''$	4.85 Å	$Ba - O_2'''$	2.9 Å
$Ba - Ba'''$	5.15	$Ba - O_1''$	2.9
$Ba - O_1$	2.8	$O_1 - O_2$	1.6
$Ba - O_2$	2.7	$O_3' - O_3''$	1.4
$Ba - O_3'$	2.7	$O_1 - O_3$	2.4
$Ba - O_3''$	2.9	$O_3' - O_2$	2.8

$\wedge\ O_1'' \ldots O_3' - O_3''$	115°
$\wedge\ O_3 \ldots O_1 - O_2$	100°
$\wedge\ O_3' \ldots O_2 - O_1$	90°
$\wedge\ O_2 \ldots O_3' - O_3''$	115°
$\wedge\ O_1'' \ldots O_3' \ldots O_2$	140°

Weissenberg photographs were taken with rotation about the c axis and a direction parallel with $[1\bar{1}0]$. The prisma axis of the crystals coincided with the c axis. The unit cell dimensions were measured from rotation and single film Weissenberg photographs, as these gave the desired accuracy. They were found to be

$$a = 8.18 \pm 0.03 \text{ Å} \qquad c = 6.35 \pm 0.03 \text{ Å}$$
$$b = 9.03 \pm 0.04 \text{ Å} \qquad \beta = 95°40' \pm 18$$
$$v = 467 \text{ Å}^3$$

With four formula units in the elementary cell, the density is calculated to 3.38 g/cm^3, in good agreement with the observed value 3.41 g/cm^3. In all photographs, reflexions from planes of the following types only were observed:

$$hkl \text{ with } h + k = 2n$$
$$h0l \text{ with } h = 2n,\ l = 2n.$$

The space group is accordingly C2/c No. 15 or Cc No. 9. β-$BaO_2 \cdot 2H_2O_2$ is probably isostructural with the corresponding strontium compound (2) since the elementary cell dimensions in Å of the latter are $a = 7.72$, $b = 8.75$, $c = 6.02$, $\beta = 93°40'$ $(86°20')$. The space group is then C2/c No. 15.

On the assumption of isomorphy between β-$SrO_2 \cdot 2H_2O_2$ and β-$BaO_2 \cdot 2H_2O_2$, the barium positions in the latter could be evaluated by trial and error methods. When the barium positions were estimated, the signs of the structure factors could be determined. Two electron density projections were then made, one on the (001) plane and the other on the (110) plane. Besides, a difference projection on (001) was made. From the observed structure factors the contributions of the barium atoms were drawn and the rest was used in a Fourier synthesis. See Fig. 2.

Owing to the crystal habit, the hhl intensities are greatly affected with absorption errors. To diminish these, the intensities were divided into two groups, each with a certain scale factor. One of the groups contained reflexions with $\varphi = 0°$–$40°$ and $120°$–$180°$ and the other $\varphi = 40°$–$120°$ $(\varphi_{hh0} = 0)$.

While the x and y parameters of the oxygen atoms could be evaluated rather accurately, the z parameters, which were determined from the hhl reflexions, were only approximate. In order to increase the accuracy, a complete three-dimensional calculation was made using the $hk0$, $hk1$, $hk2$ and $hk3$ reflexions. From the observed

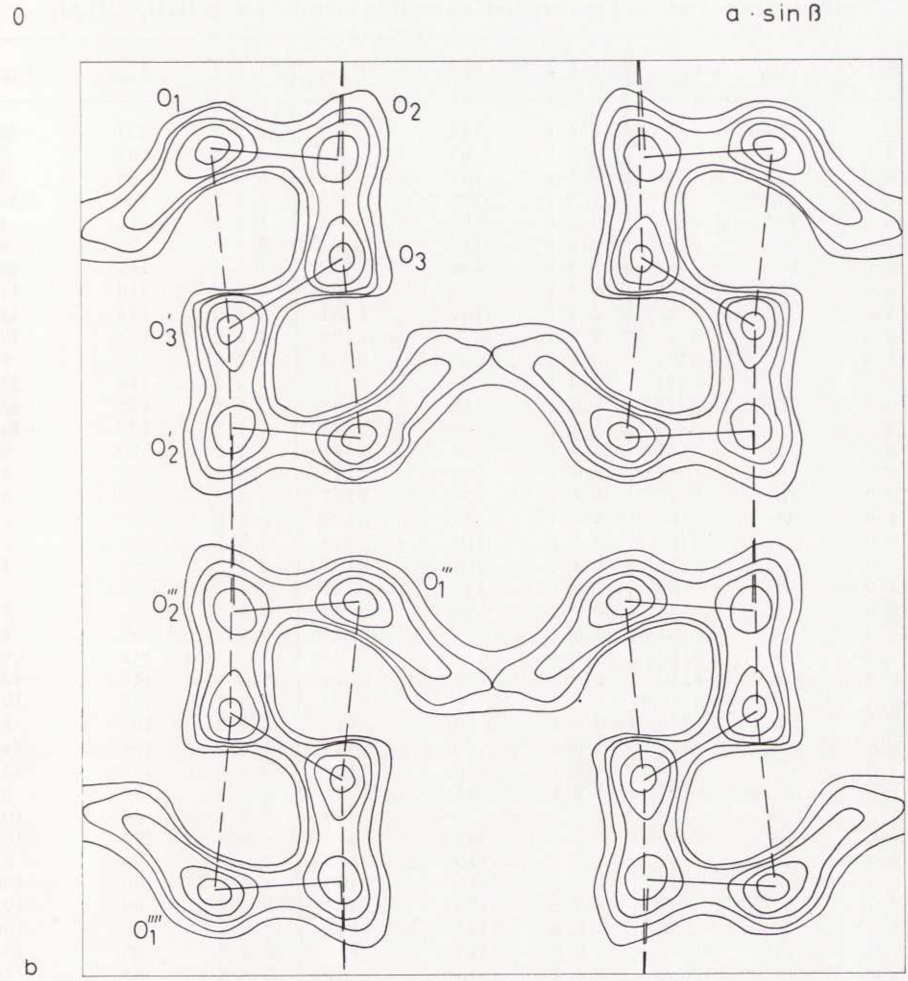


Fig. 2. β-$BaO_2 \cdot 2H_2O_2$. Difference electron density projection $\varrho_{obs} - \varrho_{Ba}$ on (001). Covalent bonds fulldrawn, hydrogen bonds broken lines.

Table 5. Atomic coordinates for β-$BaO_2 \cdot 2H_2O_2$. Space group C2/c.

	x	y	z
4 Ba in (e)	0	0.185	1/4
8 O_1 in (f)	0.158	0.090	0.658
8 O_2 in (f)	0.315	0.100	0.581
8 O_3 in (f)	0.310	0.210	0.075

Table 6. Observed and calculated structure factors for β-$BaO_2 \cdot 2H_2O_2$.

h k l	F_{obs}	F_{calc}	k h l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}
0 2 0	138	−145	$\bar{5}$ 1 1	184	−117	4 2 2	131	+124
0 4 0	45	− 45	0 2 1	97	−116	6 2 2	68	+ 74
0 6 0	71	+ 55	2 2 1	107	−148	8 2 2	88	+ 79
0 8 0	92	−138	4 2 1	103	−130	$\bar{2}$ 2 2	106	+154
0 10 0	102	+108	6 2 1	98	− 82	$\bar{4}$ 2 2	76	+ 80
1 1 0	95	+ 99	$\bar{2}$ 2 1	173	−162	$\bar{6}$ 2 2	79	+ 85
1 3 0	187	−164	$\bar{4}$ 2 1	124	−132	1 3 2	185	+200
1 5 0	134	+113	6 2 1	—	− 66	3 3 2	119	+113
1 7 0	—	− 33	1 3 1	167	+151	5 3 2	131	+128
1 9 0	81	− 63	3 3 1	—	+ 34	7 3 2	101	+123
1 11 0	111	+107	5 3 1	—	+ 4	9 3 2	78	+ 83
2 0 0	103	+121	$\bar{1}$ 3 1	—	− 16	$\bar{1}$ 3 2	146	+132
2 2 0	125	+117	$\bar{3}$ 3 1	62	+ 68	$\bar{3}$ 3 2	139	+133
2 4 0	—	− 4	$\bar{5}$ 3 1	—	+ 62	$\bar{5}$ 3 2	136	+148
2 6 0	149	+131	0 4 1	220	+221	$\bar{7}$ 3 2	99	+ 92
2 8 0	119	−117	2 4 1	104	+114	0 4 2	—	+ 15
2 10 0	75	+ 47	4 4 1	135	+157	2 4 2	—	+ 18
3 1 0	90	+ 88	6 4 1	113	+126	4 4 2	—	+ 1
3 3 0	189	−182	$\bar{2}$ 4 1	146	+150	6 4 2	—	+ 4
3 5 0	171	+153	$\bar{4}$ 4 1	101	+102	8 4 2	—	+ 16
3 7 0	78	− 60	$\bar{6}$ 4 1	176	+171	$\bar{2}$ 4 2	—	− 2
3 9 0	—	− 43	1 5 1	79	+ 68	$\bar{4}$ 4 2	—	+ 10
3 11 0	75	+104	3 5 1	—	+ 58	$\bar{6}$ 4 2	—	+ 16
4 0 0	134	+129	5 5 1	—	+ 61	1 5 2	112	− 99
4 2 0	115	−110	$\bar{1}$ 5 1	61	+ 79	3 5 2	117	−126
4 4 0	—	0.0	$\bar{3}$ 5 1	—	+ 50	5 5 2	126	−131
4 6 0	108	+116	0 6 1	95	−118	7 5 2	106	− 81
4 8 0	104	−113	2 6 1	100	− 49	$\bar{1}$ 5 2	154	−146
5 1 0	—	+ 9	4 6 1	90	−108	$\bar{3}$ 5 2	109	−135
5 3 0	105	−111	$\bar{2}$ 6 1	88	− 94	$\bar{5}$ 5 2	96	− 90
5 5 0	120	+139	$\bar{4}$ 6 1	—	− 50	$\bar{7}$ 5 2	84	−104
5 7 0	—	+ 2	1 7 1	147	−159	0 6 2	124	−108
5 9 0	78	− 77	3 7 1	113	−113	2 6 2	99	− 92
6 0 0	169	+162	$\bar{1}$ 7 1	119	−100	4 6 2	105	−100
6 2 0	91	−109	$\bar{3}$ 7 1	135	−126	6 6 2	96	−102
6 4 0	—	+ 2	2 0 2	194	−189	$\bar{2}$ 6 2	88	−106
6 6 0	94	+ 86	4 0 2	185	−172	$\bar{4}$ 6 2	96	−103
6 8 0	110	−113	6 0 2	76	— 87	$\bar{6}$ 6 2	83	− 74
7 1 0	78	+ 73	8 0 2	135	−150	1 7 2	96	+ 79
7 3 0	104	−117	$\bar{2}$ 0 2	189	−218	3 7 2	—	+ 8
7 5 0	92	+ 78	$\bar{4}$ 0 2	100	−110	5 7 2	—	+ 28
7 7 0	—	− 41	$\bar{6}$ 0 2	133	−154	7 7 2	—	+ 48
8 0 0	96	+103	$\bar{8}$ 0 2	—	−118	$\bar{1}$ 7 2	—	+ 12
8 2 0	70	− 64	1 1 2	133	−162	$\bar{3}$ 7 2	—	+ 22
8 4 0	—	− 16	3 1 2	—	− 24	$\bar{5}$ 7 2	83	+ 63
8 6 0	91	+ 80	5 1 2	—	− 41	$\bar{7}$ 7 2	—	+ 6
9 1 0	—	+ 40	7 1 2	77	− 76	0 8 2	120	+121
9 3 0	96	−105	9 1 2	—	− 27	2 8 2	127	+122
9 5 0	98	+114	$\bar{1}$ 1 2	—	− 23	4 8 2	151	+110
10 0 0	98	+111	$\bar{3}$ 1 2	—	− 39	$\bar{2}$ 8 2	102	+117
1 1 1	187	−176	$\bar{5}$ 1 2	91	−101	$\bar{4}$ 8 2	109	+112
3 1 1	191	−174	$\bar{7}$ 1 2	—	− 24	$\bar{6}$ 8 2	106	+107
5 1 1	106	−132	$\bar{9}$ 1 2	—	− 40	1 9 2	—	+ 24
$\bar{1}$ 1 1	173	−166	0 2 2	110	+100	3 9 2	—	+ 80
$\bar{3}$ 1 1	261	−195	2 2 2	97	+102	5 9 2	—	+ 53

