Acta Cryst. (1954). 7, 833

The Crystal Structure of Benzeneseleninic Acid

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(*Received* 7 *June* 1954 *and in revised form* 22 *July* 1954)

Crystals of benzeneseleninic acid, $C_6H_5SeO_2H$, are monoclinic holohedral with $a_0 = 10{\cdot}29$, $b_0 = 5{\cdot}14$, $c_0 = 12{\cdot}63$ Å and $\beta = 99°\ 15'$. The space group is $P2_1/c$ and there are four molecules in the unit. By means of projections on (010) and three-dimensional Fourier syntheses making use of 785 observed F values, the structure was completely determined. The molecule has a pyramidal configuration about the selenium atom. The Se–O distances are 1·707 and 1·765 Å and the Se–C distance is 1·903 Å. The bond angles at selenium are 99·0°, 98·5°, and 103·5°. Within the limits of error of the determination the phenyl group is a regular hexagon with a C–C distance of 1·40 Å. The molecules form infinite chains along the twofold screw axes. Within the chains the molecules are held together by strong hydrogen bonds with an O–O separation of 2·520 Å. The chains are held to one another by means of van der Waals forces.

Introduction

Benzeneseleninic acid, $C_6H_5SeO_2H$, is a white, crystalline solid which melts at 121° C. and which is moderately soluble in water, alcohol and a variety of other solvents. The material used in the present study was prepared by the method of McCullough & Gould (1949) and was of high purity. Crystals grown by the slow evaporation of an aqueous solution are lath-shaped needles elongated along b. In contrast to this, crystals grown from alcohol are needles elongated along c. It was thus possible to select crystals almost ideally suited for rotation about both the b and c axes.

This investigation was undertaken as part of a program involving structural studies of organoselenium and organotellurium compounds, and had, as its main objective, the determination of the stereochemistry of selenium in the seleninic acid group.

The unit cell and space group

Rotation and zero-level Weissenberg photographs about the b and c axes showed the crystals to be monoclinic with the following cell dimensions, based on Cu $K\alpha = 1{\cdot}542$ Å:

$$a = 10{\cdot}29 \pm 0{\cdot}03,\ b = 5{\cdot}14 \pm 0{\cdot}02,\ c = 12{\cdot}63 \pm 0{\cdot}03\ \text{Å};\quad \beta = 99°\ 15' \pm 15'\ .$$

Practically complete intensity data for Cu $K\alpha$ radiation were collected by means of multiple-film Weissenberg photographs about the b and c axes. A total of 785 independent non-zero hkl intensities were observed out of a possible 1500 within the sphere of diffraction. The possible reflections with observed intensities of zero were nearly all of the type hkl with $k+l$ odd. This was later accounted for by the nearness of the y parameter of selenium to zero. The only systematic absences were $h0l$ with l odd and $0k0$ with k odd. The space group is thus uniquely determined as $P2_1/c$–C_{2h}^5.

The approximate density of the crystals determined by a flotation method is 1·93 g.cm.$^{-3}$. The density calculated for four molecules in the unit cell is 1·908 g.cm.$^{-3}$.

Determination of the approximate structure

Owing to the shortness of the b axis it was considered best to proceed first with projections on (010). The $h0l$ intensities were accordingly estimated visually by comparison with standard intensity strips and corrected in the usual manner to obtain values of F_{h0l}. The Patterson projection showed one large peak in the asymmetric unit of height about one-third that of the origin. This peak was assumed to be due to Se–Se interaction, and its position indicated an x parameter of 0·097 and a z parameter of either 0·163 or 0·413. Since one cannot distinguish between the twofold screw axes and the centers of symmetry in this projection, it was not possible to decide between the two alternatives at this point. The second possibility was attractive because it appeared to indicate dimeric molecules about the centers of symmetry, as found in some crystalline carboxylic acids. Although this assumption proved later to be incorrect, it served equally as well as the other possibility through the $h0l$ refinement.

On the basis of the above selenium parameters, the signs of the F_{h0l} values were computed and a Fourier projection on (010) was prepared. This projection showed excellent resolution of the selenium and oxygen atoms and good indications of the locations of the carbon atoms. The signs of F_{h0l} were recalculated including the indicated oxygen and carbon parameters. Five signs were thus changed out of a total of 151 F_{h0l} values. The second Fourier projection

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(Fig. 1) showed all atoms well resolved. No further changes in sign resulted in calculating a new set of F_{h0l} values including all atoms except hydrogen. The x and z parameters corresponding to this stage of refinement are given in Table 1.

