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The Crystal Structure of Barium Peroxide*

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The lattice constants of barium peroxide have been remeasured, and at 25.0° C. the tetragonal unit cell has $a = 5.384 \pm 0.010$ and $c = 6.841 \pm 0.005$ Å. The crystal structure has been redetermined, using a complete least-squares method, as well as triple Fourier series, based upon powder-derived intensities, measured with a Geiger counter. The oxygen–oxygen bond length is 1.49 ± 0.04 Å, and there are two kinds of barium–oxygen contacts of 2.68 and 2.79 Å. The final agreement factor R_1 has the value 0.0381.

Introduction

The nature of the oxygen–oxygen bond in covalent peroxides (Kazarnovskii, 1930), in the peroxide ion (Kazarnovskii, 1940) and in the superoxide ion (Kasatochkin & Kotov, 1936) has been the subject of repeated investigation during the last two decades. The length of this bond in hydrogen peroxide has been measured by Abrahams, Collin & Lipscomb (1951) as 1.49 ± 0.02 Å, and in the hydrogen peroxide–urea addition complex by Lu, Hughes & Giguère (1941) as 1.46 Å. X-ray studies of the ion $[\text{O}-\text{O}]^-$ have been made on calcium, strontium and barium peroxide. The first study on the barium and strontium compound was reported by Bernal *et al.* (1935), who examined the powder pattern and obtained a length of 1.28 Å for the O–O bond. A contemporary, but unpublished, study had been made by Miller (1936), who found this distance to be 1.36 Å. Kotov & Raikhshtein (1941) reported only the cell constants of CaO_2 .

The apparent shortness of the $[\text{O}-\text{O}]^-$ bond prompted a re-examination of the existing data by Butuzov (1947). Using the unit cell previously measured by Bernal *et al.*, and a new set of intensities published by Hanawalt, Rinn & Frevel (1938), Butuzov calculated the O–O distance to be 1.47 Å. The method employed was to compute a line in F^2 space along $(0, 0, z)$,

whereupon recognition of the barium–oxygen vector immediately led to the oxygen parameter.

The only superoxide for which atomic coordinates appear to have been reported is that of sodium (Templeton & Dauben, 1950). Using a powder specimen of 70% purity, the superoxide ion is described as being in a disordered state. The O–O distance was estimated to be 1.33 ± 0.06 Å. Zhdanov & Zvonkova (1952) have discussed Templeton & Dauben's results; based on a new determination, they claim for the O–O distance the value 1.31 ± 0.03 Å. The unit cells of several other alkali superoxides have been measured by Kasatochkin & Kotov (1937) and by Helms & Klemm (1939).

Butuzov's (1947) study was based upon an incomplete set of intensities. Including 002, 16 lines observable with Cu X-radiation were completely omitted (for $2\theta \leq 165^\circ$). Further, the solution of a Patterson series generally does not furnish atomic positions with high accuracy. In Templeton & Dauben's study no attempt apparently was made to permit the O–O distance to vary simultaneously with the degree of disorder. Also, the range of O–O bond lengths allowed was only 1.30–1.35 Å. The present investigation has been undertaken to redetermine the O–O distance in barium peroxide under more favorable conditions.

After the present work had been completed, we found that a study of the crystal structures of $\text{CaO}_2 \cdot 8 \text{H}_2\text{O}$, $\text{SrO}_2 \cdot 8 \text{H}_2\text{O}$ and $\text{BaO}_2 \cdot 8 \text{H}_2\text{O}$ had been made by Harr (1952). The values obtained for the O–O separation in the peroxide ion were given as 1.48, 1.49 and 1.48 Å, respectively. No limits of error

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were quoted, although the agreement between the observed and calculated structure factors was very good, particularly for the last two compounds.

