angle between the least-squares planes of the phenyl ring and the central ring [C(11), C(12), C(13) and C(14)] is 91·1°. This can be seen from the torsion angle about the N–C(15) bond in Fig. 3. The O and C(21) atoms of the methoxy group are nearly coplanar with the phenyl ring. The deviations of the atoms from the two benzene rings and the phenyl ring are shown in Fig. 4.

The packing of the molecules in the crystal is shown in the stereoscopic drawing in Fig. 5. There are no intermolecular contacts less than van der Waals distances. The closest intermolecular distances are 3·58 and 3·59 Å between O and C(7) and between C(2) and C(8) respectively.

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The Crystal Structure of $Bi_{12}O_{15}Cl_6$

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The structure of $Bi_{12}O_{15}Cl_6$ has been determined by symbolic addition and Fourier methods and refined to $R = 0{\cdot}094$ for 1083 independent counter intensities. The crystals are orthorhombic, space group *Pnma*, with $a = 40{\cdot}532\ (8)$, $b = 3{\cdot}8688\ (4)$, $c = 15{\cdot}487\ (3)$ Å, $Z = 4$. The Bi atoms are of two types, one coordinated by four O atoms, the other by five. The Bi–O distances lie between 2·03 and 2·69 Å. The fourfold coordination can be described as a square pyramid with the lone pair of electrons of Bi at its apex, and the five-coordination as an octahedron with the lone pair at one corner. The coordination polyhedra are linked by sharing edges and corners to form infinite layers parallel to [010]. Between the nets are parallel trigonal prisms of Cl^- ions.

Introduction

The present study is part of an investigation of the systems Bi_2O_3–BiOCl and Bi_2O_3–BiOF–BiOCl. The intention is to prepare compounds of complex compositions but predictable structures. The investigation was started with the latter system where the structure of $Bi_6O_7FCl_3$ has been reported (Hopfgarten, 1975).

Experimental

For the preparation of $Bi_{12}O_{15}Cl_6$ a mixture of Bi_2O_3 and BiOCl in the mole ratio 1:2 was heated in a sealed gold capsule for 24 h at 860 °C. The product consisted of colourless needle-shaped crystals, elongated along **b**. Weissenberg photographs indicated orthorhombic symmetry with the systematic absences $0kl$ and $hk0$ for $k+l$ and h odd respectively, indicating the space groups *Pnma* (No. 62) or $Pn2_1a$ (No. 33).† The photographs also showed that the $Bi_{12}O_{15}Cl_6$ modification prepared had an *OD* structure, since there were intensity streaks along [100]. Several crystals prepared at different temperatures were tried. All the photographs showed streaks with more or less pronounced maxima corresponding to disorder along the [100] direction. The intensity distribution on the

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† Orientation different from that given in *International Tables for X-ray Crystallography* (1965).

streaks varied from crystal to crystal as is to be expected for an *OD* structure. Photographs obtained from two different crystals are shown in Fig. 1.

Unit cell and data collection

Cell dimensions were determined from a least-squares analysis of the positions, measured on a single-crystal diffractometer with Mo $K\alpha$ radiation, of 43 reflexions with θ values varying between 7 and 27·5°. Some crystal data are presented in Table 1.

Table 1. *Crystal data*

$Bi_{12}O_{15}Cl_6$, F.W. 2960·5
Orthorhombic, *Pnma*
$a=40{\cdot}532$ (8), $b=3{\cdot}8688$ (4), $c=15{\cdot}487$ (3) Å
$V=2428{\cdot}6$ Å^3, $Z=4$
$D_m=8{\cdot}14$, $D_x=8{\cdot}10$ g cm^{-3}
μ(Mo $K\alpha$) = 830 cm^{-1}

