

## The Crystal Structure of Bismuth(III) Formate

CLAES-IVAR STÅLHANDSKE

*Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology,  
Box 740, S-220 07 Lund 7, Sweden*

The crystal structure of bismuth(III) formate has been determined from X-ray single-crystal data. The crystals are trigonal with three formula units  $\text{Bi}(\text{OOCH})_3$  in a unit cell with the dimensions  $a = 4.1193$  and  $c = 10.5663$  Å.

The bismuth atoms are surrounded by nine oxygen atoms in the form of a trigonal prism with three extra oxygen atoms outside each prism face. The Bi—O distances fall into three ranges, and considering only the shorter ones the polyhedra may be described as deformed octahedra of a type very similar to that previously found in eulytite,  $\text{Bi}_4\text{Si}_3\text{O}_{12}$ .

The crystal structures of a number of mixed oxide halides, mixed oxides, and basic salts of bismuth have previously been reported, but relatively few neutral bismuth salts have hitherto been investigated by means of X-ray methods. As a first object of such a study bismuth(III) formate was chosen.

### EXPERIMENTAL

Bismuth formate was prepared by adding bismuth(III) oxide to a 40 % formic acid solution. The reaction mixture was refluxed for half an hour, filtered, and slowly cooled to room temperature. The pencil-shaped crystals thus obtained are colourless, and their cross-sections are hexagons. They are unstable in air and furthermore they decompose and become black when irradiated with X-rays. Thus a new single crystal had to be picked out for each recorded layer line.

Intensity data were collected for the reflections  $hk0-hk4$  (512 independent reflections) with an integrating Weissenberg camera using Zr-filtered  $\text{MoK}\alpha$  radiation. The multi-film technique was used with thin (0.05 mm) steel foils between the films. The relative intensities of the reflections, with an intensity range from 1 to 4000, were measured by means of a microdensitometer. The collected intensities were corrected for Lorentz and polarization effects in the usual way. As the linear absorption coefficient<sup>1</sup> was calculated to be  $326 \text{ cm}^{-1}$ , an absorption correction was performed with the program DATACORR.<sup>2</sup> The crystals were approximated to cylinders with cross sectional diameters varying from 0.06 to 0.09 mm. The lengths of the crystals were from 0.3 to 0.4 mm. No correction was made for extinction effects.

The density of the bismuth formate crystals,  $4.36 \text{ g}\cdot\text{cm}^{-3}$ , was determined from their loss of weight in benzene. The calculated density is  $4.30 \text{ g}\cdot\text{cm}^{-3}$ , assuming a cell content of three formula units  $\text{Bi}(\text{OOCH})_3$ .

The results of the analyses were in good agreement with the values calculated for  $\text{Bi}(\text{OOCH})_3$ . (Found: Bi 60.35; C 10.95; H 0.78. Calc.: Bi 60.74; C 10.47; H 0.88).

#### DETERMINATION OF THE CRYSTAL STRUCTURE

*Unit cell.* The powder pattern could be interpreted by means of a hexagonal unit cell with the following dimensions and standard deviations:

$$a = 10.5663 \pm 0.0004 \text{ \AA}, c = 4.1193 \pm 0.0002 \text{ \AA}, V = 328.29 \pm 0.03 \text{ \AA}^3.$$

The powder photographs were taken in a Guinier focusing camera at  $25^\circ\text{C}$  with  $\text{CuK}\alpha_1$  radiation and potassium chloride as an internal standard. Refinement of the cell parameters was performed using the least-squares program PIRUM written by P. E. Werner.<sup>3</sup>

*Space group.* No systematically absent reflections  $hki0$  were found in the Weissenberg photographs. For the  $hki0$  reflections, however, those with  $h-k \neq 3n$  were occasionally absent. A study of the intensities of the general reflections  $hki0$  revealed that  $I_{hki0} = I_{\bar{h}\bar{k}i0}$  and  $I_{hki0} = I_{\bar{h}\bar{k}i0}$ . If the symmetry of the light atoms is the same as that of the dominant bismuth atoms (*vide infra*), the Laue symmetry is  $\bar{3}m$  and at first the space groups  $P\bar{3}m$  (No. 164) and  $P3m$  (No. 156) had to be considered. From a two-dimensional Patterson projection  $P(uvp)$  the following bismuth atom positions were found:

$$\text{Bi}_1 \text{ in } 0, 0; \text{Bi}_2 \text{ in } 2/3, 1/3; \text{Bi}_3 \text{ in } 1/3, 2/3.$$

This is compatible with both  $P3m$  and  $P\bar{3}m$ . An inspection of the reflections  $hki0$  showed that it was impossible to find correct positions for the bismuth atoms in space group  $P\bar{3}m$  whereas a solution could be obtained assuming either  $P3m$  or  $P3$  (Laue symmetry 3) with the bismuth atoms in the positions  $0, 0, z_1$ ;  $2/3, 1/3, z_2$  and  $1/3, 2/3, z_3$ . It may also be noted that with space group  $P\bar{3}m$  some of the carbon atoms would have to occupy a centre of symmetry, which is incompatible with the known geometry of the formate group. The choice between  $P3$  and  $P3m$  was made on the basis of the intensities of the general reflections  $hki0$  (see above), but as the influence of the scattering of the light atoms on the intensities is small, a slight deviation from Laue symmetry  $\bar{3}m$  used here cannot be excluded.