Table 6 (cont.)

$h\ k\ l$	F_{obs}	F_{calc}	$h\ k\ l$	F_{obs}	F_{calc}	$h\ k\ l$	F_{obs}	F_{calc}
$\bar{1}$ 9 2	75	+ 78	$\bar{8}$ 2 3	65	+ 86	$\bar{3}$ 5 3	84	− 66
$\bar{3}$ 9 2	60	+ 65	1 3 3	74	− 91	$\bar{5}$ 5 3	104	− 54
$\bar{5}$ 9 2	—	+ 27	3 3 3	—	− 16	$\bar{7}$ 5 3	—	− 47
0 10 2	—	− 53	5 3 3	89	− 94	0 6 3	60	+ 46
2 10 2	62	− 66	7 3 3	—	− 34	2 6 3	95	+114
$\bar{2}$ 10 2	60	− 78	$\bar{1}$ 3 3	—	− 47	4 6 3	60	+ 69
$\bar{4}$ 10 2	63	− 42	$\bar{3}$ 3 3	—	− 4	6 6 3	—	+ 52
1 1 3	145	+134	$\bar{5}$ 3 3	103	− 94	$\bar{2}$ 6 3	103	+ 98
3 1 3	91	+122	$\bar{7}$ 3 3	—	− 17	$\bar{4}$ 6 3	124	+ 83
5 1 3	99	+142	0 4 3	132	− 99	$\bar{6}$ 6 3	113	+ 50
7 1 3	113	+ 95	2 4 3	242	−190	1 7 3	114	+137
$\bar{1}$ 1 3	171	+176	4 4 3	96	−114	3 7 3	123	+ 98
$\bar{3}$ 1 3	136	+123	6 4 3	60	− 94	5 7 3	117	+112
$\bar{5}$ 1 3	92	+117	8 4 3	111	−138	$\bar{1}$ 7 3	124	+115
$\bar{7}$ 1 3	113	+111	$\bar{2}$ 4 3	135	−146	$\bar{3}$ 7 3	122	+ 93
0 2 3	186	+140	$\bar{4}$ 4 3	132	−146	$\bar{5}$ 7 3	123	+134
2 2 3	63	+ 72	$\bar{6}$ 4 3	107	− 99	0 8 3	—	+ 11
4 2 3	93	+110	$\bar{8}$ 4 3	110	−115	2 8 3	—	+ 30
6 2 3	83	+107	1 5 3	88	− 66	4 8 3	—	+ 7
8 2 3	—	+ 56	3 5 3	—	− 67	6 8 3	—	+ 2
$\bar{2}$ 2 3	110	+124	5 5 3	—	− 42	$\bar{2}$ 8 3	—	+ 1
$\bar{4}$ 2 3	84	+ 78	7 5 3	—	− 55	$\bar{4}$ 8 3	—	+ 16
$\bar{6}$ 2 3	113	+ 94	$\bar{1}$ 5 3	—	− 50	$\bar{6}$ 8 3	—	+ 14

Table 7. Bond lengths and angles in β-$BaO_2 \cdot 2H_2O_2$.

$Ba' - Ba'$	4.61 Å	$Ba - O_1''''$	2.9 Å
$Ba' - Ba'''$	5.24	$O_1 - O_2$	1.4
$Ba - O_1$	2.9	$O_3' - O_3$	1.5
$Ba - O_2'$	2.6	$O_1 - O_3'$	2.5
$Ba - O_3'$	2.9	$O_2''' - O_3'$	2.8
$Ba - O_3$	2.9		

$\wedge\ O_3' \ldots O_1 - O_2$	100°
$\wedge\ O_1 \ldots O_3' - O_3$	95°
$\wedge\ O_2''' \ldots O_3' - O_3$	120°
$\wedge\ O_3' \ldots O_2''' - O_1'''$	85°
$\wedge\ O_2''' \ldots O_3' \ldots O_1$	135°

structure factors of these reflexions the calculated contribution of the barium ions was first drawn. The rest was then used in a three-dimensional Fourier synthesis.

The structure was now refined until $R(hk0) = 0.11$, $R(hkl) = 0.15$ and $R(hhl) = 0.22$. The parameter values obtained are tabulated in Table 5, and a comparison between observed and calculated structure factors in Table 6. Some interatomic distances are tabulated in Table 7.

The structure of β-$BaO_2 \cdot 2H_2O_2$ consists of Ba^{2+} ions and peroxide groups. The peroxide groups are held together by hydrogen bonds. These are revealed by a short oxygen–oxygen distance. The peroxide groups are linked into infinite chains, which are bonded into layers parallel with the (100) plane. See Fig. 3.

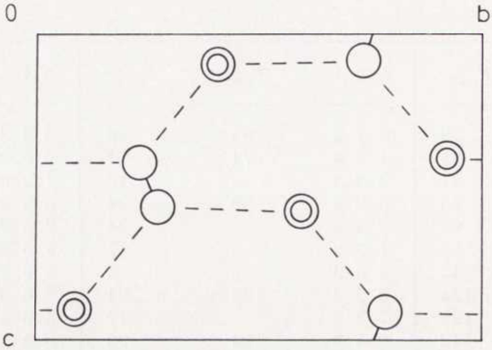


Fig. 3. Schematic representation of the peroxide layer in β-$BaO_2 \cdot 2H_2O_2$. Covalent bonds full-drawn, hydrogen bonds broken lines.

The distances between such oxygen atoms which form hydrogen bonds are 2.5 and 2.8 Å. The distances between the oxygen atoms in a peroxide group are 1.4 and 1.5 Å.

The barium atoms are surrounded by ten oxygen atoms.

The structure arrived at is, as predicted, isomorphous with β-$SrO_2 \cdot 2H_2O_2$. The barium atoms are, however, surrounded by ten oxygen atoms instead of eight (2). This is caused by a small twist of one of the peroxide ions.

The structure of γ-$BaO_2 \cdot 2H_2O_2$

The single crystals of this compound consist of short prismas or tablets. The usual decomposition was not noticeable at room temperature before six hours.

The compound appeared to be orthorhombic. The cell dimensions were determined from Guinier photographs.

$$a = 16.837 \pm 0.014 \text{ Å}$$
$$b = 6.407 \pm 0.006 \text{ Å}$$
$$c = 8.005 \pm 0.007 \text{ Å}$$
$$v = 863.5 \text{ Å}^3$$

Calculated and observed $\sin^2 \theta$ values can be found in Table 8. The measured density is 3.56 g/cm^3, the calculated 3.65 assuming eight formula units in the elementary cell. The systematic extinctions are of the following kind

$$0kl \; k \neq 2n$$
$$h0l \; l \neq 2n$$
$$hk0 \; h \neq 2n$$

The space group is accordingly Pbca No. 61.

If the dimensions of the unit cells of α-$BaO_2 \cdot 2H_2O_2$ and γ-$BaO_2 \cdot 2H_2O_2$ are compared (Table 9) it appears that the b and c axes of γ-$BaO_2 \cdot 2H_2O_2$ are of about the same lengths as those of α-$BaO_2 \cdot 2H_2O_2$ while the a axis is about twice as long.

