

The Crystal Structure of the Orthorhombic Modification of BiOHCrO_4 . A Refinement of the Structure of Monoclinic BiOHCrO_4

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On treating acid solutions of bismuth nitrate with solutions containing dichromate, selenate, or sulphate ions, salts of the general composition $\text{BiOHXO}_4 \cdot n\text{H}_2\text{O}$ ($X = \text{Cr, Se, or S}$) are formed. A survey over basic salts of these compositions hitherto studied by X-ray diffraction methods is given in a previous paper.¹ The compound BiOHCrO_4 is dimorphous, having one orthorhombic and one monoclinic form. In this paper the crystal structure of the orthorhombic modification of BiOHCrO_4 is described. The structure of the monoclinic form of BiOHCrO_4 has been published in a previous paper.² The intensity data given there have been used for the refinement of the structure. The two modifications of BiOHCrO_4 are closely related structurally, the main difference being the mode of arrangement of the formal BiOHCrO_4 layers perpendicular to the x -axis. In these layers square aggregates of the probable formula $\text{Bi}_4(\text{OH})_4^{4+}$ may be visualized. The non-tetrahedral oxygen atoms and the bismuth atoms form finite groups and not endless sheets as in BiOCl and related compounds.

The compound BiOHCrO_4 occurs in one orthorhombic and in one monoclinic modification. In the present paper the crystal structure of the orthorhombic form is treated. A least-squares refinement of the structure of the monoclinic modification given in a previous paper² has also been made.

EXPERIMENTAL

Preparation, analysis and solubility. Pure crystals of the orthorhombic form of BiOHCrO_4 were prepared in the following way: 1 part of a solution *A* containing 75 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 100 ml concentrated HNO_3 , and 300 ml H_2O was mixed with 2.5 parts of a solution *B* containing 30 g $\text{K}_2\text{Cr}_2\text{O}_7$ dissolved in 800 ml H_2O . The mixture was transferred to a glass tube which was then sealed off and heated to 130°C for one week. The sample was washed with water and dried at 110°C .

The analyses of the orthorhombic form of BiOHCrO_4 were carried out in the same way as for the monoclinic one (*cf.* Ref.²) (Found: Bi 60.8; Cr 15.1; H_2O 2.85. Calc.: Bi 61.1; Cr 15.2; H_2O 2.63).

Orthorhombic BiOHCrO_4 is less soluble than the monoclinic form. Determinations of the solubilities at 25°C in $0.05\text{ M H}_2\text{SO}_4$ indicate a solubility ratio *mon/rh* of 1.5. Thus the orthorhombic form is the more stable phase at this temperature.

Unit-cell dimensions and single crystal intensity data. The powder photographs were taken in a Guinier focusing camera of 80 mm diameter using CuK radiation and potassium chloride ($a = 6.2930\text{ \AA}$) as an internal standard. A table of observed and calculated values of $\sin^2\theta$ is given earlier.² $\sin^2\theta$ of the lines in this table were referred to the wavelength of CuKa_2 (1.5443 \AA) and not to CuKa_1 (1.5405 \AA) as stated there. The powder pattern could be interpreted by means of an orthorhombic unit cell with the following dimensions:

$$a = 11.311\text{ \AA}, b = 9.728\text{ \AA}, c = 7.314\text{ \AA} \text{ and } V = 804.8\text{ \AA}^3.$$

The observed density, 5.7 g.cm^{-3} , indicates a cell content of eight formula units BiOHCrO_4 . The calculated density is 5.646 g.cm^{-3} .

The crystals used for the single crystal investigations appeared as flat parallelepipeds with their b axes perpendicular to the plates.

Single crystals were investigated by CuK radiation (Weissenberg photographs) and MoK radiation (Buerger precession photographs). The reflections of the following layer lines were registered:

Crystal rotated around	Registered layer lines	Method
[001]	0-4	Weissenberg
[101]	0-7	»
[100]	0-1	Buerger precession
[010]	0-3	»

The multifilm technique was used for the Weissenberg photographs. Series of photographs for each zone were exposed for different times in the Buerger precession camera.

The intensities of the spots in the photographs were estimated visually compared to a calibrated scale and corrected for absorption by means of an absorption program developed by Werner.³ The digital computer FACIT EDB of the *Swedish Board for Computing Machinery* was used for these calculations.

DETERMINATION OF THE CRYSTAL STRUCTURE OF ORTHORHOMBIC BiOHCrO_4

Symmetry. From the single-crystal photographs, the Laue symmetry was found to be *mmm*. In the powder and single crystal photographs the following spectra were systematically missing:

$$hk0 \text{ with } h \neq 2n, 0kl \text{ with } k \neq 2n \text{ and } h0l \text{ with } l \neq 2n \text{ (} n \text{ is an integer).}$$

This is characteristic of the space group *Pbca* (No. 61 in the *International Tables*⁴).

The positions of the heavy atoms. In spite of the limited number of independent reflections, *viz.* 40, 41, and 59 in the $h0l$, $0kl$, and $hk0$ photographs, respectively, we tried to get a preliminary structure based mainly on Patterson and electron density *projections*. We then refined the obtained structure with the aid of three-dimensional intensity data by means of the method of least squares.

The bismuth atoms. There are eight bismuth atoms in the unit cell and they could either be situated in the general eightfold point position $8(c)$ or in a combination of the fourfold point positions $4(a)$ and $4(b)$ in the space group.

Pbca (No. 61); 8 Bi in $8(c)$: $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$
 or 4 Bi in $4(a)$: $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}$
 and 4 Bi in $4(b)$: $0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0.$

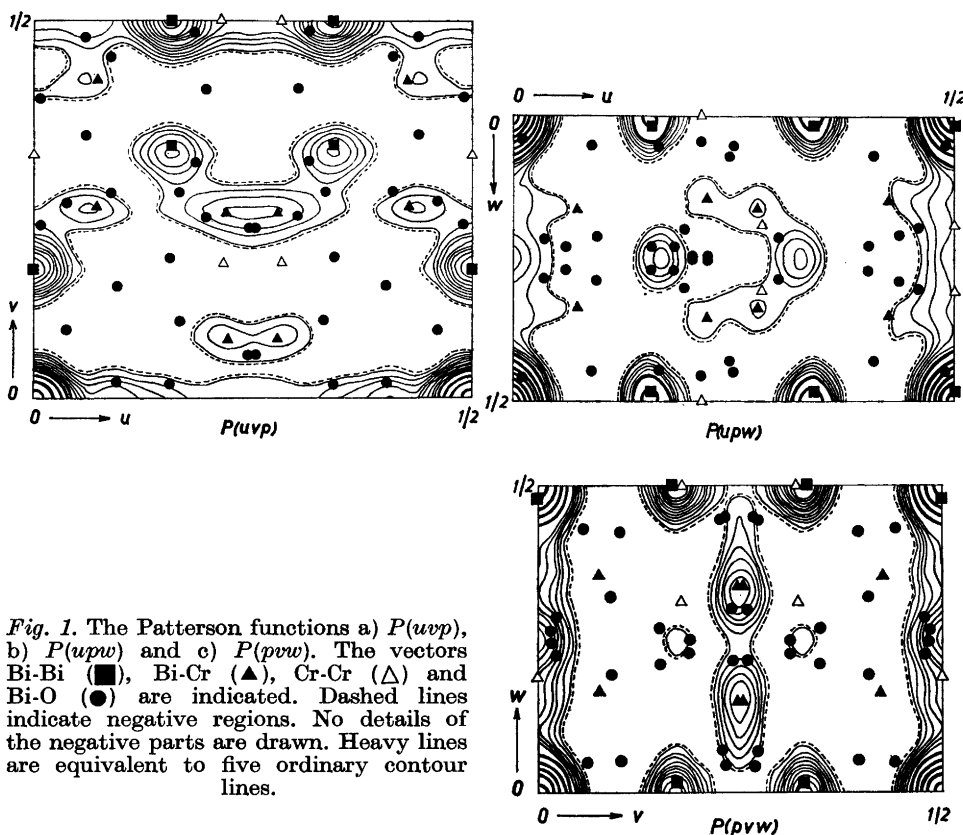


Fig. 1. The Patterson functions a) $P(uvp)$, b) $P(upw)$ and c) $P(pvw)$. The vectors Bi-Bi (■), Bi-Cr (▲), Cr-Cr (△) and Bi-O (●) are indicated. Dashed lines indicate negative regions. No details of the negative parts are drawn. Heavy lines are equivalent to five ordinary contour lines.

From the occurrence of high peaks at values of u and/or $v \neq 0, \frac{1}{2}$ in the Patterson projections $P(uvp)$, $P(upw)$ and $P(pvw)$ (Figs. 1a-c), we deduced that the eight bismuth atoms are situated in the general point position 8(c). The following restrictions could be made for the parameters of these eight bismuth atoms: $0 \leq |x| \leq \frac{1}{4}$, $0 \leq |y| \leq \frac{1}{4}$, $0 \leq |z| \leq \frac{1}{4}$. Taking this fact into account and considering the positions of the high peaks in the Patterson projections above, the following parameter values were arrived at:

8 Bi in 8(c); $x = 0.0792(0.0790)$, $y = 0.1654(0.1655)$, $z = 0(-0.0085)$.

Throughout this paper the final parameter values arrived at by least-squares refinement are given within brackets.