*The bismuth atoms.* Three-dimensional Patterson functions (program DRF<sup>2</sup>) were now computed at different heights of the  $c$ -axis in order to find the  $z$ -values for the bismuth atoms. Approximate scale factors between the different layer lines were at first calculated from the exposure times of the photographs.

The largest maxima in the sections, which undoubtedly could be ascribed to the bismuth-bismuth vectors, revealed the positional parameters 0.35 and 0.55 for  $z_2$  and  $z_3$ , respectively, when  $z_1$  was arbitrarily chosen as zero. A least-squares refinement of the parameters of the bismuth atoms and of the inter-layer scale factors was then performed using the full-matrix program LALS.<sup>2</sup> The calculations were based on the entire intensity material and gave a resulting discrepancy factor  $R = \sum |F_o| - |F_c| / \sum |F_o|$  of 0.08.

*The light atoms.* In order to find the carbon and oxygen atomic positions, three-dimensional electron density difference syntheses  $\rho'(xyz)$  were computed at different  $z$ -values, with the contributions of the bismuth atoms subtracted. Most maxima found in the maps could be explained by using a structure model for the formate groups including reasonable interatomic distances and angles. Some peaks of nearly the same height as that calculated for a carbon atom remained, however. For geometrical reasons they could not possibly indicate atoms of formate groups. They are assumed to be due to errors inherent in the intensity material and to the fact that contributions from scattering of the light atoms were not included when the scale factors were calculated.

*Refinement of the structure.* The positional parameters for all atoms, the isotropic temperature factors, and the inter-layer scale factors were now refined in a least-squares calculation. When the parameter shifts (37 variables) were well below 5 % of their standard deviations, the refinement was considered to be complete and the  $R$  value was at this point 0.053.

Since positions could be assigned to all non-hydrogen atoms, the distances found are normal, and none of the atoms has an unusually high temperature factor, it seems possible that the space group found is the correct one.

*Table Ia.* Final parameters and standard deviations (within brackets) obtained from the refinement with anisotropic temperature factors for the bismuth atoms.

The space group involves the condition  $y = -x$  for all independent atoms in this structure. The temperature factor expression used for the bismuth atom is

$$\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl),$$

where  $\beta_{11} = \beta_{22} = \beta_{12}$  and  $\beta_{13} = \beta_{23} = 0$ .

	$x$	$z$	$B$	$\beta_{11}$	$\beta_{33}$
Bi(1)	0	0		0.0024 (1)	0.0105 (24)
Bi(2)	2/3	0.3544 (6)		0.0025 (1)	0.0098 (24)
Bi(3)	1/3	0.5472 (9)		0.0035 (2)	0.0231 (13)
C(1)	0.155 (2)	0.374 (10)	1.7 (5)		
C(2)	0.822 (2)	0.754 (8)	1.3 (4)		
C(3)	0.486 (2)	0.103 (9)	1.4 (4)		
O(1)	0.198 (2)	0.620 (8)	2.2 (4)		
O(2)	0.864 (2)	0.974 (7)	1.9 (4)		
O(3)	0.527 (2)	0.340 (7)	1.9 (4)		
O(4)	0.085 (1)	0.444 (7)	1.5 (3)		
O(5)	0.751 (1)	0.800 (7)	1.5 (3)		
O(6)	0.417 (1)	0.115 (6)	1.2 (3)		

*Table Ib.* Root-mean-square components,  $R_i$  (Å), of thermal displacement along principal axes of the ellipsoids of vibration, calculated for the bismuth atoms from the  $\beta_{ij}$  values given in Table Ia.