As the agreement is striking, it seemed possible that the elementary cell of the γ-compound consists of two monoclinic twins joined along the (100) plane. Tei-Ichi

Table 8. Powder diffraction data for γ-$BaO_2 \cdot 2H_2O_2$.

$h\ k\ l$	$10^4 \sin^2 \theta_{obs}$	$10^4 \sin^2 \theta_{calc}$	I	$h\ k\ l$	$10^4 \sin^2 \theta_{obs}$	$10^4 \sin^2 \theta_{calc}$	I
2 1 0	229	228	vw	8 0 2	1712	1713	vw
2 1 1	331	332	vs	6 1 3	1738	1735	w
4 0 0	336	336	m	2 3 2	1756	1757	vw
0 0 2	372	371	m	4 0 4	1820	1819	vw
0 2 0	578	579	m	8 2 0	1919	1921	w
0 2 1	673	672	m	8 2 1	2014	2014	w
4 0 2	710	707	s	6 3 1	2151	2151	w
3 2 1	859	861	w	8 2 2	2295	2292	vw
4 2 0	911	915	m	10 1 1	2335	2335	vw
0 2 2	949	949	s	4 4 1	2739	2744	w
6 1 1	992	994	s	12 0 0	3016	3019	vw
4 2 1	1006	1007	m	12 0 2	3397	3390	vw
2 1 3	1069	1064	w	10 3 0		3400	
4 2 2	1286	1285	m	4 4 3	3485	3486	vw
8 0 0	1342	1342	w	10 3 1		3492	
2 3 0	1384	1387	vw	12 2 1	3690	3692	vvw
2 3 1	1477	1480	w	12 2 2	3970	3968	vvw
1 0 4	1504	1505	vw				

Table 9. A comparison of the unit cell dimensions of α- and γ-$BaO_2 \cdot 2H_2O_2$.

a	16.837	$2 \cdot 8.454 \cdot \sin 96° \ 32'$	$= 16.798$
b	6.407	6.398	$= 6.398$
c	8.005	8.084	$= 8.084$
v	863.5	$2 \cdot 434.4$	$= 868.9$

Ito (3, 4) has studied this kind of polymorphy very thoroughly. For instance, he has shown that if two monoclinic cells with the space group C2/c are joined through a glide reflexion across (100), at least one of the combinations of index $h/2 + k + l/2$ and $h/2 + k - l/2$ must not be an odd integer if the reflexion hkl is to occur (3).

This rule, however, is not obeyed here. On the other hand, the extinction rule $h/2 + k \neq 2n$, when h is even, is valid. Accordingly, the elementary cell of the γ-compound is centered in the same way as that of the α-compound.

In his monograph "X-ray studies on Polymorphism" Ito has described a number of polymorphic compounds, whose behavior are closely related to that of α- and γ-$BaO_2 \cdot 2H_2O_2$ (4). Especially interesting is the couple diopsid-enstatit, the space group of diopsid being C2/c and that of enstatit Pbca. The same author has shown that for the latter compound his rule is nearly satisfied. The unit cell is composed of two monoclinic elementary cells, the space group of which, however, is not C2/c but $P2_1/c$ owing to a shift in the metallic atom positions. If the same circumstances are valid for the pair α-γ-$BaO_2 \cdot 2H_2O_2$ it is quite possible that the rule of Ito fails here, too, as a consequence of the strong dependence of the intensities on the barium atom positions.

Using the assumed relation between the structures of α- and γ-$BaO_2 \cdot 2H_2O_2$, the barium atom position could be determined by trial and error methods. From these positions the signs of the structure factors of the reflexions $h0l$ and $hk0$ were deter-

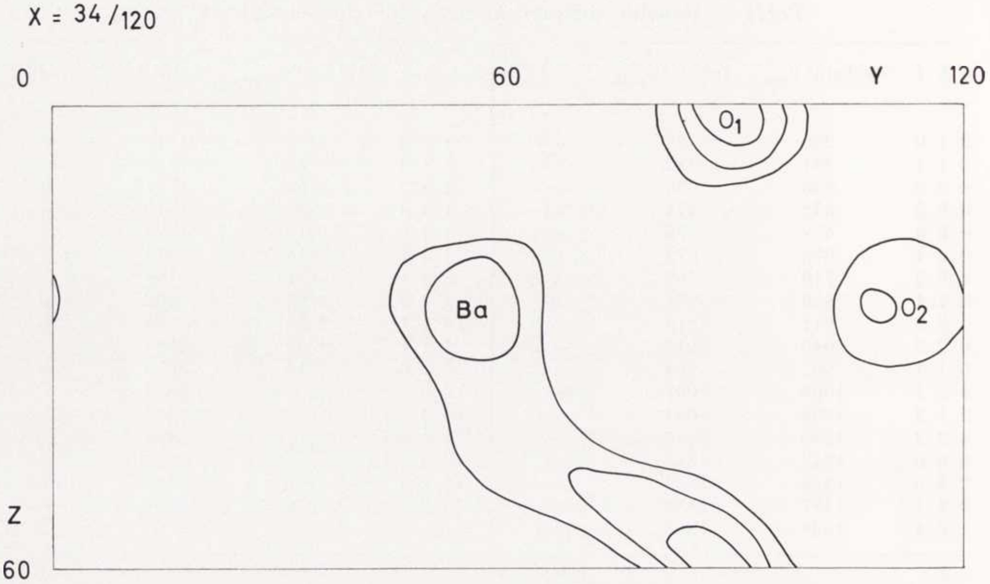


Fig. 4. Section through the unit cell of γ-$BaO_2 \cdot 2H_2O_2$. $x = 34/120$.

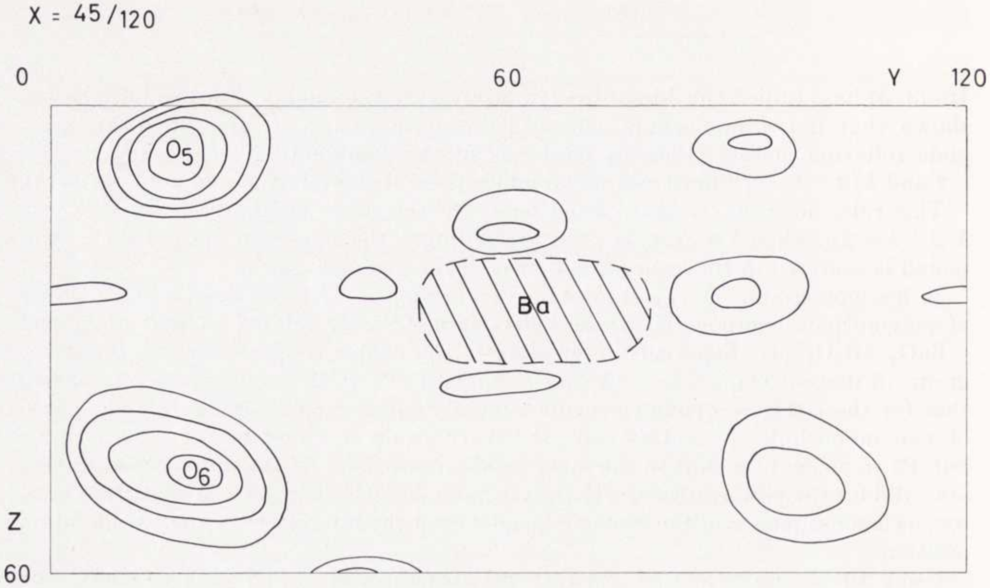


Fig. 5. Section through the unit cell of γ-$BaO_2 \cdot 2H_2O_2$. $x = 45/120$.
Negative area shaded.

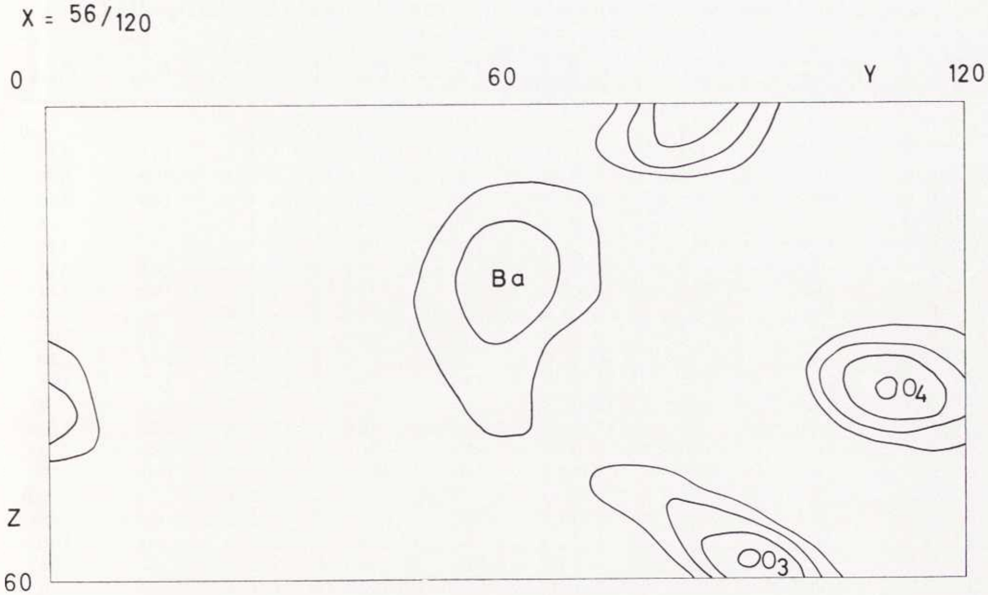


Fig. 6. Section through the unit cell of γ-$BaO_2 \cdot 2H_2O_2$. $x = 56/120$.