As the z value might deviate from zero by a small amount two points of the generalized Patterson functions were calculated, namely $P_n(0,0)$ and $P_n(\frac{1}{2},0)$. The ratio $P_n(\frac{1}{2},0)/P_n(0,0)$ should then be approximately equal to $\cos 2\pi(\frac{1}{2}-2z)n$. Calculations for the reflections $hk3-hk9$ gave $z = \pm(0.013-0.009)$ or $z = \pm(0.487-0.491)$. The negative value $z = -0.01$ was arbitrarily chosen.

Bismuth-bismuth vectors calculated according to the finally accepted parameter values are marked in Figs. 1*a-c*.

The chromium atoms. The positions of the chromium atoms were derived from the electron density projections $\rho(xyp)$, $\rho(xpz)$ and $\rho(pyz)$, where these atoms stand out clearly. Only the electron density projection $\rho(pyz)$ is given here (Fig. 2*a*). The signs of the reflections used for these calculations were obtained from the positions of the bismuth atoms. The following values of the coordinates of the chromium atoms were thus arrived at:

Pbca (No. 61); 8 Cr in 8(*c*), $x = 0.141(0.143)$, $y = 0.588(0.589)$, $z = 0.155(0.155)$.

The corresponding bismuth-chromium vectors are marked in the Patterson projections in Figs. 1*a-c*. It might be noted that not all Bi-Cr vectors do fall within positive regions in these maps. That is probably due to the combined effect of the limited number of reflections used in these projections and to the dominant scattering power of the bismuth atoms.

The oxygen atoms. Except for the maxima due to the bismuth and chromium atoms, the electron density projection $\rho(pyz)$ (Fig. 2*a*) shows one quite large maximum at $y = 0.16$ and $z = 0.25$. This peak is real since it persists in the electron density projections $\rho'(pyz)$ and $\rho''(pyz)$ (Figs. 2*b,c*) but is not present in the $(F_o - F_c)$ synthesis $\rho'''(pyz)$ (Fig. 2*d*). The distance from this peak to the nearest chromium atom in the projection is about 0.9 Å. On account of the height of this maximum it seems probable that this peak is the result of the overlapping of four oxygen atoms, two belonging to the chromium

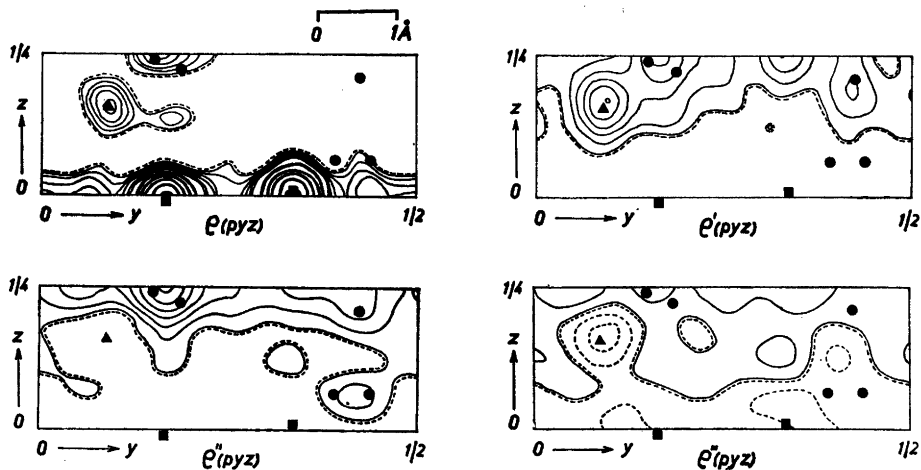


Fig. 2. a) The observed electron density projection $\rho(pyz)$, b) the projection $\rho'(pyz)$, where the contributions of the bismuth atoms are subtracted from $\rho(pyz)$, c) the projection $\rho''(pyz)$, where the contributions of the bismuth and chromium atoms are subtracted from $\rho(pyz)$, and d) the projection $\rho'''(pyz)$, where the contributions of the bismuth, chromium and oxygen atoms are subtracted from $\rho(pyz)$. The final bismuth (■), chromium (▲) and oxygen (●) atom positions are indicated. Dashed lines indicate negative values. Details of the negative regions are drawn only in $\rho'''(pyz)$. Heavy lines in $\rho(pyz)$ are equivalent to five ordinary contour lines.

atom at $x = 0.359$, $y = 0.088$, $z = 0.155$ (named Cr_{14}) and two to the chromium atom at $x = 0.859$, $y = 0.088$ and $z = 0.345$ (named Cr_{17}) (notations *cf.* Tables 2,3). From the known geometry of the CrO_4^{2-} tetrahedron (distances $\text{Cr}-\text{O} = 1.6 \text{ \AA}$, $\text{O}-\text{O} = 2.6 \text{ \AA}$) the following values for the x parameters of the oxygen atoms belonging to Cr_{14} could be expected:

$$x_1 = 0.359 + \frac{2.6}{2 \times 11.3} = 0.47 \text{ and}$$

$$x_2 = 0.359 - \frac{2.6}{2 \times 11.3} = 0.24$$

as the length of the a axis of the unit cell is 11.3 \AA . Thus from this peak in $\rho(\text{pyz})$ (Fig. 2a) and from these geometrical considerations, the positions of two of the oxygen atoms in one chromate tetrahedron should approximately be:

Pbca (No. 61); 8 O_1 in 8(c), $x = 0.47(0.48)$, $y = 0.16(0.18)$, $z = 0.25(0.22)$
8 O_2 in 8(c), $x = 0.24(0.24)$, $y = 0.16(0.15)$, $z = 0.25(0.28)$

Moreover, to complete a regular tetrahedron around the chromium atom Cr_{14} , two oxygen atom O_3 and O_4 should be situated in the plane $x = 0.359$ with such values for their y and z parameters that their distances to the chromium atom are about 1.6 \AA and all angles $\text{O}-\text{Cr}-\text{O}$ are about 110° . In this way the following approximate positions for the oxygen atoms O_3 and O_4 were arrived at:

8 O_3 in 8(c); $x = 0.36(0.33)$, $y = 0.12(0.11)$, $z = 0.95(0.93)$
8 O_4 in 8(c); $x = 0.38(0.38)$, $y = 0.92(0.92)$, $z = 0.19(0.21)$

These positions of the oxygen atoms O_3 and O_4 correspond to positive regions in $\rho''(\text{pyz})$ (Fig. 2c).

Geometrical considerations were also used to locate the remaining eight oxygen atoms O_5 of the unit cell. Using the atomic positions already determined, sections were drawn perpendicular to the b axis for different y values and such positions of the oxygen atoms O_5 were sought for so as to satisfy the conditions:

$$\text{O}-\text{O}_5 \geq 2.6 \text{ \AA}, \text{O}_5-\text{O}_5 \geq 2.6 \text{ \AA}, \text{O}_5-\text{Bi} \geq 2.3 \text{ \AA}$$

Small regions around $x = 0.38$, $y = 0.07$ and $z = 0.60$ were found to agree with these conditions. As a starting point for the subsequent refinement the equivalent position $x = 0.50 + 0.38 = 0.88(0.91)$, $y = 0.07(0.06)$ and $z = 0.50 - 0.60 + 1 = 0.90(0.93)$ was chosen. This position of O_5 also corresponds to a positive region in $\rho''(\text{pyz})$ (Fig. 2c).

Refinement of the parameters. Using all observed reflections, the parameters of all atoms found by the procedure described above were refined by means of the method of least squares, applying a program for the refinement developed by Åsbrink and Brändén.⁵ The calculations were performed by the aid of the digital computer FACIT EDB of the *Swedish Board for Computing Machinery*. The scattering factors of the bismuth, chromium and oxygen atoms (not ions) were used for the calculations.⁶ No corrections were made for the anomalous dispersion of the heavy atoms. The applied weighting scheme was that according to Cruickshank.⁷

At first the 655 observed independent reflections were treated. The discrepancy factor went down to 12.4 %. Next the 215 non-observed reflections were included in the refinement. These reflections were assigned the value of $\frac{1}{2} |F_o|_{\min}$ for the corresponding zones. Thereby small shifts occurred in the parameters, and as expected the standard deviations diminished and the discrepancy factor increased, to 15.3 %. In calculating the scale factors of the different zones and the standard deviations those reflections were excluded for which $||F_o| - |F_c|| > 128$ and $|F_o| > 3 |F_c|$. These reflections were, however, included in the calculations of the discrepancy factor. The table of the observed and calculated structure factors will be published elsewhere.⁸ For the final cycle of the refinement no shift exceeded 6 % of the corresponding standard deviations. The final weight analysis is given in Table 1, the atomic parameters, the isotropic temperature factors of all atoms and their standard deviations are listed in Table 2. The values of $w \overline{\Delta^2}$ (Table 1) deviate as much from unity as could be expected for this intensity material, which was photographically registered, and in which the heavy absorption effects may not have been

Table 1. Analysis of the weighting scheme used in the last cycle of the refinement of orthorhombic BiOHCrO_4 . w = weighting factor, $\Delta = ||F_o| - |F_c||$.