Atom	$R_1$	$R_2$	$R_3$
Bi(1)	0.101	0.101	0.095
Bi(2)	0.104	0.104	0.092
Bi(3)	0.122	0.122	0.141

Table 2. Observed and calculated structure factors.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
3	0	0	160.4	161.9	0	5	1	156.2	163.9	2	2	2	95.4	96.6	5	11	2	32.3	31.9
6	0	0	171.7	172.4	1	5	1	59.3	46.6	3	2	2	75.7	66.5	0	12	2	48.2	40.3
9	0	0	101.9	107.7	2	5	1	34.2	34.7	4	2	2	120.6	120.5	1	12	2	29.5	29.8
12	0	0	89.5	93.4	3	5	1	109.1	109.4	5	2	2	69.7	74.1	2	12	2	51.3	49.9
15	0	0	58.0	57.9	4	5	1	40.6	39.2	6	2	2	53.4	55.4	3	12	2	39.7	33.8
4	1	0	173.0	168.2	5	5	1	30.6	29.4	7	2	2	66.4	69.2	0	13	2	63.1	58.9
7	1	0	138.3	142.5	6	5	1	115.3	109.1	8	2	2	56.6	54.5	1	13	2	37.2	34.7
10	1	0	105.6	106.4	7	5	1	30.3	28.1	9	2	2	34.1	39.7	2	13	2	28.4	22.9
13	1	0	72.2	74.1	8	5	1	21.1	22.0	10	2	2	66.8	73.6	3	13	2	48.3	40.9
16	1	0	43.8	46.3	9	5	1	81.0	75.3	11	2	2	38.4	42.3	0	14	2	30.3	25.3
2	2	0	246.3	251.9	12	5	1	62.1	56.8	12	2	2	26.4	27.2	1	14	2	46.1	42.0
5	2	0	153.0	159.4	0	6	1	39.6	41.6	13	2	2	29.4	38.2	0	15	2	31.1	29.8
8	2	0	113.3	114.7	1	6	1	135.8	141.1	0	3	2	108.8	90.8					
11	2	0	85.4	85.4	2	6	1	37.7	36.7	1	3	2	79.0	72.6	2	0	3	83.6	82.2
14	2	0	56.2	55.2	3	6	1	28.6	32.3	2	3	2	139.5	137.2	3	0	3	76.2	61.7
3	3	0	194.3	200.4	4	6	1	122.2	120.5	3	3	2	86.1	85.4	4	0	3	104.3	94.6
6	3	0	133.6	134.8	5	6	1	32.1	33.2	4	3	2	59.1	56.2	5	0	3	63.5	60.9
9	3	0	103.4	102.5	6	6	1	28.7	23.9	5	3	2	101.6	104.9	6	0	3	70.7	66.6
12	3	0	62.1	65.2	7	6	1	79.5	79.7	6	3	2	63.8	65.3	7	0	3	94.9	85.0
4	4	0	185.2	184.7	10	6	1	61.1	59.9	7	3	2	41.0	43.7	8	0	3	51.1	50.1
7	4	0	106.3	100.7	13	6	1	45.7	39.5	8	3	2	73.6	73.4	9	0	3	61.1	46.8
10	4	0	75.6	77.8	0	7	1	44.0	43.7	9	3	2	46.4	48.3	10	0	3	52.8	59.1
13	4	0	43.4	45.9	1	7	1	37.6	34.3	10	3	2	29.3	34.3	11	0	3	34.3	35.0
5	5	0	143.9	144.9	2	7	1	122.0	120.1	11	3	2	47.3	51.4	12	0	3	70.7	65.7
8	5	0	84.9	84.2	3	7	1	35.0	34.0	12	3	2	30.9	32.9	13	0	3	47.2	45.0
11	5	0	65.9	66.9	4	7	1	20.6	24.5	0	4	2	103.5	95.4	1	1	3	59.8	62.3
6	6	0	96.8	100.2	5	7	1	97.0	95.9	1	4	2	90.8	84.8	2	1	3	105.0	103.6
9	6	0	76.8	74.7	6	7	1	31.7	26.2	5	5	2	68.9	66.2	3	1	3	72.3	71.8
12	6	0	54.6	51.4	8	7	1	71.3	67.7	5	4	2	107.7	104.8	4	1	3	47.1	45.2
10	7	0	60.6	59.1	11	7	1	55.3	50.4	4	4	2	69.6	68.6	5	1	3	91.3	87.0
7	7	0	96.8	95.9	0	8	1	136.1	144.3	5	4	2	51.6	52.4	6	1	3	59.9	57.5
8	8	0	79.6	76.1	1	8	1	37.8	35.9	6	4	2	92.5	90.6	7	1	3	76.2	68.9
11	8	0	49.9	44.9	2	8	1	29.2	29.1	7	4	2	52.5	53.9	8	1	3	72.8	69.3
9	9	0	60.6	59.1	3	8	1	98.7	100.4	8	5	2	35.5	36.5	9	1	3	83.1	82.7
10	10	0	40.3	42.9	4	8	1	26.9	27.2	4	4	2	50.1	53.5	10	1	3	42.8	41.2
					6	8	1	79.5	77.6	10	4	2	37.1	38.6	11	1	3	52.7	50.6
3	0	1	57.9	54.2	9	8	1	46.2	47.3	11	4	2	32.3	26.8	12	1	3	32.6	30.7
4	0	1	189.1	193.8	0	9	1	30.5	27.3	12	4	2	36.8	42.3	0	2	3	95.2	102.7