Table 10. Atomic coordinates for γ-$BaO_2 \cdot 2H_2O_2$. Space group Pbca.

	x	y	z
8 Ba in (c)	0.375	0.542	0.219
8 O_1 in (c)	0.283	0.758	0.023
8 O_2 in (c)	0.292	0.885	0.200
8 O_3 in (c)	0.472	0.767	0.483
8 O_4 in (c)	0.466	0.917	0.317
8 O_5 in (c)	0.375	0.150	0.042
8 O_6 in (c)	0.375	0.167	0.397

mined. Then two electron density projections along the *b* and *c* axis were made. From the projections, approximate oxygen positions could be obtained. To refine these, difference syntheses $\varrho_{obs} - \varrho_{Ba}$ were made which, however, gave some "ghosts". Moreover, the shift of the oxygen parameters in the *h0l* projection was considerable. Better results were obtained with a three dimensional difference synthesis. From reflexions of the type *hkl* (h max $= 15$, k max $= 3$, l max $= 10$) the barium contribution was first drawn. This contribution was not corrected for thermal vibration, as it was thought that the absorption effect would largely compensate the temperature factor. Summation was first made over *h* and *l* and then over *k*. Three different sections from this three-dimensional synthesis can be found in Figs. 4, 5 and 6. From these sections rather accurate oxygen parameters could be determined, although it appeared that the temperature factor of the barium atoms was under-estimated.

Table 11. Observed and calculated structure factors for γ-$BaO_2 \cdot 2H_2O_2$.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
2	0	0	—	0.3	0	0	8	—	−12	0	1	3	—	0.0
4	0	0	309	−384	1	0	8	141	−141	1	1	3	171	−177
6	0	0	—	−2	2	0	8	—	+0.2	2	1	3	309	−309
8	0	0	407	+369	3	0	8	145	−160	3	1	3	103	+106
10	0	0	—	−2	4	0	8	—	−10	4	1	3	—	−8
12	0	0	488	−437	5	0	8	150	+130	5	1	3	125	+148
14	0	0	—	−0.4	6	0	8	—	−7	6	1	3	261	+314
0	0	2	243	−277	7	0	8	137	+118	7	1	3	122	−111
1	0	2	103	+125	8	0	8	—	−5	8	1	3	—	−4
2	0	2	—	+3	9	0	8	137	−144	9	1	3	86	−105
3	0	2	—	+20	10	0	8	—	−9	10	1	3	274	−240
4	0	2	303	+303	11	0	8	136	−136	11	1	3	127	+122
5	0	2	97	−108	12	0	8	—	+8	12	1	3	—	+4
6	0	2	—	−22	13	0	8	129	+126	13	1	3	132	+115
7	0	2	114	−110	0	0	10	75	+107	14	1	3	182	−212
8	0	2	276	−261	1	0	10	116	+151	15	1	3	100	−75
9	0	2	—	+29	2	0	10	—	−2	0	1	4	—	0.0
10	0	2	—	−22	3	0	10	130	+125	1	1	4	62	−48
11	0	2	95	+73	4	0	10	84	−61	2	1	4	80	+100
12	0	2	245	+215	5	0	10	111	−130	3	1	4	65	+54
13	0	2	96	−87	2	1	0	58	+87	4	1	4	—	−6
14	0	2	—	+2	6	1	0	120	−122	5	1	4	—	+41
15	0	2	—	−41	10	1	0	162	−105	6	1	4	—	−12
0	0	4	257	+298	14	1	0	100	−23	7	1	4	—	−42
1	0	4	208	−166	1	1	1	71	+70	8	1	4	—	−4
2	0	4	—	−13	2	1	1	245	−315	9	1	4	—	−40
3	0	4	125	−134	3	1	1	—	−14	10	1	4	70	+97
4	0	4	201	−177	4	1	1	—	+1	1	1	5	162	+173
5	0	4	152	+164	5	1	1	60	−46	2	1	5	147	−149
6	0	4	—	−10	6	1	1	302	+383	3	1	5	133	−117
7	0	4	137	+148	7	1	1	80	+51	4	1	5	—	+9
8	0	4	224	+176	8	1	1	—	−7	5	1	5	138	−158
9	0	4	167	−101	9	1	1	—	+24	6	1	5	140	+128
10	0	4	—	−2	10	1	1	290	+240	7	1	5	144	+162
11	0	4	125	−123	11	1	1	—	−42	8	1	5	—	+10
12	0	4	204	−212	12	1	1	—	−12	9	1	5	148	+116
13	0	4	136	+185	13	1	1	—	−43	10	1	5	150	−133
14	0	4	—	+8	14	1	1	280	+227	11	1	5	147	−138
15	0	4	116	+113	15	1	1	—	+18	12	1	5	—	+5
0	0	6	88	−61	0	1	2	—	0.0	13	1	5	139	−135
1	0	6	157	+245	1	1	2	—	+21	14	1	5	132	−113
2	0	6	—	−15	2	1	2	115	+123	15	1	5	121	−96
3	0	6	179	+155	3	1	2	97	−87	1	1	6	—	+8
4	0	6	146	+161	4	1	2	—	+10	2	1	6	—	+10
5	0	6	239	−211	5	1	2	—	−24	3	1	6	60	−61
6	0	6	—	−0.04	6	1	2	131	−160	4	1	6	—	+5
7	0	6	201	−215	7	1	2	—	+7	5	1	6	—	−2
8	0	6	121	−131	8	1	2	—	+5	6	1	6	—	+56
9	0	6	153	+146	9	1	2	—	+53	7	1	6	—	−11
10	0	6	—	−11	10	1	2	65	−64	8	1	6	—	+8
11	0	6	142	+191	11	1	2	—	−26	9	1	6	—	+50
12	0	6	111	+63	12	1	2	—	−3	10	1	6	—	+22
13	0	6	175	−194	13	1	2	—	−18	11	1	6	—	−24
14	0	6	—	−10	14	1	2	100	+98	12	1	6	—	+6
15	0	6	132	−130	15	1	2	—	+40	13	1	6	—	−6

Table 11 (cont.)

h k l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}
14 1 6	—	+ 18	14 2 2	—	− 3	5 2 6	108	+ 134
15 1 6	—	+ 41	15 2 2	60	+ 67	6 2 6	—	+ 7
0 1 7	—	0.0	0 2 3	59	+ 54	7 2 6	101	+ 122
1 1 7	148	− 165	1 2 3	35	+ 17	8 2 6	83	− 67
2 1 7	60	− 65	2 2 3	—	− 11	9 2 6	85	− 131
3 1 7	147	+ 155	3 2 3	47	+ 71	10 2 6	—	+ 4
4 1 7	—	− 6	4 2 3	95	− 96	11 2 6	120	− 113
5 1 7	147	+ 172	5 2 3	42	− 25	12 2 6	68	+ 85
6 1 7	—	+ 23	6 2 3	—	+ 2	13 2 6	104	+ 112
7 1 7	142	− 169	7 2 3	—	+ 26	14 2 6	—	− 5
8 1 7	—	− 9	8 2 3	80	+ 89	15 2 6	74	+ 127
9 1 7	132	− 146	9 2 3	60	− 67	0 2 7	60	− 58
10 1 7	61	− 63	10 2 3	—	+ 10	1 2 7	83	+ 72
11 1 7	120	+ 147	11 2 3	—	− 28	2 2 7	—	− 7
12 1 7	—	− 7	12 2 3	108	− 58	3 2 7	60	− 98
13 1 7	98	+ 141	13 2 3	—	+ 16	4 2 7	—	+ 4
14 1 7	—	+ 45	14 2 3	—	+ 5	5 2 7	67	+ 87
15 1 7	71	− 45	15 2 3	87	− 43	6 2 7	—	− 5
2 2 0	—	+ 21	0 2 4	133	+ 143	7 2 7	60	+ 86
4 2 0	200	− 309	1 2 4	108	+ 147	8 2 7	—	− 15
6 2 0	—	+ 19	2 2 4	—	− 3	9 2 7	60	− 90
8 2 0	285	+ 260	3 2 4	110	+ 96	10 2 7	—	+ 0
10 2 0	—	+ 6	4 2 4	182	− 224	11 2 7	74	+ 66.6
12 2 0	275	− 182	5 2 4	133	− 142	12 2 7	—	+ 43
14 2 0	—	− 11	6 2 4	—	+ 7	13 2 7	60	+ 64
0 2 1	116	− 135	7 2 4	134	− 146	14 2 7	—	+ 6
1 2 1	—	+ 20	8 2 4	161	+ 189	0 2 8	—	− 27
2 2 1	—	+ 4	9 2 4	78	+ 90	1 2 8	88	+ 162
3 2 1	67	− 62	10 2 4	—	+ 10	2 2 8	—	− 10
4 2 1	148	+ 254	11 2 4	109	+ 109	3 2 8	96	+ 126
5 2 1	—	− 16	12 2 4	142	− 125	4 2 8	—	− 18
6 2 1	—	− 9	13 2 4	120	− 115	5 2 8	122	− 148
7 2 1	—	− 11	14 2 4	—	− 0	6 2 8	—	− 0
8 2 1	180	− 199	15 2 4	120	− 81.7	7 2 8	102	− 153.1
9 2 1	—	+ 50	0 2 5	117	− 112	8 2 8	—	+ 9
10 2 1	—	− 11	1 2 5	92	− 83	9 2 8	88	+ 128
11 2 1	—	+ 25	2 2 5	—	+ 10	10 2 8	—	+ 8
12 2 1	121	+ 111	3 2 5	106	− 139	11 2 8	63	+ 142
13 2 1	—	+ 8	4 2 5	79	+ 96	2 3 0	113	− 230
14 2 1	—	+ 0	5 2 5	67	+ 87	4 3 0	—	− 3
15 2 1	—	+ 26.3	6 2 5	—	+ 3	6 3 0	181	+ 212
0 2 2	534	− 410	7 2 5	66	+ 80	8 3 0	—	− 9
1 2 2	113	− 83	8 2 5	69	− 91	10 3 0	228	− 175
2 2 2	—	− 8	9 2 5	88	− 127	12 3 0	—	− 12
3 2 2	60	− 95	10 2 5	—	− 5	14 3 0	215	+ 182
4 2 2	212	+ 233	11 2 5	84	− 80	1 3 1	—	+ 27
5 2 2	69	+ 96	12 2 5	40	+ 86	2 3 1	184	− 273
6 2 2	—	+ 8	13 2 5	60	− 57	3 3 1	32	− 51
7 2 2	38	+ 84	14 2 5	—	− 7	4 3 1	—	+ 16
8 2 2	195	− 234	15 2 5	75	− 89	5 3 1	—	− 26
9 2 2	85	− 70	0 2 6	82	− 103	6 3 1	185	+ 220
10 2 2	—	+ 13	1 2 6	112	− 124	7 3 1	—	+ 24
11 2 2	93	− 61	2 2 6	—	+ 6	8 3 1	—	+ 13
12 2 2	330	+ 268	3 2 6	114	− 154	9 3 1	57	+ 43
13 2 2	108	+ 64	4 2 6	76	+ 67	10 3 1	255	− 216

Table 11 (cont.)