Interval $\sin \Theta$	$\overline{w \Delta^2}$	Number of independent reflections	Interval $ F_o $	$\overline{w \Delta^2}$	Number of independent reflections
0.00—0.46	1.30	83	0—29	0.85	56
0.46—0.58	0.51	78	29—59	0.82	129
0.58—0.67	0.86	71	59—88	1.21	110
0.67—0.74	0.71	64	88—118	1.47	95
0.74—0.79	0.56	64	118—147	0.94	59
0.84—0.89	1.03	62	147—176	0.62	44
0.89—0.93	1.02	61	176—206	0.59	46
0.93—0.97	1.75	58	206—235	0.96	35
0.97—1.00	1.83	40	235—265	0.54	17
			265—294	1.24	50

Table 2. The crystal structure of orthorhombic BiOHCrO_4 . Space group $Pbca$ (No. 61). 8 Bi, 8 Cr, 8 O_1 —8 O_5 in 8(c). Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement.

Atom	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	$B \pm \sigma_B \text{ \AA}^2$
Bi	0.07895 \pm 0.00013	0.16549 \pm 0.00016	0.99150 \pm 0.00017	1.370 \pm 0.028
Cr	0.14271 \pm 0.00055	0.58858 \pm 0.00058	0.15482 \pm 0.00081	1.159 \pm 0.085
O_1	0.48227 \pm 0.00246	0.18321 \pm 0.00242	0.22082 \pm 0.00360	1.251 \pm 0.402
O_2	0.23946 \pm 0.00253	0.14598 \pm 0.00253	0.25938 \pm 0.00366	1.416 \pm 0.420
O_3	0.33619 \pm 0.00283	0.10867 \pm 0.00295	0.93455 \pm 0.00447	2.072 \pm 0.474
O_4	0.38146 \pm 0.00217	0.92274 \pm 0.00243	0.20522 \pm 0.00344	1.106 \pm 0.369
O_5	0.91131 \pm 0.00231	0.06333 \pm 0.00248	0.93158 \pm 0.00371	1.150 \pm 0.376

Table 3. Interatomic distances and angles in the structure of orthorhombic BiOHCrO_4 .

The numbering of the atoms

All atoms are situated in the general point position 8(c) in *Pbca* (No. 61). Taking the oxygen atom O_5 as an example, the following symbols will be used:

O_{51} x, y, z (the coordinates given in Table 2)	O_{52} $\bar{x}, \bar{y}, \bar{z}$
O_{53} $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$	O_{54} $\frac{1}{2} - x, \frac{1}{2} + y, z$
O_{55} $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$	O_{56} $x, \frac{1}{2} - y, \frac{1}{2} + z$
O_{57} $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	O_{58} $\frac{1}{2} + x, y, \frac{1}{2} - z$

Distances O—O < 3.5 Å outside the chromate tetrahedron

$\text{O}_{11}-\text{O}_{28}$	2.94 ± 0.04
$\text{O}_{11}-\text{O}_{36}$	3.04 ± 0.05
$\text{O}_{11}-\text{O}_{45}$	2.85 ± 0.04
$\text{O}_{11}-\text{O}_{53}$	2.82 ± 0.04
$\text{O}_{11}-\text{O}_{57}$	3.10 ± 0.04
$\text{O}_{11}-\text{O}_{58}$	2.91 ± 0.04

$\text{O}_{21}-\text{O}_{36}$	2.92 ± 0.04
$\text{O}_{21}-\text{O}_{37}$	2.92 ± 0.04
$\text{O}_{21}-\text{O}_{44}$	3.05 ± 0.04
$\text{O}_{21}-\text{O}_{52}$	3.00 ± 0.04
$\text{O}_{21}-\text{O}_{58}$	3.09 ± 0.04

$\text{O}_{31}-\text{O}_{42}$	3.37 ± 0.05
$\text{O}_{31}-\text{O}_{47}$	2.99 ± 0.05
$\text{O}_{31}-\text{O}_{52}$	3.41 ± 0.05
$\text{O}_{31}-\text{O}_{53}$	3.44 ± 0.04
$\text{O}_{31}-\text{O}_{58}$	2.84 ± 0.05

$\text{O}_{41}-\text{O}_{52}$	3.46 ± 0.04
$\text{O}_{41}-\text{O}_{57}$	2.87 ± 0.04
$\text{O}_{41}-\text{O}_{58}$	3.01 ± 0.04
$\text{O}_{51}-\text{O}_{52}$	2.56 ± 0.06

Distances Me—Me < 5.0 Å

$\text{Bi}_{11}-\text{Bi}_{12}$	3.684 ± 0.004
$\text{Bi}_{11}-\text{Bi}_{16}$	4.010 ± 0.002

$\text{Cr}_{11}-\text{Cr}_{12}$	4.304 ± 0.013
$\text{Cr}_{11}-\text{Cr}_{17}$	4.715 ± 0.008
$\text{Cr}_{11}-\text{Cr}_{16}$	4.821 ± 0.008

$\text{Bi}_{11}-\text{Cr}_{14}$	3.450 ± 0.007
$\text{Bi}_{11}-\text{Cr}_{16}$	3.561 ± 0.006
$\text{Bi}_{11}-\text{Cr}_{15}$	3.769 ± 0.007
$\text{Bi}_{11}-\text{Cr}_{11}$	4.346 ± 0.006
$\text{Bi}_{11}-\text{Cr}_{17}$	4.657 ± 0.007

Distances Bi—O < 3.5 Å

$\text{Bi}_{11}-\text{O}_{13}$	2.408 ± 0.026
$\text{Bi}_{11}-\text{O}_{18}$	2.378 ± 0.027
$\text{Bi}_{11}-\text{O}_{21}$	2.678 ± 0.028
$\text{Bi}_{11}-\text{O}_{26}$	3.089 ± 0.027
$\text{Bi}_{11}-\text{O}_{31}$	2.991 ± 0.032
$\text{Bi}_{11}-\text{O}_{44}$	2.984 ± 0.025
$\text{Bi}_{11}-\text{O}_{47}$	2.307 ± 0.025
$\text{Bi}_{11}-\text{O}_{51}$	2.185 ± 0.026
$\text{Bi}_{11}-\text{O}_{52}$	2.299 ± 0.025

Distances Cr—O and O—O (in Å) within the chromate tetrahedron

$\text{Cr}_{11}-\text{O}_{14}$	1.756 ± 0.030
$\text{Cr}_{11}-\text{O}_{24}$	1.635 ± 0.029
$\text{Cr}_{11}-\text{O}_{34}$	1.640 ± 0.034
$\text{Cr}_{11}-\text{O}_{44}$	1.677 ± 0.025

$\text{O}_{14}-\text{O}_{24}$	2.784 ± 0.040
$\text{O}_{14}-\text{O}_{34}$	2.764 ± 0.042
$\text{O}_{14}-\text{O}_{44}$	2.781 ± 0.035

$\text{O}_{24}-\text{O}_{34}$	2.641 ± 0.043
$\text{O}_{24}-\text{O}_{44}$	2.730 ± 0.035

$\text{O}_{34}-\text{O}_{44}$	2.730 ± 0.040
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∠ O—Cr—O within the chromate tetrahedron

∠ $\text{O}_1-\text{Cr}-\text{O}_2$	110.4°
∠ $\text{O}_1-\text{Cr}-\text{O}_3$	108.9°
∠ $\text{O}_1-\text{Cr}-\text{O}_4$	108.2°
∠ $\text{O}_2-\text{Cr}-\text{O}_3$	107.5°
∠ $\text{O}_2-\text{Cr}-\text{O}_4$	111.0°
∠ $\text{O}_3-\text{Cr}-\text{O}_4$	110.8°

Estimated standard deviations in the angles are $\pm 1.6^\circ$.

fully compensated for. The calculated interatomic distances Bi—Bi, Cr—Cr, Cr—O, Bi—O and O—O, with their standard deviations are given in Table 3, together with the angles of interest in the structure.

The result obtained from the refinement was controlled by making three-dimensional electron density syntheses based on values of $F_o - F_c$. For these calculations programs developed by Liminga and Olovsson were used,⁹ and the calculations were performed with the aid of the aforementioned digital computer. Sections were calculated at values of y corresponding to the different sites of the atoms. All oxygen atoms stand out clearly in the F_o syntheses. A fairly deep pit occurs in the sections at $y = 0.14-0.18$. It corresponds to 0.7 times the height of an oxygen atom in the syntheses based on F_c . The corrections of the atomic sites of the oxygen atoms as calculated from the $F_o - F_c$ syntheses are always less than 1.5 times the corresponding standard deviations as obtained from the least-squares refinement. The parameter values from the least-squares refinement (Table 2) have been used throughout this paper.

THE REFINEMENT OF THE CRYSTAL STRUCTURE OF MONOCLINIC BiOHCrO_4

After the crystal structure of monoclinic BiOHCrO_4 was published² a least-squares program was developed at the Institute of Inorganic Chemistry.⁶ It therefore became possible to make a refinement of the structural data given earlier.

The observed structure factors given in a previous paper² were treated. The coordinates of all atoms given there, together with estimated overall temperature factors were chosen as a starting point for the refinement. Cruickshank's weighting function was used. The procedure was exactly the same as that given above for the orthorhombic modification. Starting with the 605 independent reflections, the discrepancy factor went down to 11.1%. On introducing the 180 non-observed reflections, within the range of $\sin \theta$

Table 4. Analysis of the weighting scheme used in the last cycle of the refinement of monoclinic BiOHCrO_4 . w is the weighting factor, $\Delta = ||F_o| - |F_c||$.