5	0	1	48.5	46.1	1	9	1	91.5	98.6	0	5	2	73.4	66.4	1	2	3	66.1	68.1
6	0	1	42.5	40.8	2	9	1	28.2	30.9	1	5	2	101.2	92.5	2	2	3	86.0	84.1
7	0	1	149.7	154.0	3	9	1	25.2	22.9	2	5	2	79.8	75.7	3	2	3	102.7	103.4
8	0	1	39.2	37.5	4	9	1	90.0	87.7	3	5	2	54.2	53.6	4	2	3	65.4	66.8
9	0	1	27.4	27.8	5	9	1	26.8	22.2	4	5	2	112.9	112.1	5	2	3	49.4	43.6
10	0	1	94.9	94.9	6	9	1	57.0	58.1	5	5	2	61.4	62.2	6	2	3	81.5	78.0
11	0	1	27.4	27.2	7	9	1	46.5	46.8	6	5	2	38.6	40.5	7	2	3	47.1	45.2
12	0	1	16.7	16.9	8	10	1	25.2	28.0	7	5	2	63.0	63.5	8	2	3	48.1	48.6
13	0	1	51.9	57.6	9	10	1	24.9	24.3	8	5	2	43.3	44.9	9	2	3	63.3	62.8
14	0	1	18.3	19.5	2	10	1	87.9	93.0	9	5	2	33.1	29.6	10	2	3	37.6	37.4
15	0	1	54.2	49.8	3	10	1	24.0	25.4	10	5	2	42.3	45.7	11	2	3	31.3	31.7
3	1	0	66.2	56.8	4	10	1	64.3	63.1	0	6	2	81.6	74.4	12	2	3	46.3	42.4
4	1	0	48.6	43.5	5	10	1	51.3	48.6	1	6	2	61.5	57.0	0	3	3	88.7	86.2
5	1	0	146.2	147.2	6	11	1	75.5	77.7	2	6	2	111.7	97.3	1	3	3	101.8	104.0
6	1	0	44.4	44.2	7	11	1	24.9	25.0	3	6	2	68.4	63.4	2	3	3	65.3	66.4
7	1	0	33.9	32.2	8	11	1	76.3	71.4	4	6	2	49.2	47.3	3	3	3	66.9	63.4
8	1	0	121.2	122.4	9	11	1	80.7	56.1	5	6	2	64.0	67.2	4	3	3	85.1	82.7
9	1	0	29.0	30.7	0	12	1	22.9	20.0	6	6	2	49.7	45.2	5	3	3	56.7	56.2
10	1	0	20.3	23.9	1	12	1	59.9	63.9	7	6	2	31.5	34.6	6	3	3	55.7	51.5
11	1	0	75.0	76.5	4	12	1	63.4	61.3	8	6	2	60.4	61.2	7	3	3	65.5	65.7
12	1	0	24.6	22.6	7	12	1	42.4	42.8	9	6	2	40.0	37.5	8	3	3	41.2	42.8
14	1	0	64.6	61.0	2	13	1	80.7	60.4	0	7	2	128.1	111.9	9	3	3	47.4	43.7
17	1	0	38.7	39.3	5	13	1	54.2	49.2	1	7	2	74.6	68.5	10	3	3	53.8	50.6
2	2	1	57.2	53.2	0	14	1	55.4	63.3	2	7	2	53.0	46.5	11	3	3	32.1	30.4
3	2	1	180.1	191.5	3	14	1	49.2	47.4	3	7	2	72.7	71.3	0	4	3	71.0	70.0
4	2	1	48.3	44.3	1	15	1	55.2	53.3	4	7	2	53.2	54.2	1	4	3	75.0	71.8
5	2	1	41.2	39.6	2	16	1	33.9	36.9	5	7	2	40.2	36.0	2	4	3	86.7	90.3
6	2	1	156.6	151.3	0	17	1	37.0	41.9	6	7	2	75.2	71.1	3	4	3	58.5	55.4
7	2	1	38.1	37.1						7	7	2	39.7	42.0	4	4	3	43.7	46.8
8	2	1	24.2	27.1	2	0	2	128.2	134.3	8	7	2	29.2	27.0	5	4	3	77.6	78.9
9	2	1	92.7	93.4	3	0	2	92.8	94.4	9	7	2	47.7	50.6	6	4	3	44.4	47.9
10	2	1	32.1	26.9	4	0	2	64.8	67.4	0	8	2	54.6	43.6	7	4	3	41.9	38.5
12	2	1	86.0	67.2	5	0	2	96.5	91.8	1	8	2	84.0	75.2	8	4	3	58.2	56.5
15	2	1	44.0	42.4	6	0	2	66.6	72.5	2	8	2	59.0	54.0	9	4	3	31.9	34.3
0	3	1	46.8	44.4	7	0	2	51.0	57.1	3	8	2	46.5	42.1	10	4	3	36.1	36.7
1	3	1	179.6	200.9	8	0	2	75.7	87.2	4	8	2	62.2	58.6	0	5	3	91.3	91.0
2	3	1	56.9	56.7	9	0	2	47.9	57.8	5	8	2	46.3	44.6	1	5	3	54.9	60.2
3	3	1	44.3	41.6	10	0	2	37.1	40.8	6	8	2	35.1	31.4	2	5	3	57.9	57.5
4	3	1	123.2	119.9	11	0	2	50.1	62.1	7	8	2	54.5	56.1	3	5	3	76.1	78.0
5	3	1	42.8	40.5	12	0	2	37.5	41.3	8	8	2	27.1	33.7	4	5	3	49.0	51.2
6	3	1	28.6	30.6	13	0	2	27.3	28.2	0	9	2	66.0	59.2	5	5	3	54.2	53.7
7	3	1	109.1	107.9	14	0	2	38.6	51.5	1	9	2	44.8	41.1	6	5	3	6	