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
11 3 1	—	− 24	1 3 4	61	+ 78	6 3 6	79	− 62
12 3 1	—	+ 0.1	2 3 4	108	− 125	7 3 6	100	− 107
13 3 1	—	− 19	3 3 4	124	− 161	8 3 6	—	− 9
14 3 1	216	+ 188	4 3 4	—	+ 9	9 3 6	89	− 101
15 3 1	—	+ 30	5 3 4	86	− 89	10 3 6	54	+ 71
1 3 2	48	− 41	6 3 4	138	+ 169	11 3 6	90	+ 92
2 3 2	185	+ 269	7 3 4	94	+ 64	12 3 6	—	− 5
3 3 2	54	+ 78	8 3 4	—	+ 9	13 3 6	90	+ 104
4 3 2	—	− 4	9 3 4	180	+ 127	14 3 6	54	− 53
5 3 2	36	− 56	10 3 4	107	− 92	15 3 6	69	− 101
6 3 2	97	− 112	11 3 4	82	− 83	1 3 7	112	− 122
7 3 2	—	− 46	12 3 4	—	+ 2	2 3 7	—	+ 29
8 3 2	—	+ 2	13 3 4	77	− 62	3 3 7	111	+ 117
9 3 2	—	− 57	14 3 4	111	+ 122	4 3 7	—	+ 4
10 3 2	227	+ 243	15 3 4	120	+ 112	5 3 7	112	+ 105
11 3 2	—	+ 35	1 3 5	70	+ 130	6 3 7	77	− 46
12 3 2	—	+ 9	2 3 5	103	− 129	7 3 7	102	− 104
13 3 2	87	+ 39	3 3 5	117	− 145	8 3 7	—	+ 4
14 3 2	173	− 156	4 3 5	—	− 2	9 3 7	107	− 109
15 3 2	77	− 58	5 3 5	98	− 113	10 3 7	—	+ 27
1 3 3	62	− 73	6 3 5	103	+ 114	11 3 7	104	+ 108
2 3 3	124	+ 132	7 3 5	104	+ 110	12 3 7	—	+ 1
3 3 3	54	+ 60	8 3 5	—	− 0.9	13 3 7	86	+ 106
4 3 3	—	− 9	9 3 5	109	+ 131	14 3 7	—	− 27
5 3 3	65	+ 45	10 3 5	100	− 113	1 3 8	89	+ 112
6 3 3	120	− 118	11 3 5	102	− 111	2 3 8	—	+ 14
7 3 3	74	− 51	12 3 5	—	+ 1	3 3 8	93	− 135
8 3 3	—	− 8	13 3 5	112	− 104	4 3 8	—	+ 5
9 3 3	53	− 56	14 3 5	115	+ 100	5 3 8	115	− 97
10 3 3	140	+ 115	15 3 5	117	+ 109	6 3 8	—	+ 43
11 3 3	84	+ 57	1 3 6	89	− 113	7 3 8	109	+ 89
12 3 3	—	− 0.4	2 3 6	83	+ 72	8 3 8	—	− 9
13 3 3	82	− 60	3 3 6	97	+ 113	9 3 8	77	+ 126
14 3 3	154	− 111	4 3 6	—	− 7	10 3 8	—	− 25
15 3 3	110	− 50	5 3 6	98	+ 106			

Table 12. Interatomic distances in γ-$BaO_2 \cdot 2H_2O_2$.

$Ba-Ba'$	4.81 Å	$Ba-O_6$	2.8 Å	O_4-O_6	2.3 Å
$Ba-Ba''$	5.31	$Ba-O_6'$	2.9	O_2-O_5	2.5
$Ba-Ba'''$	5.29	$Ba-O_3$	3.0	$O_3''-O_6'$	2.8
$Ba-O_1$	2.6	$Ba-O_4$	2.9	$O_1'''-O_5'$	2.8
$Ba-O_2$	2.6	$Ba-O_2''$	3.0	$O_3''-O_5'$	2.7
$Ba-O_3'$	2.8	$Ba-O_1'$	3.1	$O_1'''-O_6$	2.9
$Ba-O_4''''$	2.8	O_1-O_2	1.6	$O_1'-O_2$	2.8
$Ba-O_5$	2.9	O_3-O_4	1.6	O_2-O_6	2.8
$Ba-O_5'$	2.9	$O_5'-O_6$	1.6	O_5-O_6	2.8

Table 13. Angles between assumed or real bonds in γ-$BaO_2 \cdot 2H_2O_2$.

O_4	$\ldots O_6$	$-O_5'$	130°	O_1'''	$\ldots O_5'$	$-O_6$	80°
O_6	$\ldots O_4$	$-O_3$	100°	O_5'	$\ldots O_3''$	$-O_4''$	100°
O_5'	$\ldots O_2'$	$-O_1'$	90°	O_3''	$\ldots O_5'$	$-O_6$	70°
O_2'	$\ldots O_5'$	$-O_6$	140°	O_1'''	$\ldots O_6$	$-O_5$	70°
O_6	$\ldots O_3''$	$-O_4''$	110°	O_6	$\ldots O_1'''$	$-O_2'''$	110°
O_3''	$\ldots O_6$	$-O_5'$	70°	O_2	$\ldots O_1'$	$-O_2'$	160°
O_5'	$\ldots O_1'''$	$-O_2'''$	100°	O_1'	$\ldots O_2$	$-O_1$	130°

The atomic coordinates can be found in Table 10. A comparison between observed and calculated structure factors is given in Table 11. The observed structure factors have been corrected for thermal vibration by the factor exp. $\frac{B \sin^2\theta}{\lambda^2}$, where $B(h0l) = 0.6$ Å^2, $B(h1l) = 0.0$ Å^2, $B(h2l) = 0.5$ Å^2, $B(h3l) = 0.4$ Å^2.

Interatomic distances and bond angles are tabulated in Tables 12 and 13.

The structure arrived at is very similar to that of α-$BaO_2 \cdot 2H_2O_2$. It consists of Ba^{2+} ions and peroxide groups. The latter are joined by hydrogen bonds. The barium ions are surrounded by twelve oxygen atoms, in the same way as in the α-compound. See Fig. 7 or 8.

The orthorhombic cell of γ-$BaO_2 \cdot 2H_2O_2$ may be considered as composed of two monoclinic cells, the space group of which is not that of α-$BaO_2 \cdot 2H_2O_2$ C2/c but very nearly $P2_1/c$ owing to a shift in the positions of the certain atoms.

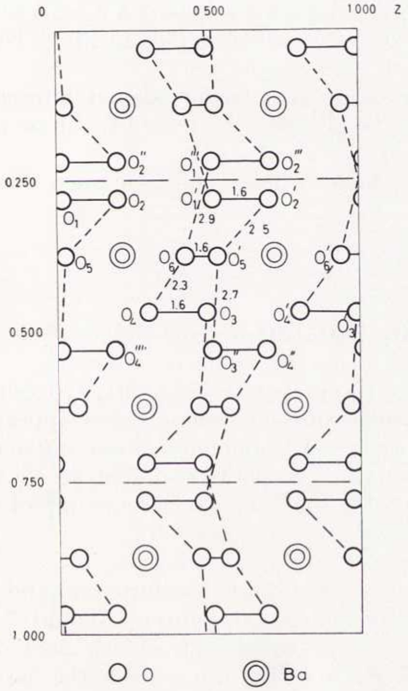


Fig. 7. The hydrogen bonding in γ-$BaO_2 \cdot 2H_2O_2$. (Alternative 1.)

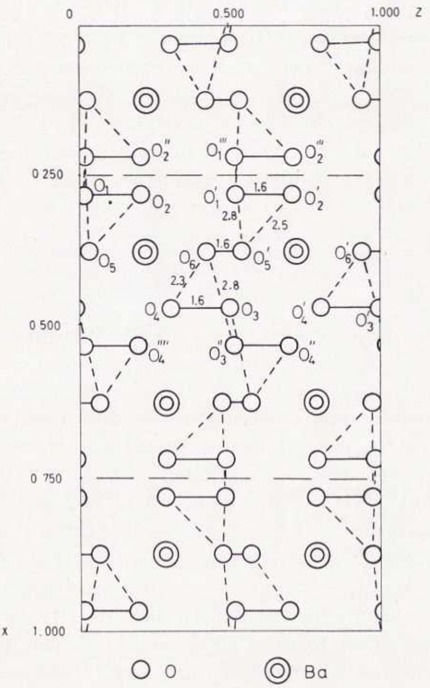
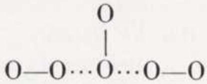


Fig. 8. The hydrogen bonding in γ-$BaO_2 \cdot 2H_2O_2$. (Alternative 2.)