Interval $\sin \theta$	$\overline{w \Delta^2}$	Number of independent reflections	Interval $ F_o $	$\overline{w \Delta^2}$	Number of independent reflections
0.00—0.46	0.98	86	0—36	1.14	41
0.46—0.58	0.78	73	36—53	0.66	93
0.58—0.67	1.10	77	53—71	0.80	113
0.67—0.74	0.82	60	71—89	1.14	75
0.74—0.79	0.80	56	89—107	1.02	92
0.79—0.84	1.05	67	107—125	1.17	48
0.84—0.89	1.05	52	125—142	1.05	45
0.89—0.93	1.49	51	142—160	0.99	23
0.93—0.97	1.05	41	160—178	1.44	64
0.97—1.00	0.96	35			

Table 5. The crystal structure of monoclinic BiOHCrO₄. Space group $P2_1/c$ (No. 14). 4 Bi, 4 Cr, 4 O₁–4 O₅ in 4(*e*): $\pm(x,y,z; x, \frac{1}{2}-y, \frac{1}{2}+z)$. Cell dimensions: $a = 5.625 \text{ \AA}$, $b = 9.592 \text{ \AA}$, $c = 7.476 \text{ \AA}$, $\beta = 93.12^\circ$. Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement. The coordinates reported earlier (*Ref.*²) are given in boldface types.

Atom	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	$B \pm \sigma_B \text{ \AA}^2$
Bi	0.15612 \pm 0.00028 0.1550	0.16770 \pm 0.00016 0.1671	0.01593 \pm 0.00021 0.0165	1.109 \pm 0.026
Cr	0.27589 \pm 0.00119 0.270₀	0.58618 \pm 0.00073 0.585₀	0.15772 \pm 0.00091 0.159₁	0.655 \pm 0.095
O ₁	0.46390 \pm 0.00581 0.482	0.15831 \pm 0.00321 0.153	0.26473 \pm 0.00447 0.263	1.146 \pm 0.510
O ₂	0.72795 \pm 0.00570 0.777	0.09271 \pm 0.00345 0.078	0.55638 \pm 0.00423 0.557	1.243 \pm 0.494
O ₃	0.96486 \pm 0.00445 0.995	0.17405 \pm 0.00245 0.173	0.26896 \pm 0.00347 0.263	0.037 \pm 0.376
O ₄	0.73611 \pm 0.00658 0.700	0.92382 \pm 0.00421 0.920	0.27643 \pm 0.00499 0.272	2.123 \pm 0.618
O ₅	0.80030 \pm 0.00547 0.807	0.06402 \pm 0.00302 0.070	0.93496 \pm 0.00422 0.910	1.060 \pm 0.476

studied, the standard deviations diminished somewhat and the discrepancy factor increased to 13.6 %. For the final cycle of the refinement no shift exceeded 15 % of the corresponding standard deviation. The weighting analysis for the final cycle is given in Table 4, and the atomic parameters, the individual isotropic temperature factors, and their standard deviations are listed in Table 5. As seen (Table 4), the weight analysis is fairly satisfactory in this case. The interatomic distances Bi–Bi, Cr–Cr, Cr–O, Bi–O, and O–O and the angles of interest in the structure, together with the standard deviations are given in Table 6. In Table 5 the coordinates arrived at by Fourier methods² are given in italics. In Table 6 the interatomic distances based on these coordinates are given in brackets. The shifts of the positions of the atoms from those given in a previous paper,² resulting from this least-squares refinement are as follows:

Bi 0.01 \AA , Cr 0.04 \AA , O₁ 0.12 \AA , O₂ 0.31 \AA , O₃ 0.18 \AA , O₄ 0.21 \AA , O₅ 0.20 \AA .

Though these shifts do alter some of the interatomic distances (Table 6), the main features of the structure of monoclinic BiOHCrO₄ as described earlier² have not changed.

As for the orthorhombic BiOHCrO₄, the results of the least-squares refinement was controlled by making three-dimensional electron density syntheses based on F_o and $F_o - F_c$. Sections were calculated at values of y corre-

Table 6. Interatomic distances and angles in the structure of monoclinic BiOHCrO_4 . Values within brackets refer to the corresponding distances obtained with the parameters given in Ref.²

The numbering of the atoms

All atoms are situated in the general point position 4(e) in $P2_1/c$. Taking O_6 as an example the following symbols will be used:

$$\begin{array}{ll} \text{O}_{51} & x, y, z \quad (= \text{the coordinates, given in Table 5}) \\ \text{O}_{53} & x, \frac{1}{2} - y, \frac{1}{2} + z \end{array} \quad \begin{array}{ll} \text{O}_{52} & \bar{x}, \bar{y}, \bar{z} \\ \text{O}_{54} & \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z \end{array}$$

The notation ' denotes the atom is situated in an adjacent unit cell.

Distances O—O < 3.5 Å outside the chromate tetrahedron

$\text{O}_{11}-\text{O}_{23}$	2.99 ± 0.05	(3.01)
$\text{O}_{11}-\text{O}_{23}$	3.22 ± 0.05	(3.47)
$\text{O}_{11}-\text{O}_{31}$	2.81 ± 0.05	(2.75)*
$\text{O}_{11}-\text{O}_{44}$	2.79 ± 0.05	(2.77)
$\text{O}_{11}-\text{O}_{52}$	2.96 ± 0.05	(2.95)
$\text{O}_{11}-\text{O}_{51}$	3.32 ± 0.05	(3.41)
$\text{O}_{11}-\text{O}_{53}$	3.47 ± 0.05	(3.37)
$\text{O}_{21}-\text{O}_{22}$	3.20 ± 0.07	(3.08)
$\text{O}_{21}-\text{O}_{33}$	3.01 ± 0.04	(3.06)
$\text{O}_{21}-\text{O}_{32}$	3.18 ± 0.05	(3.02)
$\text{O}_{21}-\text{O}_{42}$	2.96 ± 0.05	(2.96)
$\text{O}_{21}-\text{O}_{42}'$	3.20 ± 0.05	(3.14)*
$\text{O}_{21}-\text{O}_{51}$	2.85 ± 0.05	(2.64)**
$\text{O}_{21}-\text{O}_{53}$	3.45 ± 0.05	(3.69)*
$\text{O}_{31}-\text{O}_{44}$	2.96 ± 0.05	(2.95)
$\text{O}_{31}-\text{O}_{51}$	2.82 ± 0.04	(2.96)
$\text{O}_{31}-\text{O}_{53}$	2.97 ± 0.04	(2.91)
$\text{O}_{41}-\text{O}_{51}$	2.92 ± 0.05	(3.15)
$\text{O}_{41}-\text{O}_{52}$	3.13 ± 0.05	(3.08)
$\text{O}_{41}-\text{O}_{52}'$	3.33 ± 0.05	(3.09)*
$\text{O}_{51}-\text{O}_{52}$	2.70 ± 0.07	(2.82)

Distances Me—Me < 5.0 Å

$\text{Bi}_{11}-\text{Bi}_{12}$	3.667 ± 0.003	(3.652)
$\text{Bi}_{11}-\text{Bi}_{13}$	4.058 ± 0.002	(4.058)
$\text{Cr}_{11}-\text{Cr}_{12}$	3.907 ± 0.014	(3.955)
$\text{Cr}_{11}-\text{Cr}_{13}$	4.884 ± 0.009	(4.898)*
$\text{Cr}_{11}-\text{Cr}_{13}'$	4.167 ± 0.014	(4.092)*
$\text{Bi}_{11}-\text{Cr}_{12}$	3.500 ± 0.007	(3.570)*
$\text{Bi}_{11}-\text{Cr}_{14}$	3.622 ± 0.007	(3.585)*
$\text{Bi}_{11}-\text{Cr}_{11}$	4.197 ± 0.007	(4.189)*

Distances Bi—O < 3.5 Å

$\text{Bi}_{11}-\text{O}_{11}$	2.472 ± 0.033	(2.53)
$\text{Bi}_{11}-\text{O}_{13}$	3.114 ± 0.034	(3.22)*
$\text{Bi}_{11}-\text{O}_{23}$	3.326 ± 0.033	(3.27)*
$\text{Bi}_{11}-\text{O}_{31}$	2.228 ± 0.027	(2.09)*
$\text{Bi}_{11}-\text{O}_{33}$	2.579 ± 0.025	(2.57)
$\text{Bi}_{11}-\text{O}_{42}$	2.462 ± 0.036	(2.48)
$\text{Bi}_{11}-\text{O}_{44}$	2.951 ± 0.040	(2.95)
$\text{Bi}_{11}-\text{O}_{51}$	2.286 ± 0.031	(2.35)
$\text{Bi}_{11}-\text{O}_{52}$	2.265 ± 0.031	(2.35)

Distances Cr—O and O—O within the chromate tetrahedron

$\text{Cr}_{11}-\text{O}_{14}$	1.707 ± 0.032	(1.63)	$\text{O}_{11}-\text{O}_{21}$	2.617 ± 0.047	(2.78)
$\text{Cr}_{11}-\text{O}_{24}$	1.602 ± 0.032	(1.62)	$\text{O}_{11}-\text{O}_{31}$	2.820 ± 0.041	(2.89)
$\text{Cr}_{11}-\text{O}_{34}$	1.710 ± 0.025	(1.83)	$\text{O}_{11}-\text{O}_{41}$	2.720 ± 0.050	(2.52)
$\text{Cr}_{11}-\text{O}_{44}$	1.636 ± 0.041	(1.66)	$\text{O}_{21}-\text{O}_{31}$	2.705 ± 0.042	(2.73)
			$\text{O}_{21}-\text{O}_{41}$	2.650 ± 0.050	(2.63)
			$\text{O}_{31}-\text{O}_{41}$	2.725 ± 0.046	(2.94)

∠O—Cr—O within the chromate tetrahedron

$\angle \text{O}_1-\text{Cr}-\text{O}_2$	104.5°
$\angle \text{O}_1-\text{Cr}-\text{O}_3$	111.2°
$\angle \text{O}_1-\text{Cr}-\text{O}_4$	108.9°
$\angle \text{O}_2-\text{Cr}-\text{O}_3$	109.4°
$\angle \text{O}_2-\text{Cr}-\text{O}_4$	109.8°
$\angle \text{O}_3-\text{Cr}-\text{O}_4$	109.1°

Estimated standard deviations in the angles are $\pm 1.9^\circ$.