Intensities from a single crystal, 0·016 × 0·23 × 0·022 mm, were collected at 22 °C on an Enraf–Nonius computer-controlled four-circle diffractometer, CAD-4. Graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ Å) was used. The crystal was mounted with b along the φ axis of the goniometer. The ω–2θ scan technique was used with a peak scan interval $\Delta\omega=(0{\cdot}90+0{\cdot}5\tan\theta)°$. A minimum net count of 2000 was attained within a maximum measuring time of 4 min. The scan speed was calculated from the net intensity in a fast pre-scan. The background was measured for $\frac{1}{4}$ of the scan time at each end of the scan interval. In the range $3°<\theta<27{\cdot}5°$ 3183 unique reflexions were measured, of which 2100 gave net intensities $I<10$ in the fast pre-scan or resulted in $I<3\sigma(I)$, where I is the intensity and $\sigma(I)$ is the standard deviation based on counting statistics. The remaining 1083 intensities were corrected for Lorentz, polarization and absorption effects. The transmission factors, evaluated by the numerical method, varied from 0·240 to 0·453. The intensities of two standard reflexions, 18,0,4 and 604, were measured at regular intervals and were constant during the course of the data collection.

The evaluation of the intensities of the weak maxima of the diffuse streaks suffered from appreciable errors. The streaks were crossed at different angles by the ω–2θ scan motion for different reflexions. Thus both the integrated intensity within the scan interval and the background measurement contain different proportions of the continuously varying intensity streaks. However, the superposition structure obtained is of sufficient quality to allow a discussion of the architecture of the compound.

Structure determination and refinement

The Bi positions were determined by symbolic addition. The positions of all Cl and O atoms were deduced from a subsequent difference map. The centrosymmetric space group *Pnma* and the non-centrosymmetric $Pn2_1a$ are both possible, in view of the systematic absences. The least-squares refinement in *Pnma* progressed normally. As a reasonable structure and reasonable thermal parameters were obtained for *Pnma*, a refinement in $Pn2_1a$ was not considered. The final refinement in *Pnma* with anisotropic temperature factors for Bi and isotropic ones for the lighter atoms gave $R=0{\cdot}094$ and $R_w=0{\cdot}12$ where $R=\sum[|F_o|-|F_c|]/\sum|F_o|$ and $R_w=[\sum w_i(|F_o|-|F_c|)^2/\sum w_i|F_o|^2]^{1/2}$. The weights were calculated from $w_i^{-1}=\sigma^2(|F_o|^2)/4|F_o|^2+0{\cdot}0017|F_o|^2$. In the last cycle all parameter shifts were less than 0·05 of the estimated standard deviations. The value of $S=[\sum w_i(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, where m and n are

Table 2. *Positional and thermal parameters obtained in the final least-squares refinement*

The anisotropic thermal parameters are based on the expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2hl\beta_{13})]$. By symmetry $\beta_{12}=\beta_{23}=0$. The β_{ij} values are multiplied by 10^4. Estimated standard deviations are given in parentheses.