The hydrogen bonding in γ-$BaO_2 \cdot 2H_2O_2$

Hydrogen atoms cannot be detected by X-ray methods in structures like that of γ-$BaO_2 \cdot 2H_2O_2$. A hydrogen bond, however, may be indicated by a short distance between oxygen atoms. In the α- and β-compound there were just enough such short distances to account for the hydrogen atoms. In the γ-compound, however, there are four hydrogen atoms in the asymmetric unit to nine oxygen–oxygen distances which may indicate hydrogen bonds. Among these distances, two rather certainly indicate hydrogen bonding (O_2–O_5, O_4–O_6), as they are very short. There is probably no hydrogen bond between the oxygen atoms O_2–O_6, because this would give a chain of the following kind



$$\begin{array}{c} \mathrm{O} \\ | \\ \mathrm{O{-}O\cdots O\cdots O{-}O} \end{array}$$

which is not stable. Further, if there really were a hydrogen bond between the oxygen atoms O_2 and O_1', the bond angles would be 130° and 160°, which should be compared with the bond angle 100° found in β-$SrO_2 \cdot 2H_2O_2$ (2). There can be no hydrogen bonding between O_5 and O_6, as this would cause a barium–hydrogen distance of only 2.8 Å. Then there are four short oxygen–oxygen distances left, but only two hydrogen atoms. Two structures can be proposed, both very plausible (Figs. 7, 8). Both the bond distances and angles are probable. At this stage it is impossible to choose between them, but it may be pointed out that the structure described in Fig. 7 corresponds to that of the α-compound.

It must also be mentioned that both structures can be included if bifurcated hydrogen bonds are accepted. However, such bonds are very rare. Until now they have only been encountered in one structure (5).

The structures arrived at consist of short double chains linked in such a way, that a layer is formed (Figs. 9, 10).

The structure of $BaO_2 \cdot H_2O_2 \cdot 2H_2O$

As previously reported (1) during one attempt to prepare α-$BaO_2 \cdot 2H_2O_2$, together with needle-like crystals of this compound, some tiny crystalline flakes appeared. The flakes were easily separated by the aid of a sieve. The amount was about five mg. All attempts to reproduce the synthesis have failed. A qualitative analysis showed that the crystals contained barium and peroxide ions, The small amount of the compound at hand made it difficult to establish the composition.

A quantitative analysis was performed, however, in the following way:

About 0.7 mg of the compound was dissolved in cool diluted sulfuric acid and the peroxide content determined by titration with permanganate solution. About 0.7 mg was then treated in a weighed crucible with concentrated hydrochloric acid. The crucible was heated until only $BaCl_2$ was left. By weighing the crucible the barium content could be determined. The water content was obtained as rest of weight, the hydrogen peroxide content from the charge balance.

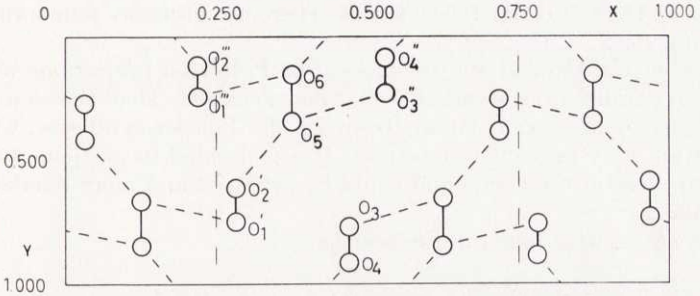


Fig. 9. The "layers" in γ-$BaO_2 \cdot 2H_2O_2$. (Alternative 1.)

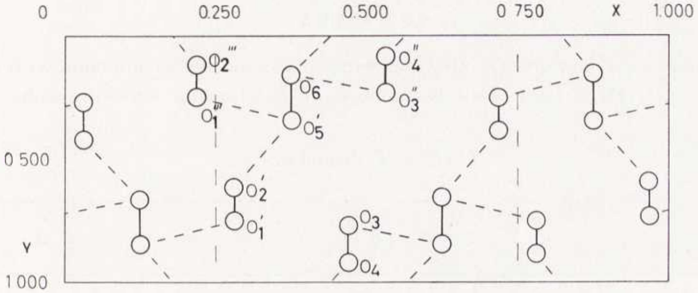


Fig. 10. The "layers" in γ-$BaO_2 \cdot 2H_2O_2$. (Alternative 2.)

	% Ba	% O_2
	66	25
	50	30
	49	24
Mean	55	26

If the rest is assumed to be water, the formula $BaO_2 \cdot H_2O_2 \cdot 2H_2O$ is arrived at as may be seen from the following figures.

	% Ba^{2+}	% O_2^{2-}	% H_2O_2	% H_2O
Observed	55	13	14	18
Calculated for $BaO_2 \cdot H_2O_2 \cdot 2H_2O$	57	13	14	15

Weissenberg photographs were taken with rotation about three axes. From these photographs it was concluded that the unit cell had monoclinic symmetry with the cell dimensions

$$a = 10.39 \pm 0.04 \text{ Å} \qquad c = 6.58 \pm 0.03 \text{ Å}$$
$$b = 8.36 \pm 0.03 \text{ Å} \qquad \beta = 95°0' \pm 18'$$

The systematic extinctions were of the following kind:

$$0k0 \text{ when } k = 2n + 1$$
$$h0l \text{ when } l = 2n + 1$$

The space group is accordingly $P2_1/c$ No. 14. There are probably four formula units in the elementary cell.

With the aid of the *hk*0 and *h*0*l* reflexions, two Patterson projections were made, from which the barium atom positions could be calculated. Then the sign of almost all the reflexions could be calculated. However, the Fourier syntheses, which were then made, were very difficult to interpret. It was decided to postpone further calculations until more of the compound could be prepared and more reliable analytical data obtained.

The barium atoms were found in the position

$$x = 0.202 \qquad y = 0.033 \qquad z = 0.071.$$

SUMMARY

The structure of α-, β- and γ-$BaO_2 \cdot 2H_2O_2$ and the space group of a compound with the possible formula $BaO_2 \cdot H_2O_2 \cdot 2H_2O$ have been determined. The following crystallographic data were evaluated.

Unit cell dimensions.

	a	*b*	*c*	*β*	Space group
α-$BaO_2 \cdot 2H_2O_2$	8.454 ± 0.006 Å	6.398 ± 0.004 Å	8.084 ± 0.005 Å	96° 32′ ± 4′	C2/c
β-$BaO_2 \cdot 2H_2O_2$	8.18 ± 0.03 Å	9.03 ± 0.04 Å	6.35 ± 0.03 Å	95° 40′ ± 18′	C2/c
γ-$BaO_2 \cdot 2H_2O_2$	16.837 ± 0.014 Å	6.407 ± 0.006 Å	8.005 ± 0.007 Å	—	Pbca
$BaO_2 \cdot H_2O_2 \cdot 2H_2O$	10.39 ± 0.04 Å	8.36 ± 0.03 Å	6.58 ± 0.03 Å	95° 0′ ± 18′	$P2_1/c$

Atomic parameters.

	α-$BaO_2 \cdot 2H_2O_2$		C2/c	β-$BaO_2 \cdot 2H_2O_2$		C2/c
4 Ba (e)	0	0.206	1/4	0	0.185	1/4
8 O (f)	0.179	0.975	0.026	0.158	0.090	0.658
8 O (f)	0.173	0.865	0.202	0.315	0.100	0.581
8 O (f)	0.458	0.060	0.059	0.310	0.210	0.075

	γ-$BaO_2 \cdot 2H_2O_2$		Pbca
8 Ba (c)	0.375	0.542	0.219
8 O (c)	0.283	0.758	0.023
8 O (c)	0.292	0.885	0.200
8 O (c)	0.472	0.767	0.483
8 O (c)	0.466	0.917	0.317
8 O (c)	0.375	0.150	0.042
8 O (c)	0.375	0.167	0.397

	$BaO_2 \cdot H_2O_2 \cdot 2H_2O$		$P2_1/c$
4 Ba (c)	0.202	0.033	0.071

The compounds α-, β- and γ-$BaO_2 \cdot 2H_2O_2$ contain Ba^{2+} ions and infinite double chains or layers of hydrogen bonded peroxide groups.

ACKNOWLEDGEMENTS

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Nils-Gösta Vannerberg

The infrared spectra of some peroxide hydrates and peroxidates

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1959

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Communicated 8 April 1959 by ARNE WESTGREN

The infrared spectra of some peroxide hydrates and peroxidates

By NILS-GÖSTA VANNERBERG

With 1 figure in the text

Introduction

Ionic crystal studies by infrared absorption technique have been relatively infrequent so far. This is partly due to the fact that such compounds generally give uncharacteristic infrared absorption spectra. Crystals consisting of single atomic ions only give lattice vibrations, i.e. such vibrations that arise from the motion of the ions relative each other. In the infrared absorption spectra the lattice vibrations are noticeable as broad strong bands at long wavelengths. Polyatomic ions, on the other hand, may give internal vibrations characteristic of a special ion (1, 2). Thus, the hydroperoxide ion, $H-O-O^-$, which has been studied in this investigation, could be expected to give two stretching vibrations, one corresponding to the O–O bond and one to the O–H bond. The O–H vibration is well known but in the case of O–O there is some uncertainty. From comparative investigations of the infrared spectra of H_2O_2 and D_2O_2, Giguère has estimated the frequency[1] of the O–O stretching vibration to 877 cm^{-1} (3). However, according to Luft, no such vibration band exists (4). Brame *et al.* have investigated a number of peroxide compounds searching for the O–O vibration frequency at about 880 cm^{-1}, but could not generally find a peak (5). In those cases where a peak really appeared, it could be attributed to carbonate ions.