Table 2. Continued.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
5	7	3	56.5	57.4	4	0	4	64.6	60.0	0	3	4	51.6	54.7	3	6	4	37.2	36.8
6	7	3	37.2	35.2	5	0	4	83.6	82.3	1	3	4	37.9	38.3	4	6	4	31.8	32.5
7	7	3	35.5	37.1	6	0	4	50.1	46.4	2	3	4	86.3	87.3	5	6	4	62.5	60.7
0	8	3	69.1	75.3	7	0	4	35.1	33.1	3	3	4	50.2	47.9	6	6	4	31.3	31.7
1	8	3	45.7	48.3	8	0	4	71.7	68.8	4	3	4	37.6	41.5	8	6	4	50.6	46.5
2	8	3	42.7	45.0	9	0	4	41.0	36.2	5	3	4	70.3	72.5	0	7	4	73.8	73.9
3	8	3	62.4	64.2	10	0	4	29.2	25.4	6	3	4	42.2	40.0	1	7	4	36.0	39.1
4	8	3	35.1	37.1	11	0	4	57.1	53.5	7	3	4	39.1	39.6	2	7	4	38.8	38.4
5	8	3	46.5	39.5	12	0	4	32.6	26.2	8	3	4	59.8	55.1	3	7	4	62.0	61.2
6	8	3	48.9	48.1	1	1	4	48.3	55.6	9	3	4	31.2	29.6	4	7	4	31.3	35.3
0	9	3	47.1	50.3	2	1	4	40.6	47.7	11	3	4	45.2	41.0	5	7	4	26.4	28.1
1	9	3	58.0	63.6	3	1	4	67.4	89.7	0	4	4	84.8	85.1	6	7	4	46.0	47.6
2	9	3	38.3	40.5	4	1	4	47.5	47.5	1	4	4	49.4	51.9	0	8	4	42.9	46.4
3	9	3	47.6	48.5	5	1	4	48.6	46.1	2	4	4	41.6	40.8	1	8	4	64.5	65.4
4	9	3	49.8	50.5	6	1	4	77.5	73.6	3	4	4	76.5	78.5	2	8	4	39.3	36.4
5	9	3	33.0	32.4	7	1	4	43.9	42.4	4	4	4	47.1	44.1	3	8	4	29.1	25.9
0	10	3	37.5	41.1	8	1	4	31.5	32.5	5	4	4	35.4	36.3	4	8	4	52.2	52.9
1	10	3	35.3	38.2	9	1	4	58.4	57.0	6	4	4	64.3	65.2	0	9	4	31.7	34.6
2	10	3	57.1	55.6	10	1	4	34.4	31.7	7	4	4	36.5	31.7	1	9	4	36.1	33.8
3	10	3	34.0	32.7	11	1	4	39.2	30.3	8	4	4	36.1	34.3	2	9	4	53.3	54.0
4	10	3	37.4	33.7	12	1	4	47.3	42.0	9	4	4	52.1	50.4	3	9	4	29.3	31.1
0	11	3	47.6	51.9	0	2	4	48.4	49.0	0	5	4	32.5	36.8	5	9	4	40.4	44.0
1	11	3	31.2	35.1	1	2	4	87.4	90.4	1	5	4	79.3	79.5	0	10	4	52.6	56.3
2	11	3	35.5	39.3	2	2	4	54.4	56.6	2	5	4	41.6	44.5	1	10	4	30.2	30.1
3	11	3	42.6	44.8	3	2	4	47.8	50.8	3	5	4	36.5	41.5	2	10	4	26.5	29.0
0	12	3	26.6	27.5	4	2	4	81.7	83.1	4	5	4	69.0	66.1	3	10	4	51.7	49.2
1	12	3	43.0	46.4	5	2	4	45.6	44.9	5	5	4	39.6	37.3	0	11	4	29.7	33.2
2	12	3	30.9	27.9	6	2	4	30.3	32.9	6	5	4	36.6	37.6	1	11	4	53.3	49.3
0	13	3	31.6	29.2	7	2	4	70.5	67.3	7	5	4	53.2	52.8	0	12	4	20.3	26.9
					8	2	4	37.6	35.5	0	6	4	50.6	47.8	2	12	4	34.5	41.3
					9	2	4	26.1	31.9	1	6	4	44.1	43.3	0	13	4	38.8	39.6
					10	2	4	57.6	52.6	2	6	4	71.9	71.6	0	14	4	30.6	21.7