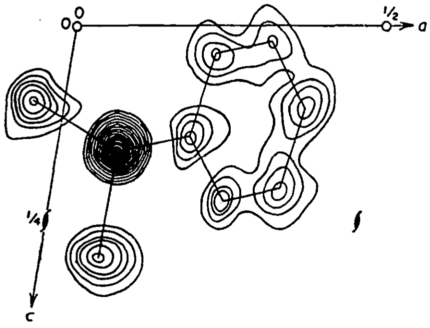

Fig. 1. Fourier projection on (010). Contour interval 1·5 e.Å^{-2} for carbon and oxygen and 4 e.Å^{-2} for selenium. The zero contour is not shown.

Table 1. *Atomic parameters from final Fourier projection on* (010)

	x	z
Se	0·097	0·162
O_1	0·092	0·297
O_2	0·949	0·096
C_1	0·211	0·142
C_2	0·276	0·224
C_3	0·365	0·214
C_4	0·388	0·105
C_5	0·321	0·024
C_6	0·232	0·038

In order to determine the temperature factor and also to put the observed F values on an absolute basis, a plot of the logarithm of F_o/F_c against $\sin^2\theta/\lambda^2$ was prepared. The best straight line through the points corresponded to a value of $B = 3{\cdot}01\times10^{-16}$ cm.^{2} in the temperature factor, $\exp(-B\sin^2\theta/\lambda^2)$. There was no indication that an anisotropic temperature factor was needed. The value of R in the expression

$$R = \Sigma|(|F_o|-|F_c|)|\div\Sigma|F_o|$$

was at this point 0·155, including all observed $h0l$ reflections.

In order to settle the ambiguity with regard to the position of the molecules with respect to the twofold screw axes and the centers of symmetry, it was necessary to consider the y parameters. The fact that the reflections with $k+l$ odd tend to be weak or missing is of help here. Of the 785 observed reflections, only 128 are of the type $k+l$ odd. This may be taken as an indication that the y parameter of selenium is very close to zero (or $\frac{1}{2}$) since the structure factor for these reflections contains the factor $\sin 2\pi ky$. With a selenium atom at either $y = 0$ or $y = \frac{1}{2}$ and at $x = 0{\cdot}097$ and $z = 0{\cdot}412$, two selenium atoms will be separated by only 3·16 Å across centers of symmetry. On the other hand, if $z = 0{\cdot}162$, the closest approach of two selenium atoms is 4·11 Å; this across the twofold screw axis. This latter situation is much more reasonable inasmuch as twice the van der Waals radius of selenium is 4·0 Å.

The y parameters of the carbon and oxygen atoms presented somewhat of a problem. Although it was possible to get fair ideas of the y parameters of the carbon atoms on the assumption of normal C–C and Se–C distances, a regular plane hexagon for the benzene ring, and the known x and z parameters, the y parameters of the oxygen atoms caused more difficulty. To be sure, Se–O distances were available from the known structures of selenium dioxide (McCullough, 1937) and selenious acid (Wells & Bailey, 1949) but the distances range from 1·72 to 1·78 Å. Also, the direction of the y component of the Se–O bonds relative to the y component of the Se–C bond could not be predicted with certainty. However, it appeared possible that the y parameters of the oxygen atoms might be determined by making linear Fourier summations parallel to the b axis at the x and z parameters of the oxygen atoms provided by the (010) projection. For this purpose $h1l$ and $h2l$ data were employed. The phases of reflections for which $k+l$ is even were taken the same as those of the selenium contributions, while those for reflections with $k+l$ odd were taken as the phases of the carbon atom contribution. For this purpose approximate y parameters for carbon were computed as indicated above. These y parameters for carbon and the y parameters for oxygen indicated by the linear summations are given in Table 2.