If hydrogen bonds are present in the investigated compound, they are revealed in a very characteristic manner. The stretching vibration frequency of an unperturbed O–H bond is 3700 cm^{-1} (1). If the O–H group is involved in hydrogen bond formation, for instance such as $O-H\cdots O$, the frequency is shifted towards lower wave numbers (6). This shift can be as large as 1900 cm^{-1} (7). At the same time, this infrared vibrational band grows broader and sometimes much more intense (8, 1).

The shift of the stretching vibration frequency has been shown to be a sensitive function of the hydrogen bond length, in this case the $O\cdots O$ distance. This gives a useful method to determine certain oxygen–oxygen distances in a crystal lattice (7, 8, 9, 10, 11).

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[1] The frequency throughout this paper was used to denote the wave number in accordance with Anglo-American usage.

The first work in this field was done by Rundle and Parasol (9). They have given an empirical curve describing the relation between the $O \cdots O$ bond distance in $O–H \cdots O$ and the O–H stretching frequency. The curve is based on eleven different relation values.

Independently Lord and Merrifield (10) have shown the existence of a linear relation between the hydrogen bond distance $M_1 \cdots M_2$ in $M_1–H \cdots M_2$ and the frequency shift. This frequency shift is defined as the difference between the M–H stretching frequency in the actual compound and that of an unperturbed M–H bond, M being F, O, N or Cl. For the basic frequency of the unperturbed O–H bond they have assumed the value 3700 cm^{-1}. The linear curve is based on twelve points including such compounds as potassium hydrofluoride and pyridine hydrochloride.

Lippincott and Schroeder (7) have theoretically calculated a relationship between the O–H frequency shift and $O \cdots O$ distance in the bond $O–H \cdots O$. Their calculation is in good agreement with empirical values.

Pimentel and Sederholm (11) have given a linear function relating the frequency shift to the hydrogen bond distance. The frequency shift is here defined as the difference between the O–H frequency of a compound in the solid state and that of the corresponding monomer in gas phase. For those compounds, which do not exist in gas phase, the frequency in dilute CCl_4 or $CHCl_3$ solution has been used. The relation given by Pimentel and Sederholm is expressed by the formula $\Delta\overline{V} = 4.43 \cdot 10^3 (2.84 - R)$, where $\Delta\overline{V}$ (cm^{-1}) is the frequency shift and R (Å) the hydrogen bond distance. However, the relation does not hold for weak hydrogen bonds, and for most inorganic compounds the frequency shift must be defined according to Lord and Merrifield (10).

Finally, Nakamoto, Margoshes and Rundle (8) have determined empirical curves describing the hydrogenic stretching frequency versus bond distance for various types of hydrogen bonds. The curves, relating the $O \cdots O$ bond distance to the stretching frequency or the stretching frequency shift, are based on 26 measurements.

In the present paper, an investigation will be described, aiming to use the relation between the O–H frequency shift and hydrogen bond length to determine the latter in atomic configurations such as $O–O–H \cdots O–O$ or $O–O \cdots H–O–H$ (the representation is schematic), which have been encountered in a series of peroxides and peroxiidates investigated by X-ray methods by the author (12–16). In one case ($SrO_2 \cdot 8H_2O$) all the above-mentioned relations have been used, in the other only that of Nakamoto *et al.* because this seems to be the most accurate. Unfortunately, the method is limited to the most stable of these compounds since the infrared technique demands the samples to be very finely ground. It is very difficult to achieve this without causing decomposition of the peroxidates.

The compounds investigated are $SrO_2 \cdot 8H_2O$ (12), $BaO_2 \cdot H_2O_2$ (13), α-$BaO_2 \cdot 2H_2O_2$ (14), γ-$BaO_2 \cdot 2H_2O_2$ (14), and $Na_2O_2 \cdot 2H_2O_2$. Besides, the spectra of $MgO_2 \cdot 2H_2O$ (15) and $ZnO_2 \cdot 0.5H_2O$ (16) are recorded to examine whether the difference in constitution between these and the above mentioned compounds can be shown.

The infrared spectrum of $Na_2O_2 \cdot 8H_2O$ and some other peroxides has been published previously by Brame *et al.* (5). They could not find any correlation between the infrared spectra of the different peroxides.

Experimental

$BaO_2 \cdot H_2O_2$, α-$BaO_2 \cdot 2H_2O_2$, γ-$BaO_2 \cdot 2H_2O_2$, $MgO_2 \cdot 2H_2O$, $ZnO_2 \cdot 0.5H_2O$ and $SrO_2 \cdot 8H_2O$ were prepared in ordinary ways (loc. cit.). $SrO_2 \cdot 8D_2O$ was prepared in the following manner: 0.2 g $Sr(NO_3)_2$ and 0.1 g Na_2O_2 were dissolved in two portions of 2 ml D_2O (99 %). The solutions were chilled separately and mixed together. The crystals formed were filtered and washed with alcohol (99.5 %) and ether.

The infrared spectra were scanned with a Perkin-Elmer infrared spectrophotometer. 2 mg of a sample were either ground and suspended in hexachlorobutadien or ground with KBr and pressed to a KBr disc. A modification by Brame *et al.* (5) of the KBr disc procedure was used. The spectra were scanned between 2 and 15 micron when the KBr procedure was used and between 2 and 6 micron when the samples were suspended in hexachlorobutadien.

Results

The infrared spectrum of $SrO_2 \cdot 8H_2O$, $SrO_2 \cdot 8D_2O$, $BaO_2 \cdot H_2O_2$, α-$BaO_2 \cdot 2H_2O_2$, γ-$BaO_2 \cdot 2H_2O_2$, $MgO_2 \cdot 2H_2O$ and $ZnO_2 \cdot 0.5H_2O$ can be seen in Fig. 1.

$SrO_2 \cdot 8H_2O$ exhibits peaks at 3330 (strong, sharp) 2730 (strong, broad), 2180 (weak, broad), 1590 (weak, broad), 1465 (medium, sharp), 1100–870 (strong, very broad), 853 (weak, sharp), 820–670 (very strong, very broad).

The spectrum of $SrO_2 \cdot 8D_2O$ contains peaks at 3330 cm^{-1} (weak, sharp), 2480 (strong, sharp), 2060 (strong, broad), 1680 (weak, broad), 1465 (strong, medium sharp), 1390 (varying, sharp), 1200 (medium, broad), 1100–870 (medium, very broad), 853 (medium, sharp), 820–670 (very strong, very broad). The peak at 1390 cm^{-1} and probably that at 853 are nitrate bands.

A comparison of the spectra of $SrO_2 \cdot 8H_2O$ and $SrO_2 \cdot 8D_2O$ described above indicates that the peaks of the former at 3330 and 2730 cm^{-1} must be related to the hydrogen atoms. For the deuterated compound the corresponding peaks are found at 2480 and 2060 cm^{-1}. This gives the values 1.34 and 1.33 to the relation of the wave numbers of the peaks $\overline{V}_H/\overline{V}_D$. According to (1) it seems justified to attribute these peaks to O–H viz. O–D stretching vibrations. However, the hydrogen and deuterium atoms in the compounds investigated are involved in hydrogen bond formation (O–H···O and O–D···O), which implies a strong perturbation of the O–H and O–D vibrations.

The frequences of the unperturbed O–H and O–D vibrations are 3700 and 2730 cm^{-1} (1). When hydrogen or deuterium bonds are present the corresponding frequences are shifted towards smaller wave numbers. The perturbed frequency in the hydrogenated compound are 3330 viz. 2730 cm^{-1} (see above). Consequently the shift of the first peak is $3700-3330=370$ cm^{-1} and of the second $3700-2730=970$ cm^{-1}.

As mentioned above, several authors have studied the relation between the frequency shift and the hydrogen bond length. The bond lengths O–H···O in $SrO_2 \cdot 8H_2O$, calculated from the measured frequency shift with functions given by the various authors, can be found in Table 1. Crystallographic investigations by the present author (12) have given mainly two values of the bond lengths O–H···O, namely 2.84 Å and 2.68 Å, the latter is a weighed mean value of 2.66 and 2.71 Å. Accordingly, as can be seen from Table 1, the structure proposal by Vannerberg are strongly supported. Especially the function of Nakamoto *et al.* and Lord *et al.* give values which agree well with those obtained from the crystallographic data.

In Table 2, the O–H stretching frequencies, the intensity and shape of the corresponding peaks, the frequency shifts and the calculated O···O distances for $BaO_2 \cdot 2H_2O_2$, α-$BaO_2 \cdot 2H_2O_2$, γ-$BaO_2 \cdot H_2O_2$ and $Na_2O_2 \cdot 2H_2O_2$ can be found. In the last column the O···O distances obtained from crystallographic data are tabulated.

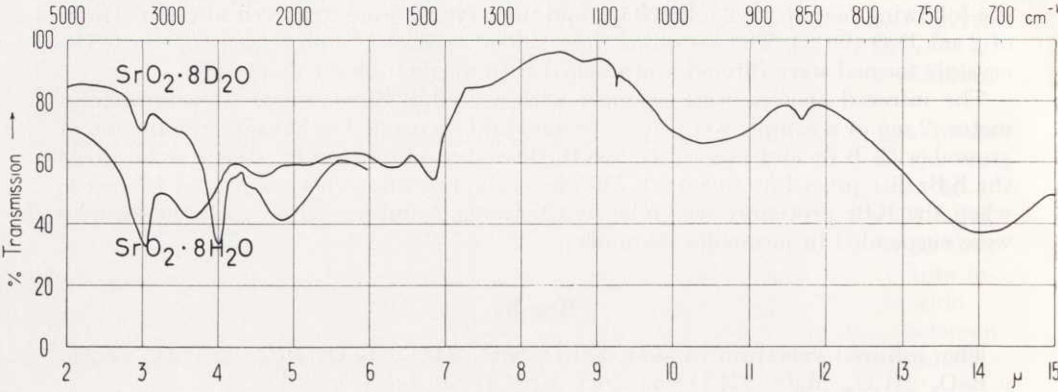

Fig. 1 a.