Experimental

Anhydrous barium peroxide was prepared by the method of Becker (1909) in which $\text{BaO}_2 \cdot 8 \text{H}_2\text{O}$ is first obtained by the addition of 3% H_2O_2 to a saturated solution of pure $\text{Ba}(\text{OH})_2$. After filtration and washing in a nitrogen atmosphere, the precipitate was dried in vacuo at 60° C. over silica gel, and then at 100° C. over P_2O_5 . The resulting product yielded a poor X-ray diffraction pattern, especially at high angles. The pattern was greatly improved by calcining the powder in a stream of oxygen for several hours at 550–600° C., and cooling slowly. It is necessary to pass the oxygen through concentrated H_2SO_4 and over granular KOH to maintain about 0.001 g.l.⁻¹ water vapor in the CO_2 -free gas, for producing BaO_2 in maximum yield. Freshly prepared samples of this white microcrystalline material were analysed by Mattner's (1952) method, and found to be 97.9–98.3% pure. The percentage of active oxygen was found to diminish slowly with time.

The experimental arrangements used for the determination of the lattice constants with the Norelco wide-range diffractometer and X-ray tube current stabilizer have previously been described (Abrahams & Kalnajs, 1954). The relatively high error limits in the lattice constants were introduced by the flat profiles of the diffraction peaks at high angles, and the consequent uncertainty in the positions of their centers of gravity. The intensities of the lines were measured by cumulatively adding the Geiger counter output starting at background level, scanning through the line profile to background level again at 0.125° 2θ per min. and then subtracting the corresponding integrated background count. The shape of the background curve had previously been determined with an accuracy of c. 1%. By suitable adjustment of the total number of counts, an overall accuracy of c. 1–2% was maintained in the intensity of each line. Peaks diffracted at 2θ > 90° were measured using 4° divergence and scatter slits and a 0.006 in. receiving slit; for 2θ < 90°, 1° slits and a 0.003 in. receiving slit were used. The ratio of the intensity of a line using the narrower slits to the same line using the wider slits was determined to be 0.129:1.

All measurements were made within 24 hr. to avoid sample deterioration. The atmosphere surrounding the samples was kept free of H_2O and CO_2 by sealing the X-ray beam entrance to the scatter shield with a 1 mil sheet of Mylar, and maintaining a dish of granular KOH within the resulting cavity. After all the intensities had been placed on the same scale they were reduced to structure factors in the usual way. In those cases where two lines overlapped, the ratios of the heights of the turning points in the profile of the

double line was taken as the ratio of the intensities. The experimental arrangement insured that all lines had the same absorption correction. Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used throughout. James & Brindley's (1931) atomic form factors for Ba and O were taken. Structure-factor and least-squares calculations were made on International Business Machines and the Fourier series were summed using Beevers–Lipson strips.

Crystal data

Barium peroxide, BaO_2 ; starts to dissociate above c. 650° C.; $D_o = 5.43 \text{ g.cm.}^{-3}$ (Raikhshtein & Kazarnovskii, 1932); $D_c = 5.672 \text{ g.cm.}^{-3}$; tetragonal with $a = 5.384 \pm 0.010$ and $c = 6.841 \pm 0.005 \text{ \AA}$. Absent spectra, (hkl) only for $h+k$, $k+l$, $l+h = 2n+1$. Space group $F4/mmm$, No. 139, (Bernal *et al.*, 1935). This is not unique, but the other possible space groups also contain the coordinates used that permit the best fit between observed and calculated structure factors. Four formula molecules per unit cell. Volume of the unit cell = 198.3 \AA^3 . Absorption coefficient for X-rays ($\lambda = 1.5418 \text{ \AA}$) = 1665.3 cm.^{-1} . Total number of electrons per unit cell, $F(000) = 288$.

Analysis of the structure

The barium atom in this structure is at $(0, 0, \frac{1}{2})$, and the oxygen atoms at $(0, 0, z)$; $(0, 0, \bar{z})$. Bernal *et al.* (1935) had obtained $z = 0.086$ and Butuzov (1947), $z = 0.11$. The initial method chosen in the present study for the refinement of the sole positional parameter was that of least squares. Of the 46 powder lines observable with Cu $K\alpha$ radiation (Table 1), 30 were separable. The remainder formed 8 sets of doublets, and the least-squares analysis was confined throughout to the singlets. An examination of the observed structure factors in Table 1 indicated a very small degree of thermal vibration, and, in the structure-factor expression

$$F(hkl) = 8f_o \exp \left[-B_1 \left(\frac{\sin \theta}{\lambda} \right)^2 \right] \\ \times \cos 2\pi lz \pm 4f_{\text{Ba}} \exp \left[-B_2 \left(\frac{\sin \theta}{\lambda} \right)^2 \right],$$

a value of 0.10 \AA^2 was assigned to B_1 and B_2 . The first value of z chosen was also 0.10, and structure factors evaluated on the basis of these two parameters immediately gave excellent agreement with the observed data, for $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0449$.