* not given in Ref.²

** miscalculation in Ref.²

sponding to the different atomic sites. All oxygen atoms stand out clearly in the F_o syntheses. The slopes at the sites of the oxygen atoms in the syntheses based on $F_o - F_c$ correspond to corrections which are less than 1.5 times the standard deviations obtained for the corresponding atoms by means of the method of least squares. The parameter values obtained from the least-squares refinement (Table 5) are used throughout this paper in the discussion of monoclinic BiOHCrO_4 .

DISCUSSION OF THE STRUCTURES OF THE TWO MODIFICATIONS OF BiOHCrO_4

As the structures of monoclinic and orthorhombic BiOHCrO_4 are very much alike they will be discussed together.

Main features of the structures. In both structures, the bismuth atoms may be said to form layers perpendicular to the x axis. Within each of these layers, the bismuth atom forms a puckered, two-dimensional network of condensed hexagons like a honeycomb. For the monoclinic form a drawing showing these hexagons is given in Fig. 3a. In the orthorhombic modification two identical layers of hexagons exist in each unit cell. They are, however, moved with

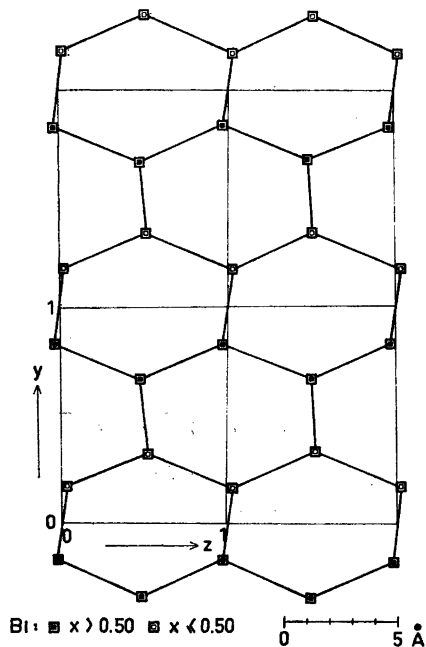


Fig. 3a. The arrangement of the bismuth atoms in the monoclinic modification of BiOHCrO_4 .

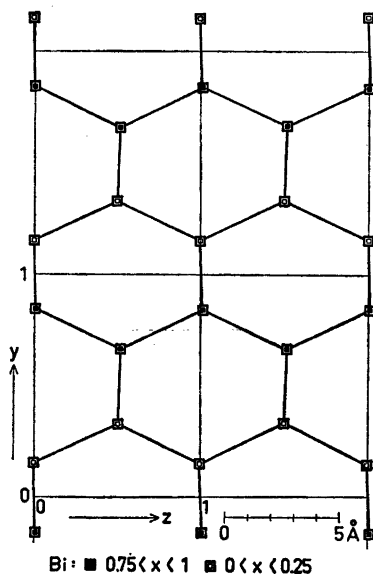


Fig. 3b. The arrangement of the bismuth atoms in the orthorhombic modification of BiOHCrO_4 . The positions of the bismuth atoms of one layer for which $-\frac{1}{4} < x < \frac{1}{4}$ are given.

respect to each others in the yz plane (*vide infra*). One of these bismuth layers is shown in Fig. 3b. The shortest bismuth-bismuth distances within the hexagons are 3.67 Å and 4.06 Å for monoclinic BiOHCrO_4 and 3.68 Å and 4.01 Å for orthorhombic BiOHCrO_4 . The shortest distances between bismuth atoms belonging to adjacent layers are 5.63 Å and 5.89 Å for the two modifications, respectively.

For both the monoclinic and orthorhombic forms the bismuth atoms having the shortest mutual distance are bridged by means of a pair of oxygen atoms or hydroxide groups at relatively short bismuth-oxygen distances, namely 2.27, 2.29 Å, and 2.19, 2.30 Å, respectively. In this way square aggregates of formula $\text{Bi}_2\text{O}_2^{2+}$ or $\text{Bi}_2(\text{OH})_2^{4+}$ are formed. The assumption made

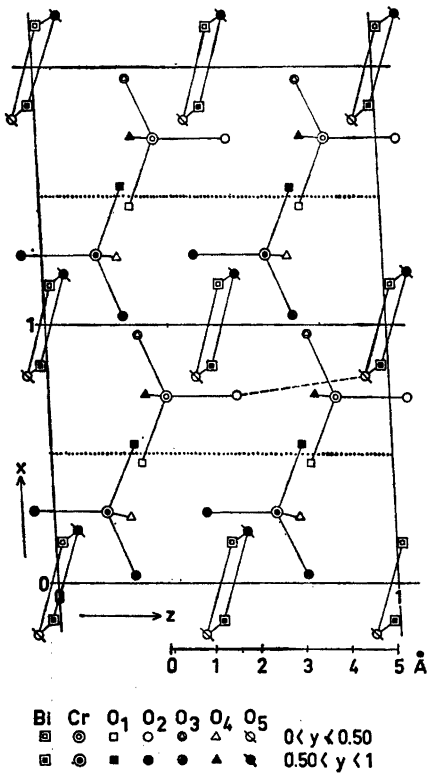


Fig. 4. Projection of the structure of monoclinic BiOHCrO_4 on the ac plane. All atoms are shown. The chromate tetrahedra and the $\text{Bi}_2(\text{OH})_2^{4+}$ (or $\text{Bi}_2\text{O}_2^{2+}$) groups are indicated. The dotted lines enclose one formal bismuth-oxygen "layer". The hydrogen bond supposed between the atoms O_{21} and O_{51} (*cf.* p. 1949) is indicated by a dashed line. The positive y axis points upwards.

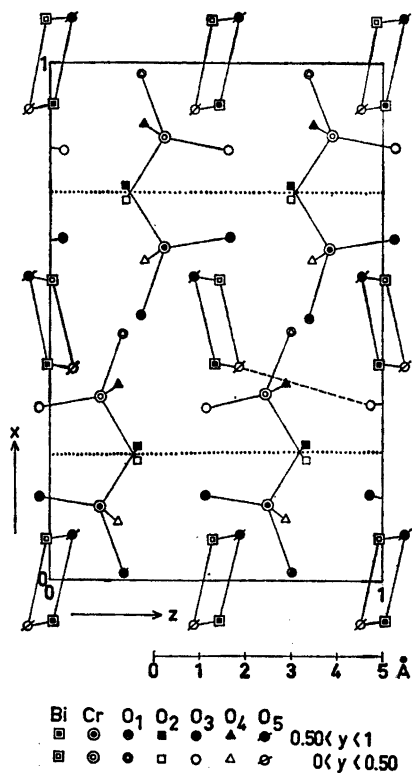


Fig. 5. Projection of one unit cell of orthorhombic BiOHCrO_4 on the ac plane. As in Fig. 6 the positive y axis points upwards. Dotted lines comprise one formal BiOHCrO_4 layer. Full lines indicate the chromate tetrahedra and the square aggregates $\text{Bi}_2\text{O}_2^{2+}$ or $\text{Bi}_2(\text{OH})_2^{4+}$. The hydrogen bond supposed between the atoms O_{31} and O_{53} (*cf.* p. 1949) is indicated by a dashed line.

earlier,² that the hydrogen atoms are situated so as to form a hydrogen bond between the atoms O_{51} and O_{21} in monoclinic BiOHCrO_4 , seems to be reasonable, the distance $\text{O}_{51}-\text{O}_{21}$ being 2.85 Å (Table 6). These atoms are joined by a dashed line in Fig. 4. The equivalent pairs of atoms $\text{O}_{52}-\text{O}_{22}$ etc. are not joined in the drawing. The corresponding distance $\text{O}_{31}-\text{O}_{58}$ in orthorhombic BiOHCrO_4 is 2.84 Å (Table 3), therefore it seems probable that a hydrogen bond also exists between these atoms. These bonds may, however, be weak. The atoms $\text{O}_{31}-\text{O}_{58}$ are joined by a dashed line in Fig. 5. Like in Fig. 3 the equivalent atoms are not joined.