Table 2. *Preliminary y parameters*

Atom	y	Atom	y
Se	0·00	C_2	0·45
O_1	0·10	C_3	0·65
O_2	0·10	C_4	0·65
C_1	0·18	C_5	0·45
C_1	0·25	C_6	0·25

By use of these parameters, the phases of all $hk0$ reflections were calculated and a complete Fourier projection on (001) was prepared. On this projection the general location of the benzene ring was indicated and one oxygen atom was partially resolved. The other oxygen atom, O_1, was completely obscured by the selenium atom. Accordingly, no satisfactory improvement of the parameters in Table 2 could be obtained from this projection.

Refinement of the structure by three-dimensional Fourier synthesis

Complete three-dimensional Fourier synthesis appeared to be the only method by which a satisfactory set of y parameters could be obtained. This was accordingly undertaken, using the complete Weissenberg data about the b and c axes. The intensities were

Table 3. *Final atomic parameters, backshift corrections and peak heights*, ϱ_o

	x	y	z	Δx	Δy	Δz	ϱ_o (e.Å^{-3})
Se	0·0966	0·9979	0·1614	0·0000	−0·0006	−0·0003	79·8
O_1	0·094	0·041	0·295	0·000	0·021	−0·003	11·4
O_2	0·949	0·144	0·099	0·000	0·002	0·000	10·0
C_1	0·215	0·270	0·140	0·000	−0·005	0·000	7·1
C_2	0·282	0·406	0·227	0·003	0·001	0·000	6·9
C_3	0·371	0·597	0·209	−0·001	−0·002	0·001	6·4
C_4	0·388	0·673	0·103	0·001	−0·004	0·001	6·7
C_5	0·317	0·548	0·017	0·000	0·023	0·002	5·9
C_6	0·228	0·345	0·036	0·000	−0·008	−0·002	6·2

estimated by visual comparisons with standard intensity strips and were corrected in the usual manner to give F_o values. These were put on an absolute basis by reference to the $h0l$ values. The phases of the 657 observed reflections with $k+l$ even were taken as those of the selenium contribution. The phases of the other 128 reflections (for which $k+l$ was odd) were determined by use of the oxygen and carbon parameters in Tables 1 and 2.

The preceding two-dimensional projections were carried out by use of Patterson–Tunell strips (Patterson & Tunell, 1942). Owing to the greater amount of labor involved in the three-dimensional work, however, this was carried out by punched-card methods on the IBM equipment at the National Bureau of Standards Institute for Numerical Analysis on the U.C.L.A. campus. The summation gave well-resolved peaks for each atom. From these Parameter Set 2 was obtained.

At this time the National Bureau of Standards Western Automatic Computor, SWAC, became available for crystallographic computations. The machine was coded for structure-factor and three-dimensional series computations in such a way as to handle any space group. Structure-factor calculations on all of the observed reflections at this stage of refinement and on the basis of an isotropic temperature factor with $B = 3{\cdot}01$ Å^2 as before led to $R = 0{\cdot}16$ for all observed reflections. However, it was found that 15 out of the 785 phases were wrong and that the scale factor needed adjustment. After making these corrections, a second three-dimensional Fourier synthesis was computed on SWAC. A composite diagram of this synthesis by means of sections through the Fourier peaks is given in Fig. 2. From the positions of the peaks, Parameter Set 3 was derived. Calculation of the structure factors from these parameters led to $R = 0{\cdot}140$ for all observed reflections.

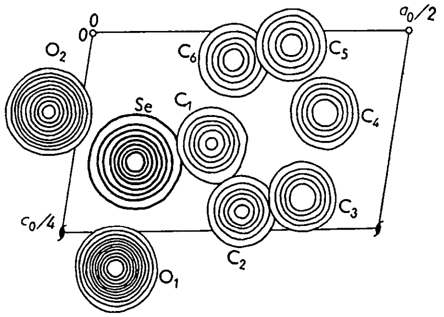

Fig. 2. Composite diagram of sections through atomic positions in the three-dimensional Fourier summation. Contour interval 1 e.Å^{-3} for carbon and oxygen and 10 e.Å^{-3} for selenium. The zero contour is omitted throughout. On carbon the 1 e.Å^{-3} contour is omitted to minimize overlapping.