The first least-squares analysis reduced R_1 to 0.0392, and the second iteration to 0.0384. In this least-squares process, since there were only three unknowns, it was easy to evaluate the coefficients of all terms in the three normal equations, and then to solve exactly the resulting determinant. In the final least-squares procedure, the possibility that the two kinds of atoms present might possess anisotropic temperature vibrations was

Table 1. Observed and calculated spacings and structure factors

<i>hkl</i>	<i>d_o</i> (Å)	<i>d_c</i> (Å)	<i>F_o</i>	<i>F_c</i>
002	3.43	3.43	210	+206
111	3.34	3.33	157	-155
200	2.701	2.696	210	+227
202	2.118	2.115	171	+177
113	1.958	1.956	182	-178
220	1.908	1.903	202	+195
004	1.712	1.710	151	+128
222	1.663	1.663	282	+159
131	1.654	1.652		-129
204	1.446	1.444	108	+118
133	1.366	1.410	151	-149
400	1.349	1.346	151	+161
115	1.288	1.280	160	-154
224	1.274	1.272	112	+113
402	1.255	1.253	253	+135
331	1.250	1.247		-113
240	1.206	1.204	147	+149
006	1.138	1.140	263	+113
242	1.135	1.136		+128
333	1.111	1.111	130	-130
135	1.068	1.088	132	-136
404	1.056	1.058	104	+104
206	1.050	1.050	210	+109
151	1.045	1.044		-105
244	0.986	0.984	98	+99
226	0.979	0.978	101	+103
153	0.959	0.958	114	-118
440	0.953	0.952	132	+126
117	0.947	0.947	111	-111
335	0.932	0.930	123	-123
442	0.918	0.917	218	+112
351	0.916	0.915		-98
600	0.898	0.897	120	+120
406	0.870	0.879	202	+97
602	0.869	0.868		+107
353	0.857	0.856	216	-109
008		0.855		+112
260	0.852	0.851	118	+116
137	0.849	0.848	102	-103
155	0.836	0.836	109	-114
444	0.833	0.832	100	+91
246	0.827	0.826	186	+95
262	0.829	0.828		+105
208	0.815	0.815	104	+108
604	0.795	0.795	75	+87
228	0.780	0.780	116	+104

explored. Where B^p is the temperature factor parallel with the c axis, and B^n the factor normal to this axis, the isotropic temperature factor could be replaced by $B_j = B_j^p \sin^2 \varphi + B_j^n \cos^2 \varphi$, in which φ is the angle between the normal to the (hkl) plane and the c -axis direction.

The final least-squares analysis thus contained five unknowns: z , B_O^p , B_O^n , B_{Ba}^p and B_{Ba}^n . Complete evaluation of the five normal equations, and solution of the resultant fifth-order determinant gave these unknowns the values 0.1079; 0.33, 0.63, 0.10 and 0.07 Å², respectively, z having changed by 0.0002. This set of values produced the smallest value of R_1 obtained, 0.0381, corresponding to the calculated structure factors in Table 1. In the correct use of the least-squares method, each equation of condition should be reduced to equal weight, by a suitably derived weighting fac-

tor. In the present analysis all weights were placed equal throughout, since each powder line intensity was obtained as a difference between two sets of counts, adjusted to keep the precision in each line about equal.