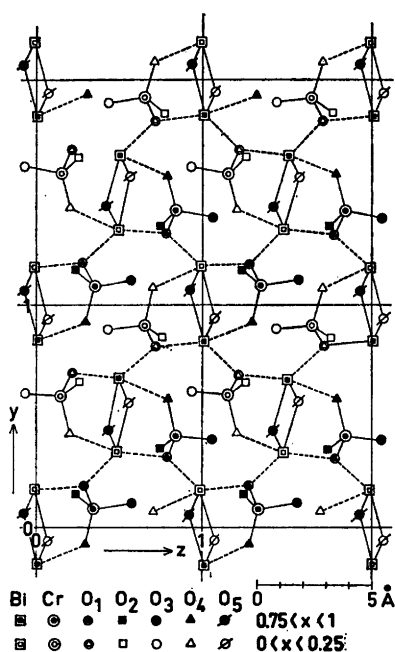


Fig. 6. Projection of four unit cells of orthorhombic BiOHCrO_4 on the bc plane. All atoms except the oxygen atoms O_2 lie within the planes $-\frac{1}{2} < x < \frac{1}{2}$. The atoms O_2 fall outside these planes (cf. Fig. 7, *vide infra*) but as the deviations are small no separate notations have been used for them in the drawing. Dashed lines indicate three of the short distances between bismuth atoms and chromate oxygen atoms. Full lines indicate the chromate tetrahedra and the square aggregates $\text{Bi}_2\text{O}_2^{2+}$ or $\text{Bi}_2(\text{OH})_2^{4+}$. The positive direction of the x axis points downwards in this drawing as in Fig. 7 (*vide infra*).

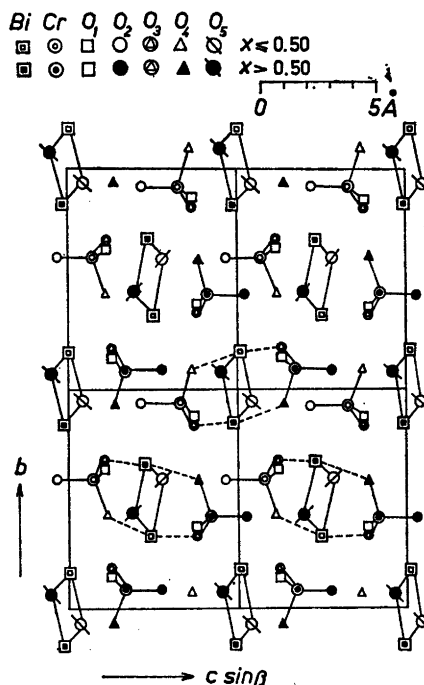


Fig. 7. Projection of the structure of monoclinic BiOHCrO_4 on the bc plane perpendicular to the x axis. All atoms are marked. The chromate tetrahedra and the groups $\text{Bi}_2\text{O}_2^{2+}$ or $\text{Bi}_2(\text{OH})_2^{4+}$ are indicated by full lines. Dashed lines indicate two of the short $\text{Bi}-\text{O}(\text{CrO}_4)$ distances.

The minimum chromium-chromium distance is 3.91 Å for the monoclinic form and 4.30 Å for the orthorhombic one. The two chromate groups lying close to a bismuth hexagon are situated on opposite sides of the layers in the x direction and at a minimum Cr—Cr distance. The arrangement of the chromate groups and the square bismuth-oxygen groups in *one* layer is shown for the orthorhombic form in Fig. 6 and for the monoclinic modification in Fig. 7. Both structures may formally be regarded as layer structures with BiOHCrO_4 layers perpendicular to the x axis (Figs. 4, 5). Thus the layers comprise the bismuth hexagons, their oxygen atoms or hydroxide groups and the chromate groups lying close to the hexagons. Though these layers are not quite separated from each other their main extensions are from $x = -\frac{1}{2}$ to $x = +\frac{1}{2}$ for the monoclinic form (Fig. 4) and from $x = -\frac{1}{4}$ to $x = +\frac{1}{4}$ and also from $x = +\frac{1}{4}$ to $x = +\frac{3}{4}$ for the orthorhombic form (Fig. 5).

In monoclinic BiOHCrO_4 adjacent layers are exactly equal and each atomic position x, y, z in one layer corresponds to an equivalent position $x+1, y, z$ in the next layer. In orthorhombic BiOHCrO_4 an atomic site in one layer x, y, z corresponds to an equivalent position $x+\frac{1}{2}, \frac{1}{2}-y, \bar{z}$ in the adjacent layer. Thus the second layer can be made identical with the first one by a rotation of 180° around an axis parallel to the direction of the x axis and passing through the point $0, \frac{1}{2}, 0$. The stacking mechanism of the layers implies a rotation of them around a normal to their planes and is of the same type as that occurring in ZnS and SiC.¹⁰ It therefore does not seem unlikely that additional forms of BiOHCrO_4 , corresponding to other sequences of stacking, might exist.

The stacking of the layers constitutes the main difference between monoclinic and orthorhombic BiOHCrO_4 since the arrangement in the first layer is about the same for both modifications (Table 7). On making this comparison it must be remembered that the monoclinic angle is close to 90° and that the a axis of the orthorhombic modification is about twice the a axis of the monoclinic one.

The volume of one formula unit BiOHCrO_4 is about the same for both modifications, *viz.* 100.6 \AA^3 for the orthorhombic form and 100.7 \AA^3 for the monoclinic one. The atoms are, however, more evenly distributed in the orthorhombic form and therefore large holes throughout the whole structure, as found in the monoclinic structure, do not occur.

Table 7. Comparison between the parameters of equivalent atoms in the monoclinic and orthorhombic modifications of BiOHCrO_4 .

Monoclinic BiOHCrO_4			Orthorhombic BiOHCrO_4				
Atom	x	y	z	Atom	$2x$	y	z
Bi_{11}	0.1561	0.1677	0.0159	Bi_{11}	0.1579	0.1655	0.9915
Cr_{11}	0.2759	0.5862	0.1577	Cr_{11}	0.2854	0.5886	0.1548
O_{14}	0.536	0.658	0.235	O_{24}	0.521	0.646	0.259
O_{24}	0.272	0.593	0.944	O_{34}	0.328	0.609	0.935
O_{34}	0.035	0.674	0.231	O_{14}	0.035	0.683	0.221
O_{44}	0.264	0.424	0.224	O_{44}	0.237	0.423	0.205
O_{51}	0.800	0.064	0.935	O_{51}	0.911	0.063	0.932

The bismuth-oxygen distances less than 3.5 \AA found for both structures are given in Tables 3 and 6. If two distances $\text{Bi}-\text{O}$ are considered to be different only when their separation is larger than 5σ , the coordination of oxygen around bismuth might formally be described as $6 + n$ for monoclinic BiOHCrO_4 and as $5 + 1 + n$ for the orthorhombic form. The coordinated atoms are ordered after increasing $\text{Bi}-\text{O}$ distances in these groups. The difference in the coordination of the bismuth atoms in the two modifications are, however, small and the description as $6 + n$ will be used in the following discussions for both modifications.

For the above structures short $\text{Bi}-\text{O}$ distances occur both for chromate and non-chromate oxygen atoms and significant differences between these two types of distances are not found. Therefore, at the present stage the correct way of describing these structures seems to be that they are extended bismuth hydroxide chromate complexes, stacked in different ways in the two modifications.

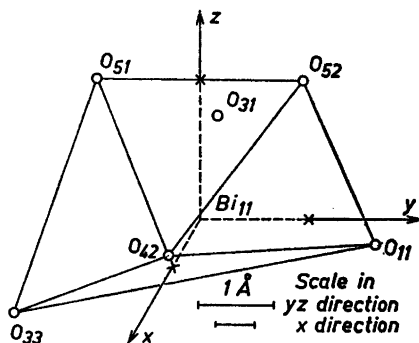


Fig. 8a The spatial arrangement of the oxygen atoms O_{11} , O_{31} , O_{33} , O_{42} , O_{51} , and O_{52} around the bismuth atom Bi_{11} in monoclinic BiOHCrO_4 . The oxygen atom O_{31} is a corner of the polyhedron situated on its backside. The bismuth atom Bi_{11} is taken as the origin of a Cartesian coordinate system. The axes are chosen so as to fulfill the following conditions: 1) The line $\text{O}_{51}-\text{O}_{52}$ lies in the yz plane with its midpoint on the positive z axis. 2) The y coordinate of O_{52} is positive. It might be remarked that the midpoint of the line $\text{O}_{51}-\text{O}_{52}$ coincides with the origin of the crystallographic coordinate system. The x , y and z axes are not parallel to the crystallographic axes. The resulting coordination polyhedron is shown perspectively and is regarded as a solid body. The points where the positive coordinate axes intersect visible faces of this body are notated by crosses.