In order to correct for series-termination errors, another complete three-dimensional Fourier synthesis was carried out by use of the calculated F values for the observed reflections. Backshift corrections were then made on Parameter Set 3, giving the final parameters. These are listed in Table 3, together with the backshift corrections and peak heights, ϱ_o, from the final three-dimensional F_o Fourier synthesis. A final set of F_c values was computed for all possible reflections within the sphere of diffraction. These were based on the Thomas–Fermi scattering factors for selenium and the James and Brindley scattering factors for oxygen and carbon. The final value of the R factor for the 785 observed reflections was 0·136. The 750 unobserved reflections had an average value of F_c of 2·9, which is about half of the average value of the lower limit of observation. The calculated and observed F values are compared in Table 4.*

The strongest reflections, notably 100, 102, $10\bar{4}$, and $20\bar{4}$, have calculated F values which average about 60% above the observed values, an effect presumed to be due to extinction. Since these reflections all involve low index values, the resulting errors in the atomic positions should be slight. Accordingly, no attempt was made to correct for the effect. These terms were included in all calculations and in the estimation of errors. If the above four reflections are omitted when computing the R factor, the value drops from 0·136 to 0·130 for the remaining 781 observed reflections.

Errors in the atomic coordinates

It was considered of interest to estimate the accuracy of the determination by use of the equations of Booth (1946, 1947) and of Cruickshank (1949).

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* Table 4 has been deposited as Document No. 4332 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $5·00 for photoprints, or $2·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. A copy may also be obtained from the author.

For the three-dimensional case, Booth gives the equation for the error in the coordinate of the atom j:

$$\varepsilon_j < \frac{5\cdot18}{N_j\sqrt{V}}\left(\frac{\pi}{\lambda p_j}\right)^{\frac{5}{2}}\Delta e\,,$$

where N_j is the atomic number, V is the volume of the unit cell, λ the wavelength of the X-rays, p_j is a parameter fit to the shape of the peaks of the F_o series by the electron-density equation $\varrho(r) = \varrho_o \exp\,(-pr^2)$ and Δe is the probable error in the $F_o(hkl)$ values, taken in the present case as $\sqrt{(\pi/2)}.\overline{(|F_o|-|F_c|)}$.

The peaks in the final F_o synthesis were closely spherical in symmetry down at least to $\frac{1}{2}\varrho_o$ and in most cases much below this. Values of p_j were computed for the various atoms from the half-widths of the peaks. The values for a given kind of atom were fairly consistent and were averaged. The values of p_j and the resulting values of ε_j are listed in Table 5.

Cruickshank's equations are of the type:

$$\sigma\left(\frac{\partial\varrho}{\partial x}\right) = \frac{2\pi}{aV}\left\{\sum_3 h^2(\Delta F)^2\right\}^{\frac{1}{2}},$$

where the symbols have their usual crystallographic significance. The quantities $\sigma(\partial\varrho/\partial x)$ are related to the standard deviations in the atomic coordinates as follows in the monoclinic system:

$$\sigma(x_j) = \frac{\{\sigma^2(\partial\varrho/\partial x)-\cos^2\beta\,\sigma^2(\partial\varrho/\partial z)\}^{\frac{1}{2}}}{\sin^2\beta\,(\partial^2\varrho/\partial x^2)_j}\,,$$

$$\sigma(y_j) = \frac{\sigma(\partial\varrho/\partial y)}{(\partial^2\varrho/\partial y^2)_j}\,,$$

$$\sigma(z_j) = \frac{\{\sigma^2(\partial\varrho/\partial z)-\cos^2\beta\,\sigma^2(\partial\varrho/\partial x)\}^{\frac{1}{2}}}{\sin^2\beta\,(\partial^2\varrho/\partial z^2)_j}\,.$$

The nearly spherical symmetry of the peaks permits one to take the second derivatives for a given kind of atom as equal to each other. The resulting deviations are shown in Table 5.

Table 5. *Estimation of errors in the atomic coordinates*

	p (Å^{-2})	ε (Å)	$\partial^2\varrho/\partial r^2$ (e.Å^{-5})	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Se	5·32	0·0025	−840	0·0013	0·0014	0·0013
O	4·5	0·016	−90	0·012	0·013	0·012
C	4·5	0·021	−52	0·021	0·022	0·020

Description of the structure

A projection of the crystal structure of benzeneseleninic acid on (010) is shown in Fig. 3. The structure consists of chains of molecules along the twofold screw axes which are held together by strong hydrogen bonds. The structure of a chain is indicated in Fig. 4. The chains are presumably held to one another laterally by means of van der Waals forces. The pronounced cleavage of the crystals into needle-like fragments along the b axis is consistent with this chain structure. The structure of the benzeneseleninic acid molecule is shown in Fig. 5, and the observed bonded distances together with their standard deviations are given in Table 6. The observed bond angles with their deviations are shown in Table 7 while intermolecular packing distances are listed in Table 8. The standard deviations of the bond angles were computed by means of the equations given by Cruickshank & Robertson (1953).