The value of z was also obtained by the alternative method of triple Fourier series using all the F_o terms in Table 1. Since the oxygen and the barium atom both lay along the line $(0, 0, z)$, the electron density in this line was computed by means of the relation

$$\rho(0, 0, z) = \frac{1}{\text{Vol.}} \sum_{-h}^{+h} \sum_{-k}^{+k} \sum_{-l}^{+l} F(hkl) \cos 2\pi lz,$$

and is shown in Fig. 1 (lower curve). The very low

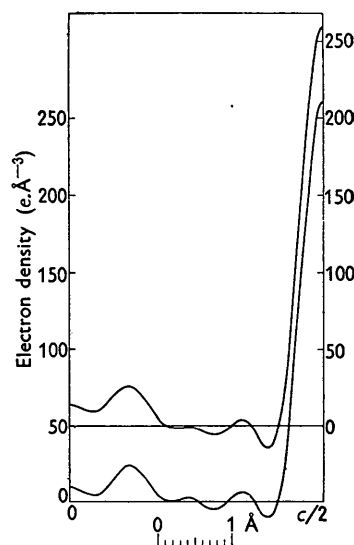


Fig. 1. Electron density profile along the line $(0, 0, z)$, computed with triple Fourier series. Upper curve has calculated $F(hkl)$ as coefficients in the series, lower curve has observed $F(hkl)$. Left-hand scale refers to lower curve.

values of the atomic thermal vibrations suggested that this series might suffer considerably from the effect of the sharp experimental cut-off. Fig. 1 (upper curve) gives the electron density obtained using the calculated structure factors, instead of the observed, as the coefficients in the triple Fourier series. This second series was used to correct the first, for errors due to the artificial termination, by the backshift method. Both series were evaluated at intervals of 0.11 Å. On correction for the termination effect, which was 0.0038, the value of z became 0.1099. R_1 for this z and the final values for B was 0.0396. The effects of the small temperature vibrations upon the sharpness of the atomic peaks, to which attention has been drawn by Burbank (1953), is very noticeable in Fig. 1. The maximum peak heights for Ba and O are respectively 260 and 24 e.Å⁻³. The corresponding number of electrons associated with each atom, however, is very close to the theoretical value.

Oxygen-oxygen bond length

The length of the O-O bond, based upon the least-squares derived value of $z = 0.1079$ and the triple Fourier series value of $z = 0.1099$ is respectively 1.48 and 1.50 Å; the mean value is 1.49 Å. R_1 , for $z = 0.1089$ and the final values for B , remained 0.0381.

Uncertainties in the parameters

An advantage of the least-squares method is the easy computation of the error to be feared in each parameter determined by the method. Solution of the fifth-order determinant, and of the minors of the coefficients of each unknown parameter, permitted an accurate evaluation of these errors. Expressing these uncertainties as probable errors in z , B_0^p , B_0^n , B_{Ba}^p and B_{Ba}^n , respectively, we have ± 0.02 Å, ± 0.65 , ± 1.07 , ± 0.08 , ± 0.09 Å². Since each oxygen atom has a probable error of ± 0.02 Å, the O-O bond length has a probable error of ± 0.04 Å.

Using Cruickshank's (1949) method for determining the error in z obtained by the triple Fourier series method, and retaining the nomenclature of that paper, $p = 13.7$, $(A_1) = 2.52 \text{ e.Å}^{-4}$ and $(A_{11}) = 1993 \text{ e.Å}^{-5}$, so that the error in the position of each oxygen atom is 0.009 Å. The corresponding error in the O-O bond length is therefore about 0.02 Å.

It is of some interest that the uncertainties, computed by the method of least-squares, in the values of z and in the temperature factors for the oxygen atom are so large. Similar large errors have previously been found in similar circumstances in barium titanate (Evans, 1953) and hydrogen cyanide (Dulmage & Lipscomb, 1951). In all these cases it appears that there may be some interaction between the sets of positional and vibrational parameters, resulting in an increase in the uncertainty of each.

The final value for the uncertainty in the O-O bond length is taken to be ± 0.04 Å.

Interionic distances

Each barium ion is surrounded by ten oxygens (Fig. 2). The barium-oxygen contacts parallel with c are 2.68 Å, and the contacts in directions approximately normal to c are 2.79 Å.