	x	y	z	B (Å^2)
Bi(1)	0·1598 (2)	¼	0·0906 (4)	For β_{ij}, see below
Bi(2)	0·1529 (2)	¼	0·3713 (5)	
Bi(3)	0·5077 (1)	¼	0·5976 (3)	
Bi(4)	0·5922 (2)	¼	0·7349 (6)	
Bi(5)	0·6727 (1)	¼	0·8482 (3)	
Bi(6)	0·2543 (1)	¼	0·2199 (4)	
Bi(7)	0·7606 (1)	¼	0·9758 (3)	
Bi(8)	0·3393 (2)	¼	0·3595 (8)	
Bi(9)	0·4174 (2)	¼	0·4752 (3)	
Bi(10)	0·0967 (2)	¾	0·2453 (4)	
Bi(11)	0·0070 (2)	¼	0·5945 (3)	
Bi(12)	0·0900 (2)	¾	0·5271 (6)	
Cl(1)	0·5558 (9)	¼	0·377 (2)	0·9 (6)
Cl(2)	0·5556 (8)	¼	0·136 (2)	0·9 (6)
Cl(3)	0·4693 (7)	¼	0·247 (2)	1·1 (5)
Cl(4)	0·7222 (9)	¼	0·630 (2)	1·0 (6)
Cl(5)	0·8029 (8)	¼	0·751 (2)	0·9 (6)
Cl(6)	0·8074 (8)	¼	0·497 (2)	1·1 (6)
O(1)	0·227 (2)	¼	0·085 (5)	1 (1)
O(2)	0·066 (2)	¼	0·587 (5)	1 (1)
O(3)	0·482 (1)	¼	0·463 (4)	1·3 (9)
O(4)	0·822 (2)	¼	0·982 (5)	1 (1)
O(5)	0·730 (2)	¼	0·859 (5)	3 (1)
O(6)	0·558 (1)	¼	0·586 (4)	1 (1)
O(7)	0·118 (2)	¾	0·644 (5)	1 (1)
O(8)	0·126 (3)	¾	0·366 (8)	3 (1)
O(9)	0·649 (2)	¼	0·732 (4)	1 (1)
O(10)	0·015 (2)	¾	0·535 (5)	2 (1)
O(11)	0·124 (2)	¼	0·484 (6)	3 (2)
O(12)	0·312 (2)	¼	0·237 (5)	1 (1)
O(13)	0·126 (2)	¼	0·252 (5)	2 (1)
O(14)	0·122 (4)	¾	0·108 (9)	3 (1)
O(15)	0·393 (1)	¼	0·346 (4)	1 (1)

	β_{11}	β_{22}	β_{33}	β_{13}
Bi(1)	5·6 (5)	690 (60)	2 (2)	−5·6 (8)
Bi(2)	2·2 (4)	110 (38)	46 (4)	−6·5 (9)
Bi(3)	0·4 (3)	10 (8)	0 (2)	−0·1 (5)
Bi(4)	0·7 (3)	180 (41)	97 (6)	−2·5 (7)
Bi(5)	3·4 (4)	200 (38)	6 (2)	−0·7 (7)
Bi(6)	2·1 (3)	160 (33)	9 (2)	2·3 (6)
Bi(7)	2·2 (3)	220 (36)	6 (2)	−2·1 (6)
Bi(8)	3·3 (6)	210 (52)	120 (8)	1·7 (8)
Bi(9)	4·3 (4)	310 (42)	3 (1)	−5·8 (7)
Bi(10)	3·2 (4)	50 (30)	32 (3)	7·5 (8)
Bi(11)	5·2 (5)	20 (8)	0 (2)	1·7 (6)
Bi(12)	3·2 (5)	130 (10)	58 (5)	−8·1 (1)

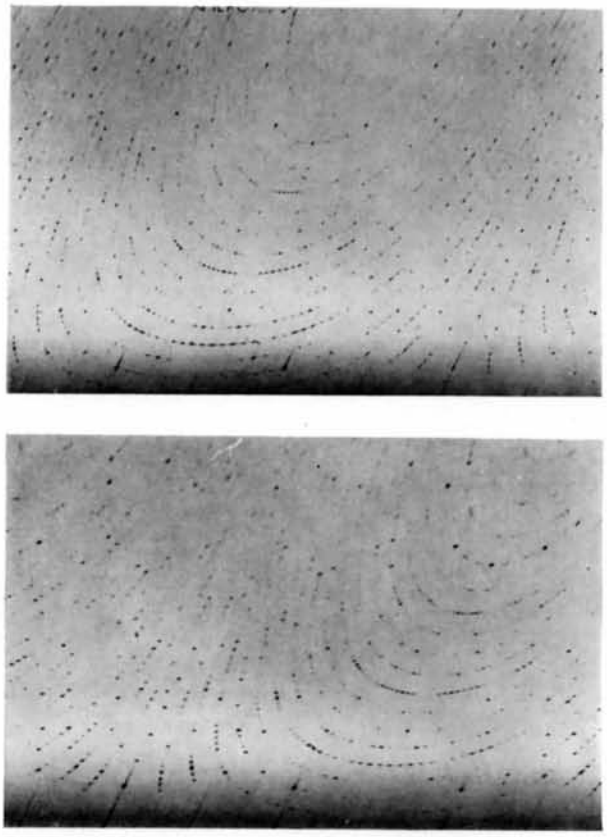

Fig. 1. Weissenberg photographs (*h*0*l*) obtained from two different $Bi_{12}O_{15}Cl_6$ crystals. The top photograph was obtained from the crystal used for the data collection.