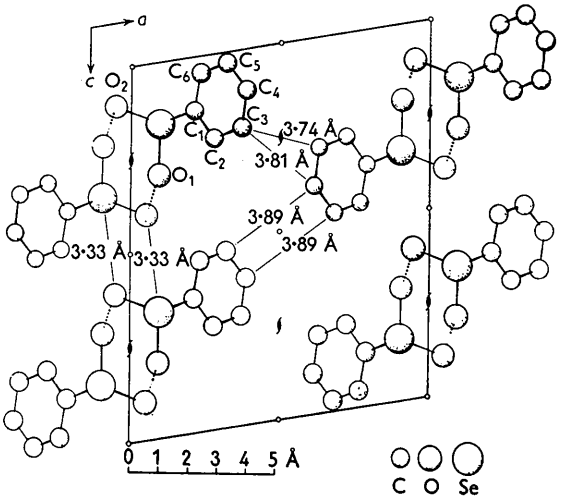

Fig. 3. View of the benzeneseleninic acid structure looking down the b axis.

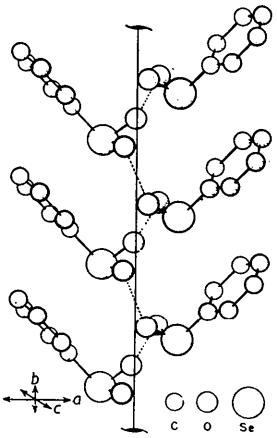

Fig. 4. Perspective view of one of the chains in benzeneseleninic acid.

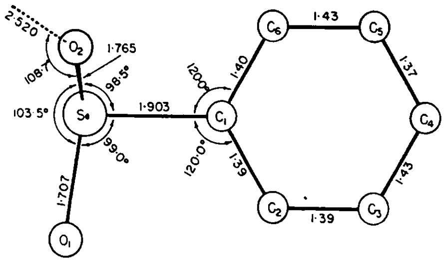

Fig. 5. The structure of the benzeneseleninic acid molecule.

Table 6. *Bonded distances in benzeneseleninic acid*

Bond	Length (Å)	Standard deviation (Å)
Se–C_1	1·903	0·021
Se–O_1	1·707	0·015
Se–O_2	1·765	0·015
C_1–C_2	1·388	0·030
C_2–C_3	1·386	0·030
C_3–C_4	1·432	0·030
C_4–C_5	1·367	0·030
C_5–C_6	1·433	0·030
C_6–C_1	1·395	0·030
$\overline{\text{C–C}}$	1·400	0·012
O_2–HO_1'	2·520	0·020

Table 7. *Bond angles in benzeneseleninic acid*

Bonded atoms	Bond angle (°)	Standard deviation (°)
O_1–Se–C_1	99·0	0·9
O_2–Se–C_1	98·5	0·9
O_1–Se–O_2	103·5	0·7
Se–C_1–C_2	120·0	1·7
Se–C_1–C_6	120·0	1·7
C_6–C_1–C_2	119·7	2·2
C_1–C_2–C_3	119·0	2·2
C_2–C_3–C_4	122·0	2·2
C_3–C_4–C_5	119·0	2·2
C_4–C_5–C_6	119·0	2·2
C_5–C_6–C_1	121·3	2·2
Se–O_2–O_1'	108·7	0·7

Table 8. *Non-bonded distances in benzeneseleninic acid*

In same chain

Atoms	Distance (Å)	Sum of van der Waal's radii (Å)
Se–Se′	4·12	4·00
Se–O_1'	3·51	3·40
Se–O_1''	3·17	3·40
Se–O_2'	3·63	3·40
O_1–O_1'	3·30	2·80
Se–C_1'	3·96	—
Se–C_2'	3·61	—
Se–C_3'	3·47	—
Se–C_4'	3·61	—
Se–C_5'	3·89	—
Se–C_6'	4·04	—