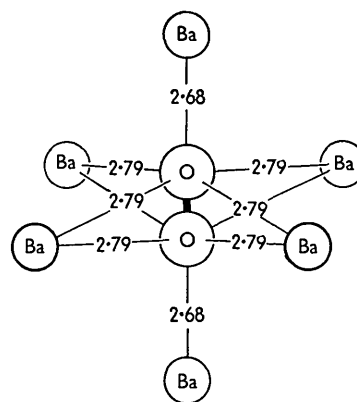


Fig. 2. Octahedral environment of peroxide ion showing closest contact distances (in Ångström units).

Discussion

There are two aspects of particular interest in the present study. One is the rather short barium-oxygen approach of 2.68 Å, and the other is the value found for the bond length of the peroxide ion. The contact of 2.79 Å between barium and eight of the ten closest oxygen neighbors may be compared with the corresponding distance of 2.76 Å in BaO, and of 2.80 Å in BaS₄.H₂O. It appears that this distance is typical of a normal ionic contact. The shorter distance seems to indicate a rather more powerful attraction between the two ions.

Unlike the heavier members of the VI_b group, oxygen exhibits a very limited tendency to form long chains. However, the single-link O-O is found under a variety of conditions, as shown in Table 2.

Magnetic susceptibility measurements indicate that cases (a) and (c) contain three electron bonds; (e) is primarily a single bond. However, the electronic structures of (b) and (d) are not well established. It appears that any attempt at expressing the O-O bond length in terms of its electronic structure, as has been done for carbon and sulfur, should perhaps be deferred until a more accurate length for case (c), and more information concerning the structures of (b) and (d) are available.

We would like to thank Mr R. Steinberg, Office of Statistical Services of this Institute, who carried out

Table 2. Oxygen-oxygen bond types and lengths

Case	Bond	Example	Bond length (Å)	Reference
(a)	O-O	O ₂	1.2074 ± 0.0001	Babcock & Herzberg (1948)
(b)	-O-O	O ₃	1.278 ± 0.003	Trambarulo <i>et al.</i> (1953)
(c)	[O-O] ⁻	β-NaO ₂	1.33 ± 0.06	Templeton & Dauben (1950)
(d)	[O-O] ⁼	BaO ₂	1.31 ± 0.03	Zhdanov & Zvonkova (1952)
		CaO ₂ · 8 H ₂ O	1.49 ± 0.04	Present paper
		SrO ₂ · 8 H ₂ O	1.48	
		BaO ₂ · 8 H ₂ O	1.49	
(e)	-O-O-	H ₂ O ₂	1.48	Harr (1952)
			1.49 ± 0.02	Abrahams <i>et al.</i> (1951)

the I.B.M. calculations, and Prof. A. von Hippel for his interest in this work.

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The Geometrical Basis of Crystal Chemistry. Part 3

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Examples are given of some of the 3- and 4-connected three-dimensional nets derived in Parts 1 and 2, with special reference to certain groups of hydrogen-bonded structures. The general types of crystal structure are indicated for long molecules such as those of dihydroxy compounds and those containing terminal $-\text{CO.NH}-$ groups. The crystal chemistry of P, P_2O_5 , and the trioxides and trisulphides of Group 5B elements is discussed.

Introduction

In this Part we show how 3- and 4-connected nets form the basis of the structures of crystals of very diverse types. Some examples, such as the structures of elements, are obvious and well known, but other relationships have not been pointed out. They emphasize the elegant simplicity of the principles underlying the structures of many crystals, a simplicity which is not always evident from the usual descriptions of structures. Moreover, these systematic studies of the topological structure types which are possible for a given compound are necessary if we hope eventually to understand why a particular structure is adopted.

In order to divide a plane surface into convex polygons at least three lines must meet at each point. The

plane hexagonal net is the unique way of partitioning the plane with this minimum number of lines into polygons all having the same number of sides. The importance of the hexagonal net in crystals is well known. In three dimensions continuous frameworks can be formed with the same minimum number of links meeting at each point, and some of the simpler ones have been derived and illustrated in Part 1 (Wells, 1954a). It might be expected that these nets also would be important in crystal chemistry, in particular the 3-dimensional analogues of the plane hexagonal net. These are the 'uniform' 3-connected nets, which have the property that the shortest circuit from any point back to itself always passes through the same total number (N) of points, N being 8, 9, 10, or 12.