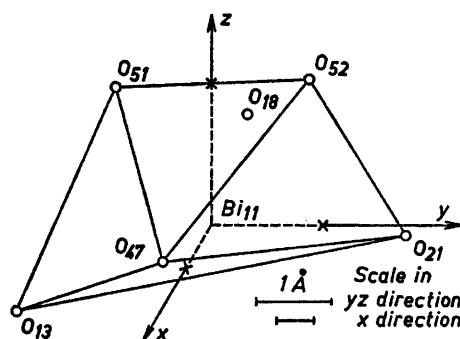


Fig. 8b The spatial arrangement of the oxygen atoms O_{13} , O_{18} , O_{21} , O_{47} , O_{51} , and O_{52} around the bismuth atom Bi_{11} in orthorhombic BiOHCrO_4 . The oxygen atom O_{18} is a corner of the polyhedron situated on its backside. The bismuth atom Bi_{11} is taken as the origin of a Cartesian coordinate system and the axes are chosen so as to fulfill the following conditions: 1) The line $\text{O}_{51}-\text{O}_{52}$ lies in the yz plane with its midpoint on the positive z axis. 2) The y coordinate of O_{52} is positive. As for the monoclinic modification the midpoint of the line $\text{O}_{51}-\text{O}_{52}$ coincides with the origin of the crystallographic coordinate system. The x , y and z axes are not parallel to the crystallographic axes. The resulting coordination polyhedron is shown perspectively and is regarded as a solid body. The points where the positive coordinate axes intersect visible faces of this body are notated by crosses.

The coordination of the bismuth atoms. The spatial arrangements of the six oxygen atoms lying close to the bismuth atoms are shown for the two structures in Figs. 8a and 8b. The Bi₁₁ atoms are taken as the origins of the coordinate systems used for these drawings. The directions of the z axes are chosen as to join these Bi atoms with the midpoints of the lines O₅₁—O₅₂ in each case (cf. Tables 3 and 6). These midpoints are in each case identical with the origins of the respective *crystallographic* coordinate systems. The axes chosen for Figs. 8a and 8b bear no simple relations to the *crystallographic axes*. In both cases the z axes are identical with the lines joining the bismuth atoms in the aggregates Bi₂(OH)₂⁴⁺ in the real structures. Considering now first the six oxygen atoms which lie close to the bismuth atoms and are shown in Figs. 8a and 8b, it is seen that they mainly lie in the direction of positive z values, thus the bismuth atoms are one-sidedly coordinated by these atoms. This is a very common situation for mixed bismuth oxides and for bismuth oxide salts. The symmetry of the arrangement is low and as seen from Figs. 8a and 8b the z axes of the coordinate systems given here are only approximate 2-fold axes. The deviation from diagonal symmetry around the z axes in Figs. 8a and 8b may be estimated on comparing Figs. 8a with 9b, for which the z axis is a true 2-fold axis and where six out of the eight oxygen atoms shown correspond to those marked in Fig. 8a, likewise to those marked in Fig. 8b but with other notations. The point symmetry of the sites of the bismuth

Table 8. Comparison between observed and calculated distances O—O and angles O—Bi—O for the six oxygen atoms surrounding Bi₁₁ at close distances in the structures of monoclinic and orthorhombic BiOHCrO₄.

The coordination polyhedra (cf. Figs. 8a, 8b) are compared both to a regular square antiprism oriented as in Fig. 9b and to a regular octahedron oriented as in Fig. 9a. The distances are given in Å.

Distance between the oxygen atoms		Observed distances O—O for the modifications		Calculated distances O—O for the case of square antiprism		Calculated distances O—O for the case of octahedron	
<i>mono-clinic</i>	<i>ortho-rhombic</i>	<i>mono-clinic</i>	<i>ortho-rhombic</i>	<i>mono-clinic</i>	<i>ortho-rhombic</i>	<i>mono-clinic</i>	<i>ortho-rhombic</i>
O ₃₃ —O ₅₁	O ₁₃ —O ₅₁	2.97 ± 0.04	2.82 ± 0.04	2.94	2.93	—	—
O ₃₁ —O ₃₃	O ₁₈ —O ₁₃	4.01 ± 0.02	3.88 ± 0.02	4.16	4.14	—	—
O ₁₁ —O ₃₃	O ₂₁ —O ₁₃	4.80 ± 0.05	4.85 ± 0.04	4.57	4.55	—	—
O ₃₃ —O ₄₂	O ₁₃ —O ₄₇	2.96 ± 0.05	2.85 ± 0.04	2.94	2.93	—	—
O ₅₁ —O ₄₂	O ₅₁ —O ₄₇	3.12 ± 0.05	2.87 ± 0.04	2.94	2.93	3.00	2.97
O ₄₂ —O ₅₂	O ₄₇ —O ₅₂	2.93 ± 0.05	3.01 ± 0.04	2.94	2.93	3.00	2.97
O ₁₁ —O ₄₂	O ₂₁ —O ₄₇	4.21 ± 0.05	4.33 ± 0.04	4.16	4.14	—	—
O ₁₁ —O ₅₂	O ₂₁ —O ₅₂	2.96 ± 0.05	3.00 ± 0.04	2.94	2.93	—	—
O ₁₁ —O ₅₁	O ₂₁ —O ₁₈	2.81 ± 0.05	2.94 ± 0.05	2.94	2.93	—	—
O ₃₁ —O ₅₂	O ₁₈ —O ₅₂	3.08 ± 0.04	3.09 ± 0.04	2.94	2.93	3.00	2.97
O ₃₁ —O ₅₁	O ₁₈ —O ₅₁	2.82 ± 0.04	2.91 ± 0.04	2.94	2.93	3.00	2.97
O ₅₁ —O ₅₂	O ₅₁ —O ₅₂	2.70 ± 0.07	2.56 ± 0.05	2.94	2.93	3.00	2.97
O ₃₁ —O ₄₂	O ₁₈ —O ₄₇	4.59 ± 0.05	4.59 ± 0.04	4.57	4.55	4.24	4.20

Table 8. Continued.

The angles O—Bi—O of the atoms		Obs. angles. Standard deviations < ± 1.9°		Calc. angles O—Bi—O for the case of	
mono- clinic	ortho- rhombic	mono- clinic	ortho- rhombic	square antiprism	octa- hedron
O ₁₁ —Bi—O ₃₁	O ₂₁ —Bi—O ₁₈	73.3	70.7	74.9	—
O ₁₁ —Bi—O ₃₃	O ₂₁ —Bi—O ₁₃	143.9	145.6	141.6	—
O ₁₁ —Bi—O ₄₂	O ₂₁ —Bi—O ₄₇	117.3	120.4	118.5	—
O ₁₁ —Bi—O ₅₁	O ₂₁ —Bi—O ₅₁	138.6	134.7	141.6	—
O ₁₁ —Bi—O ₅₂	O ₂₁ —Bi—O ₅₂	76.1	73.7	74.9	—
O ₃₁ —Bi—O ₃₃	O ₁₈ —Bi—O ₁₃	113.0	108.5	118.5	—
O ₃₁ —Bi—O ₄₂	O ₁₈ —Bi—O ₄₇	156.6	156.7	141.6	180.0
O ₃₁ —Bi—O ₅₁	O ₁₈ —Bi—O ₅₁	77.3	77.9	74.9	90.0
O ₃₁ —Bi—O ₅₂	O ₁₈ —Bi—O ₅₂	86.7	82.9	74.9	90.0
O ₃₃ —Bi—O ₄₂	O ₁₃ —Bi—O ₄₇	71.8	74.3	74.9	—
O ₃₃ —Bi—O ₅₁	O ₁₃ —Bi—O ₅₁	75.0	75.8	74.9	—
O ₃₃ —Bi—O ₅₂	O ₁₃ —Bi—O ₅₂	137.0	140.7	141.6	—
O ₄₂ —Bi—O ₅₁	O ₄₇ —Bi—O ₅₁	82.2	79.5	74.9	90.0
O ₄₂ —Bi—O ₅₂	O ₄₇ —Bi—O ₅₂	75.2	81.5	74.9	90.0
O ₅₁ —Bi—O ₅₂	O ₅₁ —Bi—O ₅₂	72.6	69.5	74.9	90.0

atoms is 1 in both structures. Orgel¹¹ has discussed the stereochemistry of a number of bismuth compounds with non-cubic environments of the bismuth atoms. He has suggested that the inert electron pair of the bismuth atom occupies a mixed sp_x orbital and has in this way accounted for the irregular coordination of the bismuth atoms in these compounds. Thus according to Orgel, in an ideal *octahedron*, deformations may occur along the 2-, 3-, or 4-fold axes. Starting from a *cube* or a *square antiprism* the deformations may occur along the 4-fold axes. For example, in the case of a deformation of an octahedron along one of its 4-fold axes, a five coordination results, the sixth oxygen atom, initially lying on the 4-fold axis being repelled by the inert electron pair.

Table 9. Distances Bi—O as obtained from the mean value of the edges of the polyhedra.

Modification	Calculated distance for the case of	
	square antiprism	octahedron
Monoclinic	2.42 Å	2.12 Å
Orthorhombic	2.41 Å	2.10 Å

Arguments of this kind will lead one to expect configurations around the bismuth atoms such that the nearest ligands form only part of complete coordination polyhedra. If only the nearest ligands are considered the central atoms will be one-sidedly coordinated.

It seemed of interest to investigate if the irregular Bi—O coordinations found in the two forms of BiOHCrO_4 could be interpreted as resulting from a deformation of regular coordination polyhedra.