Between chains

Atoms	Distance (Å)	Sum of van der Waal's radii (Å)
Se–Se	4·24	4·00
Se–O_2	3·33	3·40
O_2–O_2	3·22	2·80
C_3–C_3	3·74	—
C_3–C_4	3·81	—
C_4–C_5	3·89	—

The observed bond distances and packing distances are all reasonable. The pyramidal configuration about selenium is very similar to that found in selenium dioxide (McCullough, 1937) and selenious acid (Wells & Bailey, 1949). In selenium dioxide, selenium is bonded to three oxygen atoms at 1·73, 1·78 and 1·78 Å with bond angles of 90°, 98°, and 98°. In selenious acid, selenium is bonded to three oxygen atoms at 1·72, 1·75 and 1·76 Å with bond angles of 93°, 97°, and 112°. The difference between the two observed Se–O distances of 1·707 and 1·765 Å in benzeneseleninic acid is significant since it is approximately four times the standard deviation of 0·015 Å for these bonds.

The Se–C distance of 1·903 Å is shorter than the sum of the normal single covalent bond radii, 1·94 Å. This difference is of possible significance since it is about twice the standard deviation for the bond. The observed Se–C (aromatic) distances in the di-*p*-tolylselenium dihalides (McCullough & Marsh, 1950) are 1·93 and 1·95 Å. However, the probable error is greater in these determinations since they were based on projections.

Within the errors of the present determination, the phenyl group is planar with the expected distances and bond angles. In order to get an idea of the deviations of the observed carbon atom locations from planarity, a plane was passed through the selenium atom, the midpoint between C_2 and C_3, and the midpoint between C_5 and C_6. The equation of this plane in the rectangular coordinates:

$$X = xa_0 \sin\beta\,, \quad Y = yb_0\,, \quad Z = zc_0 + xa_0 \cos\beta$$

is

$$5{\cdot}9372X - 5{\cdot}2564Y - 0{\cdot}7579Z - 4{\cdot}4591 = 0\,.$$

Distances of the carbon atoms from this plane are:

C_1:	0·018 Å	C_4:	0·032 Å
C_2:	−0·031	C_5:	0·010
C_3:	0·031	C_6:	−0·011

which are all well under $2\sigma(r)$ for the carbon atoms. If a least-squares plane had been found, the differences would have been even less. The average C–C distance in the ring is 1·400 Å and the deviations of the individual values from this are no greater than the standard deviation for the bond. The plane of the ring makes an angle of 47° with the *B* face of the unit cell.

The oxygen atom O_1 is at a distance of −0·325 Å from the plane of the ring. This corresponds to a rotation about the Se–C bond of approximately 10° from the plane.

The authors wish to acknowledge their indebtedness, with thanks, to the following:

1. The Institute for Numerical Analysis of the National Bureau of Standards for making I.B.M. equipment and SWAC available for computations.
2. Messrs F. H. Kruse, R. J. Prosen, and R. A. Sparks for coding the three-dimensional syntheses and structure-factor calculations so that these could be carried out on SWAC. The three-dimensional refinement would not have been possible without the many hours contributed by these workers.
3. The Office of Naval Research for financial aid during the early part of this work, under Task Order I

of Contract N6 onr-275 with the University of California at Los Angeles.

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Acta Cryst. (1954). **7**, 838

The Crystal Structure of Barium Peroxide*

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(*Received* 28 *June* 1954)

The lattice constants of barium peroxide have been remeasured, and at 25·0° C. the tetragonal unit cell has $a = 5{\cdot}384 \pm 0{\cdot}010$ and $c = 6{\cdot}841 \pm 0{\cdot}005$ 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 $[O\text{–}O]^=$ 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 $[O\text{–}O]^=$ 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 $2\theta \leqslant 165°$). 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 perioxide under more favorable conditions.

After the present work had been completed, we found that a study of the crystal structures of $CaO_2 . 8\,H_2O$, $SrO_2 . 8\,H_2O$ and $BaO_2 . 8\,H_2O$ 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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* Sponsored by the Office of Naval Research, the Army Signal Corps, and the Air Force under ONR Contract N5ori-07801.

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