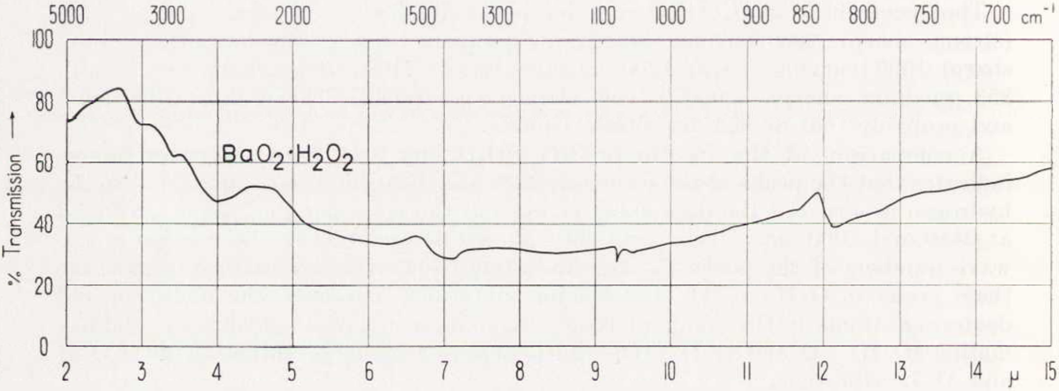

Fig. 1 b.

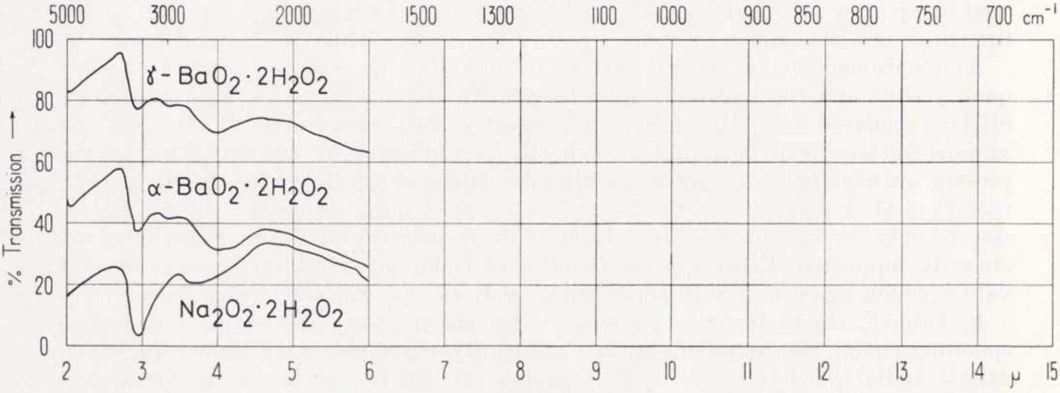

Fig. 1 c.

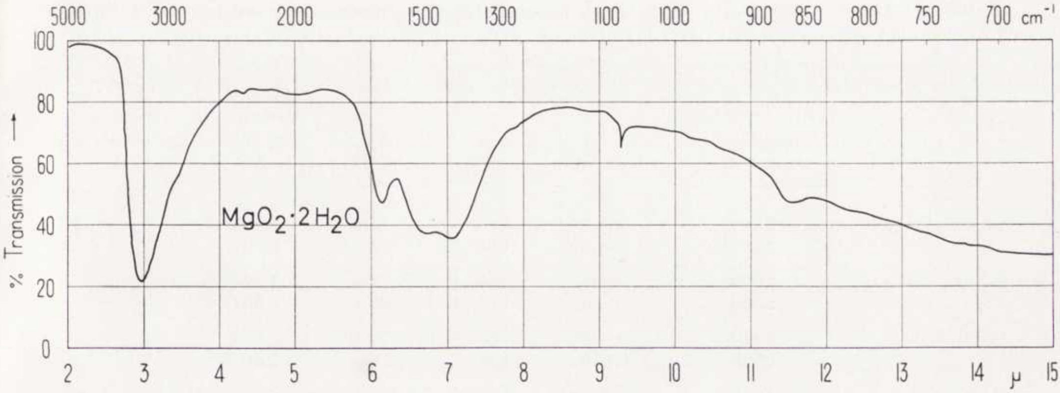

Fig. 1 d.

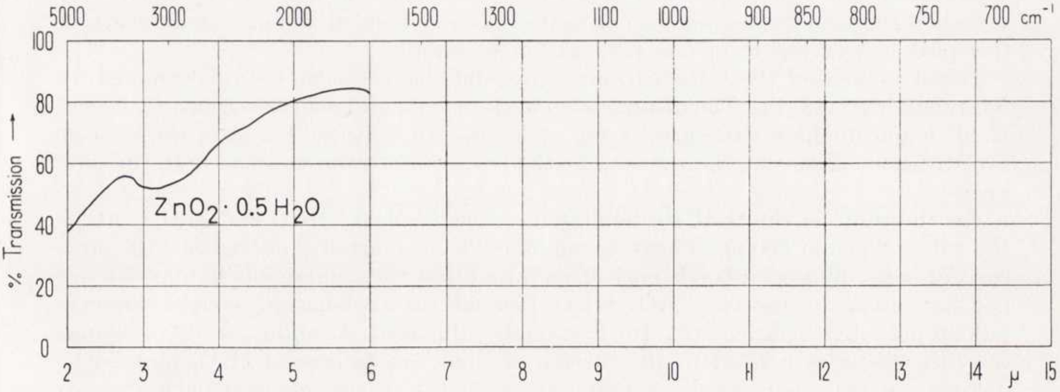

Fig. 1 e.

Fig. 1. Infrared spectra of $SrO_2 \cdot 8D_2O$, $SrO_2 \cdot 8H_2O$, $BaO_2 \cdot H_2O_2$, $\gamma\text{-}BaO_2 \cdot 2H_2O_2$, $\alpha\text{-}BaO_2 \cdot 2H_2O_2$, $Na_2O_2 \cdot 2H_2O_2$, $MgO_2 \cdot 2H_2O$ and $ZnO_2 \cdot 0.5H_2O$. (For the compounds $\gamma\text{-}BaO_2 \cdot 2H_2O_2$ and $Na_2O_2 \cdot 2H_2O_2$ the transmission scale has been displaced.)

Table 1. The hydrogen bond lengths in $SrO_2 \cdot 8H_2O$, calculated from functions given by various authors.

Authors	Bond length calculated from measured frequencies	
	3330 cm⁻¹	2730 cm⁻¹
Rundle, Parasol (9)	2.75 Å	2.61 Å
Lord, Merrifield (10)	2.82	2.67
Lippincott, Schroeder (7)	2.82	2.63
Pimentel, Sederholm (11)	2.77	2.63
Nakamoto, Margoshes, Rundle (8)	2.83	2.67

Table 2. Data concerning the O–H stretching frequencies in some peroxidates. The O···O distances are calculated from a function given by Nakamoto *et al.* (8).

Compound	O-H stretching frequency cm^{-1}	Intensity	Shape	$\Delta\bar{V}$ cm^{-1}	O···O distance infrared Å	O···O distance cryst. Å
α-$BaO_2 \cdot 2H_2O_2$	2940	weak	broad	760	2.70	2.4–2.8
	2450	strong	broad	1250	2.59	
γ-$BaO_2 \cdot 2H_2O_2$	2960	weak	broad	740	2.71	2.3–2.9
	2500	strong	broad	1200	2.60	
$BaO_2 \cdot H_2O_2$	2920	weak	broad	780	2.69	2.3–2.7
	2500	strong	broad	1200	2.60	
$Na_2O_2 \cdot 2H_2O_2$	2650	medium	broad	1050	2.64	—

The peak at 3400 cm^{-1} (not mentioned in Table 2) which undoubtedly is an O–H vibration frequency is assumed to arise from loosely bonded water. The intensity of this peak is varying from one preparation to another.

The structures of the three barium compounds have earlier been determined by X-ray methods (13, 14). The distances between oxygen atoms involved in a hydrogen bond, found in these structures, agree rather well with those found in the present investigation. However, the infrared method is certainly the most accurate in such cases.

For the shifts in the O–H stretching vibrations of $MgO_2 \cdot 2H_2O$ and $ZnO_2 \cdot 0.5H_2O$ the values 250 and 500 cm^{-1} have been observed. Such small shifts indicate the presence of weak hydrogen bonds only. This shows that the compounds in question are not built up as, for instance, $SrO_2 \cdot 8H_2O$. Instead, the explanation given by the crystallographic investigations (15, 16) is strongly supported. According to this explanation, the water is bonded to the surface of small crystallites of MgO_2 and ZnO_2.

Finally it may be pointed out that in none of the spectra investigated there was any frequency attributable to the O–O stretching vibration. As could be expected, the O_2^{2-} ion, which is homopolar, is not infrared-active. The peak at 862 cm^{-1}, which appeared in some of the infrared spectra, may be due to the carbonate or nitrate ion.

SUMMARY

The infrared spectra of one peroxide octahydrate and some peroxidates have been studied. The distances between hydrogen bonded oxygen atoms have been calculated using the O–H frequency shift. The values obtained agree with those calculated from X-ray data. No strong hydrogen bonds have been found in $MgO_2 \cdot 2H_2O$ or $ZnO_2 \cdot 0.5H_2O$.

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