Anisotropic temperature factors were now introduced for the bismuth atoms. The parameters of all atoms, thus including anisotropic temperature factors for the bismuth atoms and isotropic ones for the light atoms, were refined together with an overall scale factor, the total number of variables being 36. The overall scale factor was obtained by fixing the inter-layer scale factors to the values found in the last cycle of the preceding refinement. The resulting *R* factor was 0.052.

By comparing the results of the two refinements it was found that the largest movements of the bismuth atoms were less than 0.003 Å and of the light ones less than 0.01 Å, and furthermore the standard deviations of all parameters were somewhat smaller in the last refinement. The final atomic parameters with standard deviations are given in Table 1a and in Table 1b the root-mean-square components of thermal vibration along the principal axes of the ellipsoids of the bismuth atoms. As  $R_1=R_2$  (Table 1b) the *xy* sections of the ellipsoids are circular. The component  $R_3$  ( $\neq R_1, R_2$ ) coincides with the crystallographic *z*-axis. The r.m.s. components were calculated with the program OR FFE.<sup>2</sup> The observed and calculated structure factors are presented in Table 2.

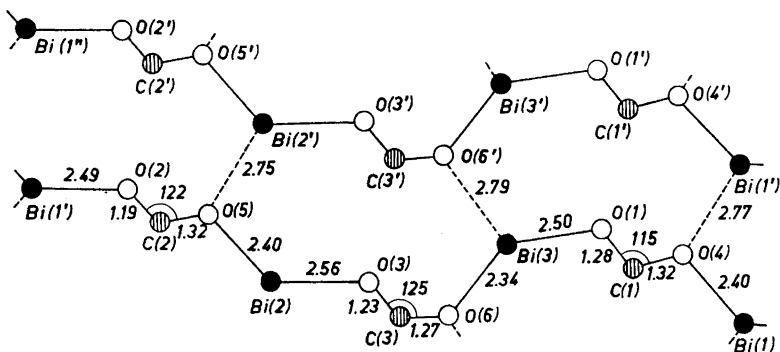
The least-squares refinement performed was based on *F* values, minimizing the function  $\sum w \cdot (|F_o| - |F_c|)^2$  with the weighting factor  $w = 1/(a + |F_o| + c|F_o|^2)$ . The values 45 and 0.008 for *a* and *c*, respectively, were found suitable for the final refinement. Only the observed reflections were included in all calculations. The atomic scattering factors used for neutral bismuth were those given by Cromer and Waber.<sup>4</sup> They were not corrected for anomalous dispersion, because the material includes most certainly both  $hkl$  and  $\bar{h}\bar{k}l$  reflections alternatively, as different crystals had to be used (see above) when collecting the intensity material. For neutral oxygen and carbon atoms the atomic scattering factors given by Hanson *et al.*<sup>5</sup> were used.

After the last least-squares refinement was performed, electron density sections were computed with the contributions of all atoms subtracted. In these sections there were residual peaks smaller than those found in  $\rho'(xyz)$ . They were located very close to the threefold axes and could therefore not possibly be caused by atoms not found in the refinement of the structure.

*Computer programs.* Most calculations were performed on the computer CD 3600 in Uppsala, using programs briefly described by Liminga.<sup>2</sup>

### DESCRIPTION OF THE STRUCTURE

*The bismuth atoms.* In bismuth formate the three non-equivalent bismuth atoms, each on a three-fold axis, are surrounded by oxygen atoms in nearly the same way. All oxygen atoms of the structure are connected to metal atoms (Fig. 1). Every bismuth atom has three different distances to the



*Fig. 1.* A section of the structure of  $\text{Bi}(\text{OOCH})_3$  along the diagonal  $[110]$  showing all independent atoms in the unit cell with some bond distances and angles. The two chains drawn with full lines correspond to endless sheets in the three-dimensional structure. These are held together by Bi—O bonds (range III), marked by dashed lines in the drawing.

oxygen atoms (Table 3). These distances fall within three distinct ranges: I. 2.34–2.40 Å, II. 2.49–2.56 Å, and III. 2.75–2.79 Å, the standard deviations being  $\pm 0.02$  Å in all cases.