From the fact that a few bismuth compounds are isostructural with the corresponding Ce^{3+} and La^{3+} compounds, the conclusion might be drawn that a relationship to a cube, a square antiprism or generally to a polyhedron involving a 7-, 8-, or 9-coordination would be probable for the coordination around bismuth in the compounds now discussed. In Tables 8 and 9 there is given a comparison between observed and calculated distances O—O and angles O—Bi—O for the six nearest oxygen atoms to bismuth in the two forms of BiOHCrO_4 using the following assumptions:

(1) The deformation of a regular *octahedron* is assumed to occur along the twofold axis, which can only explain the positions of four of the six oxygen atoms (cf. Figs. 8a, 9a).

(2) The deformation of a *regular square antiprism* is assumed to occur along one of its twofold axes (cf. Figs. 8a, 9b), explaining the positions of all six oxygen atoms belonging to the inner coordination sphere.

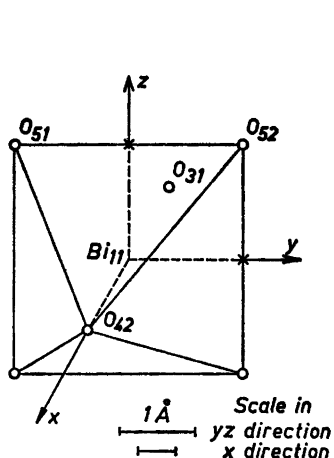


Fig. 9a. The relationship is shown between a regular octahedron and the positions of the oxygen atoms around bismuth in monoclinic BiOHCrO_4 . A regular *octahedron* is described by means of a coordinate system in which one of its fourfold axes coincides with the x axis and one of its twofold axes with the z axis. The atoms are numbered as for monoclinic BiOHCrO_4 (cf. Fig. 8a).

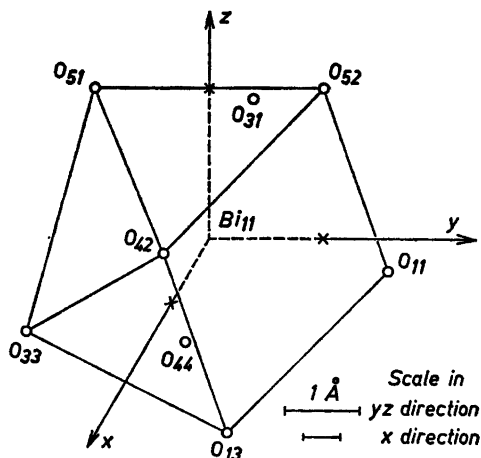


Fig. 9b. The relationship is shown between a regular square antiprism and the positions of the oxygen atoms around bismuth in monoclinic BiOHCrO_4 . A regular *square antiprism* is described by means of a coordinate system in which one of its twofold axes coincides with the z axis and one of the prism edges, perpendicular to the twofold axis, lies in the yz plane. The atoms are numbered as for monoclinic BiOHCrO_4 (cf. Figs. 8a and 10, *vide infra*).

In both cases the twofold axis is taken as the line joining the central bismuth atom and the midpoint of the line $\text{O}_{51}-\text{O}_{52}$. As pointed out before this axis is only approximately twofold.

The *square antiprism* gives a better agreement between observed and calculated data than does the octahedron (*cf.* Tables 8, 9). Other eight-coordinations were tested, but the deformations were less obvious and the agreement between observed and calculated distances and angles not so good as for the square antiprism.

A deformation along a fourfold axis in a regular octahedron was also tested. In this case the "fourfold" axis was assumed to pass along the line joining Bi_{11} and O_{51} or Bi_{11} and O_{52} (*cf.* Figs. 8*a*, 8*b*). Although this explains

Table 10. The lengths (in Å) of the edges of the deformed square antiprisms formed by one bismuth atom and eight oxygen atoms in the structures of monoclinic and orthorhombic BiOHCrO_4 . Estimated standard deviation of the distances are $\sim \pm 0.05$ Å. Figures in italics correspond to distances which are considerably longer than the expected values of 2.9 Å.

Prism edges

The oxygen atoms		Distances (in Å)	
<i>monoclinic</i>	<i>orthorhombic</i>	<i>monoclinic</i>	<i>orthorhombic</i>
$\text{O}_{51}-\text{O}_{52}$	$\text{O}_{51}-\text{O}_{52}$	2.70	2.56
$\text{O}_{52}-\text{O}_{31}$	$\text{O}_{52}-\text{O}_{18}$	3.08	3.09
$\text{O}_{31}-\text{O}_{11}$	$\text{O}_{18}-\text{O}_{21}$	2.81	2.94
$\text{O}_{11}-\text{O}_{44}$	$\text{O}_{21}-\text{O}_{44}$	2.79	3.05
$\text{O}_{44}-\text{O}_{13}$	$\text{O}_{44}-\text{O}_{26}$	3.75	3.56
$\text{O}_{13}-\text{O}_{33}$	$\text{O}_{26}-\text{O}_{13}$	2.81	2.94
$\text{O}_{33}-\text{O}_{42}$	$\text{O}_{13}-\text{O}_{47}$	2.96	2.85
$\text{O}_{42}-\text{O}_{51}$	$\text{O}_{47}-\text{O}_{51}$	3.12	2.87

Base edges

The oxygen atoms		Distances (in Å)	
<i>monoclinic</i>	<i>orthorhombic</i>	<i>monoclinic</i>	<i>orthorhombic</i>
$\text{O}_{51}-\text{O}_{31}$	$\text{O}_{51}-\text{O}_{18}$	2.82	2.91
$\text{O}_{31}-\text{O}_{44}$	$\text{O}_{18}-\text{O}_{44}$	2.96	2.85
$\text{O}_{44}-\text{O}_{33}$	$\text{O}_{44}-\text{O}_{13}$	3.83	3.63
$\text{O}_{33}-\text{O}_{51}$	$\text{O}_{13}-\text{O}_{51}$	2.97	2.82
$\text{O}_{52}-\text{O}_{11}$	$\text{O}_{52}-\text{O}_{21}$	2.96	3.00
$\text{O}_{11}-\text{O}_{13}$	$\text{O}_{21}-\text{O}_{26}$	4.13	4.18
$\text{O}_{13}-\text{O}_{42}$	$\text{O}_{26}-\text{O}_{47}$	2.79	3.05
$\text{O}_{42}-\text{O}_{52}$	$\text{O}_{47}-\text{O}_{52}$	2.93	3.01

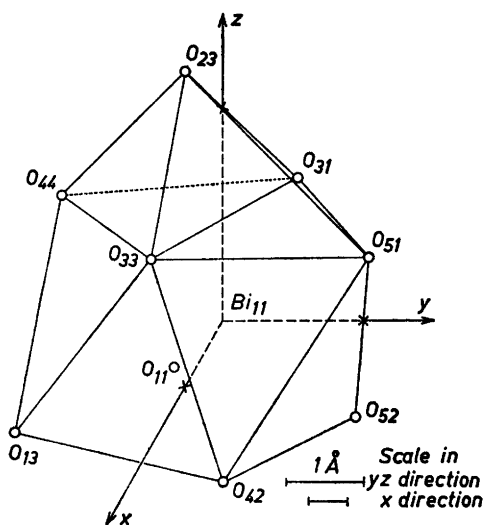


Fig. 10. The spatial arrangement of nine oxygen atoms around the bismuth atom Bi_{11} in monoclinic BiOHCrO_4 . The coordinate system used is chosen so that the midpoint of the line $\text{O}_{31}-\text{O}_{33}$, a full line in the drawing, is situated on the positive z axis and that the line $\text{O}_{51}-\text{O}_{52}$ has a common point with the positive y axis. Neglecting the ninth oxygen atom O_{23} the z axis then corresponds to the fourfold axis of a regular square antiprism and the y axis corresponds to a twofold axis. The x , y and z axes are not parallel to the crystallographic axes. The dotted line $\text{O}_{44}-\text{O}_{31}$ in the drawing indicates one base edge in a deformed square antiprism which would result if the oxygen atom O_{23} is neglected. The oxygen atom O_{11} is a corner of the polyhedron situated on its backside. The points where the positive coordinate axes intersect visible faces of the coordination polyhedron are notated by crosses.

the positions of 5 of the 6 oxygen atoms the agreement between observed and calculated data is less convincing than that obtained for the cases already treated.

Thus according to the model discussed here the coordination polyhedron of bismuth in both modifications of BiOHCrO_4 results from a deformation of a *square antiprism* along one of its twofold axes. This would explain why only six oxygen atoms lie close to one bismuth atom. In the actual structures two more distant oxygen atoms occur, *viz.* the atoms O_{13} and O_{44} in the monoclinic form and O_{26} and O_{44} in the orthorhombic one (*cf.* Tables 3, 6 and 10). These two pairs of oxygen atoms complete a rather deformed square antiprism in the two respective structures and the lines joining them will then form prism edges approximately perpendicular to the "twofold" axis.

If these deformations of a regular square antiprism are ascribed to the presence of the inert electron pair it might be supposed to be directed along the "twofold" axis mentioned.

The complete coordination polyhedra around bismuth also include a ninth oxygen atom violating the "twofold" axis. This atom is situated outside one of the base faces (Fig. 10). In this respect the coordinations of bismuth in the two chromates are similar to those found for lead in PbFCl and bismuth in BiOCl and related compounds.

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