*Table 3.* Distances (Å) and angles ( $^\circ$ ) with estimated standard deviations in bismuth(III) formate.

Around the bismuth atoms					
Bi(1)—O(4)	2.40 (2)	Bi(1)—O(2')	2.49 (2)	Bi(1)—O(4')	2.77 (2)
Bi(2)—O(5)	2.40 (2)	Bi(2)—O(3)	2.56 (2)	Bi(2)—O(5')	2.75 (2)
Bi(3)—O(6)	2.34 (2)	Bi(3)—O(1)	2.50 (2)	Bi(3)—O(6')	2.79 (2)
Mean value	2.38	Mean value	2.52	Mean value	2.77

## Distances and angles within the formate groups

Distances			
C(1)—O(1)	1.28 (5)	C(1)—O(4)	1.32 (3)
C(2)—O(2)	1.19 (4)	C(2)—O(5)	1.32 (2)
C(3)—O(3)	<u>1.23 (4)</u>	C(3)—O(6)	<u>1.27 (2)</u>
Mean value	1.23	Mean value	1.30

Angles	
O(1)—C(1)—O(4)	115 (3)
O(2)—C(2)—O(5)	122 (3)
O(3)—C(3)—O(6)	<u>125 (3)</u>
Mean value	121

If only ranges I and II are considered, the metal atom is six-coordinated and the polyhedron may be described as a distorted octahedron. Two triangular faces of one octahedron are perpendicular to the three-fold axis and the bismuth atom is situated close to the larger of the triangles. Each oxygen of the octahedron is bonded *via* a carbon atom of a formate group to an oxygen atom of another octahedron (Fig. 2). Thus the structure may be regarded as being built up of endless sheets of formula  $[\text{Bi}(\text{OOCH})_3]_n$  being held together solely by bonds belonging to range III.

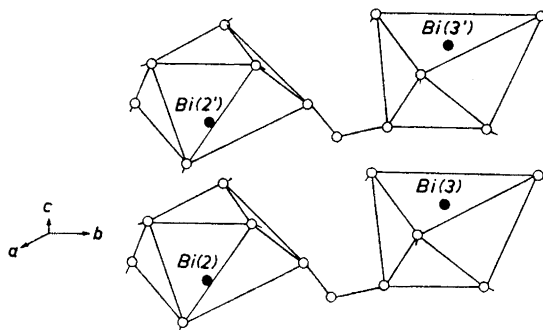


Fig. 2. Perspective view of the arrangement of Bi—O octahedra in separate layers. The separate octahedra are connected *via* carbon atoms of the formate groups.

If Bi—O distances belonging to all three ranges are considered as bonding distances, the central metal atom may be described as nine-coordinated and the polyhedron as a trigonal prism with one atom outside each prism face. The polyhedra are linked together in the *z*-direction by sharing the base triangular faces, thus forming endless strings (Fig. 3). Furthermore, all oxygen atoms in the polyhedra are in the endless strings connected *via* carbon atoms of formate groups building up a three-dimensional network.

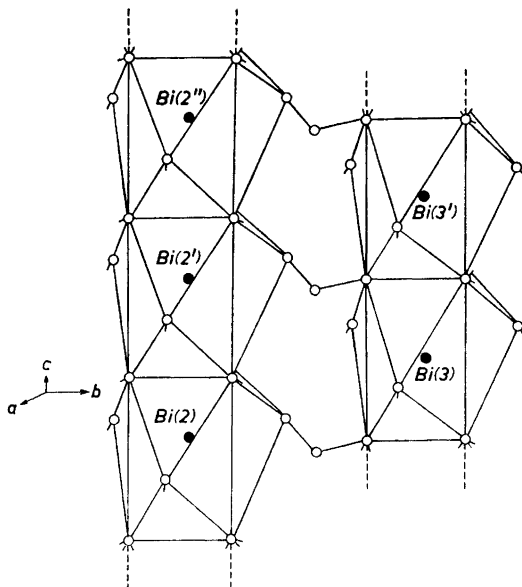


Fig. 3. Perspective view of endless strings of linked Bi-9 O polyhedra connected by carbon atoms of the formate groups.

*The formate groups.* There are three independent formate groups in the structure. Selected distances and angles within them are given in Fig. 1 and Table 3. Mean values of the dimensions of the formate groups are as follows:

$$\text{C}-\text{O}' = 1.23 \text{ \AA}, \text{C}-\text{O}'' = 1.30 \text{ \AA}, \angle \text{O}'-\text{C}-\text{O}'' = 121^\circ$$

(notations;  $\text{O}' = \text{O}(1), \text{O}(2), \text{and } \text{O}(3)$ ;  $\text{O}'' = \text{O}(4), \text{O}(5), \text{and } \text{O}(6)$ , cf. Table 3). It may be noted that the atoms  $\text{O}'$  and  $\text{O}''$  are crystallographically non-equivalent. The atom  $\text{O}'$  is in contact with one bismuth atom (range II), while  $\text{O}''$  has two neighbouring bismuth atoms (range I and III). The geometry of the formate group found in this work is in good agreement with information for similar structures reported in the literature.<sup>6-8</sup>

## DISCUSSION

Bismuth atoms are often coordinated by ligands in a very irregular way. It is very unusual with bismuth atoms on three-fold axes, which is the case in the present structure and also in eulytite,  $\text{Bi}_4\text{Si}_3\text{O}_{12}$ . A redetermination of the last structure, using neutron diffraction powder data has recently been performed by Segal *et al.*<sup>9</sup> Each bismuth atom in eulytite is coordinated by three oxygen atoms at 2.15 Å and three more oxygens at 2.62 Å, forming a distorted octahedron. This deformation is almost the same as that found



in the present structure, if the bismuth atoms are considered to be six-coordinated. The differences between the two short Bi—O bonds (2.38 and 2.52 Å) are less pronounced in bismuth formate than in eulytite, however. Such deformations of coordination octahedra on three-fold axes can according to Orgel<sup>10</sup> be explained by the influence of the pair of unshared electrons in the bismuth ions.

The bismuth atoms in bismuth formate may, as mentioned earlier, also be described as nine-coordinated, giving a rather regular polyhedron. Such coordination is fairly common among bismuth and rare earth compounds, for example YF<sub>3</sub>.<sup>11</sup> A similar coordination polyhedron has previously been reported to exist in monoclinic NH<sub>4</sub>BiF<sub>4</sub>.<sup>12</sup> In this structure the bismuth atoms, having the point symmetry 1, are surrounded by nine fluorine atoms at distances varying from 2.19 to 2.86 Å. By comparing the bond lengths within the two coordination polyhedra, it is seen that the variations in the distances Bi—F are larger than in Bi—O (2.34–2.79 Å), and thus the first prism is more irregular.

In the crystal structure of a lanthanoid formate, Gd(OOCH)<sub>3</sub>,<sup>13</sup> the gadolinium atom is reported to have nine oxygen neighbours, forming a prism of very similar appearance to that found in Bi(OOCH)<sub>3</sub>. In the Gd—9 O polyhedron there are only two crystallographically independent distances, 2.3 and 2.5 Å, and the metal atom is located in the centre of the trigonal prism. The main difference between the gadolinium and the bismuth compound seems to be that the Bi—O polyhedron is deformed along the three-fold axis, whereas the Gd—O polyhedron is fairly regular. The difference may be due to the influence of the inert electron pair in the bismuth atoms.

The author wishes to thank Professor Bengt Aurivillius for his stimulating and helpful interest and Dr. Karin Aurivillius for valuable discussions and comments on this work. Thanks are also due to Dr. Robert E. Carter for correcting the English text and to the *Computer Division of the National Rationalization Agency* for giving free time on the computer CD 3600 in Uppsala.

This investigation forms part of a research program on bismuth salts, financially supported by the *Swedish Natural Science Research Council*.

#### REFERENCES

1. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
2. Liminga, R. *Acta Chem. Scand.* **21** (1967) 1206.
3. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., (1966), No. 6027.
4. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
5. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
6. Krogmann, K. and Mattes, R. *Z. Krist.* **118** (1963) 291.
7. Bukowska-Strzyzewska, M. *Acta Cryst.* **19** (1965) 357.
8. Barclay, G. A. and Kennard, C. H. L. *J. Chem. Soc.* **1961** 3289.
9. Segal, D. J., Santoro, R. P. and Newnham, R. E. *Z. Krist.* **123** (1966) 73.
10. Orgel, L. E. *J. Chem. Soc.* **1959** 3815.
11. Zalkin, A. and Templeton, D. H. *J. Am. Chem. Soc.* **75** (1953) 2453.
12. Aurivillius, B. and Lindblom, C.-I. *Acta Chem. Scand.* **18** (1964) 1554.
13. Pabst, A. *J. Chem. Phys.* **11** (1943) 145.

Received November 1, 1968.