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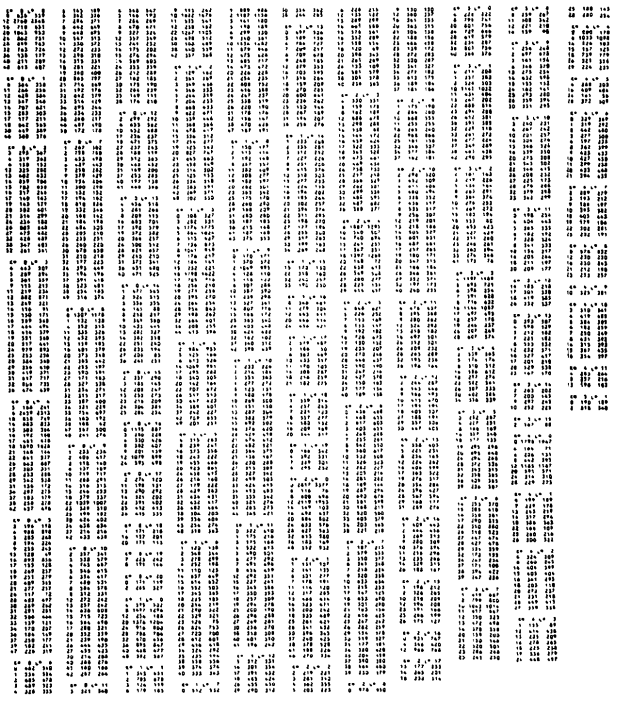
Table 3. *Observed and calculated structure factors*

The columns list h, F_o and $|F_c|$.



the number of observations and parameters, respectively, was 2·32. Scattering factors for spherically symmetric atoms were used, those given by Cromer & Waber (1965) for neutral Bi and by Hanson, Herman, Lea & Skillman (1964) for neutral Cl and O. Final positional and thermal parameters are given in Table 2, and observed and calculated structure factors in Table 3. All computations were made on the Univac 1108 computer in Lund. A short account of the program system has been given by Stålhandske (1974).

Table 4. *Interatomic distances and angles*

Interatomic distances (Å) in $Bi_{12}O_{15}Cl_6$ compared with the corresponding distances in BiOCl (Aurivillius, 1964) and $Bi_6O_7FCl_3$ (Hopfgarten, 1975). Estimated standard deviations are given in parentheses.

	$Bi_{12}O_{15}Cl_6$	$Bi_6O_7FCl_3$	BiOCl
Bi–Bi	≥3·553 (9)	≥3·584 (3)	≥3·71 (1)
Bi–Cl	3·05 (3)–3·26 (3)	3·135 (9)–3·247 (8)	≥3·07 (2)
Bi–O	2·03 (6)–2·69 (6)	2·19 (3) –2·51 (4)	≥2·309 (4)
Cl–Cl	3·72 (5)–4·04 (5)	3·84 (2) –3·90 (2)	3·48 (5)
O–O	2·52 (7)–3·15 (9)	2·69 (3) –3·00 (4)	2·7457 (5)

Four-coordinated Bi, *e.g.* Bi(1)		Five-coordinated Bi	
Bi(1)—2 O(4)	2·36 (5)	Bi(12)–2 O(2)	2·36 (5)
Bi(1)—2 O(14)	2·49 (9)	Bi(12)–2 O(11)	2·46 (6)
		Bi(12)– O(7)	2·13 (8)

Selected angles (°)			
In the 'square planes'		In the 'trigonal prisms'	
O–O–O	87·5 (1·8)–92·8 (1·7)	Cl–Cl–Cl	57·5 (0·7)–62·5 (0·7)

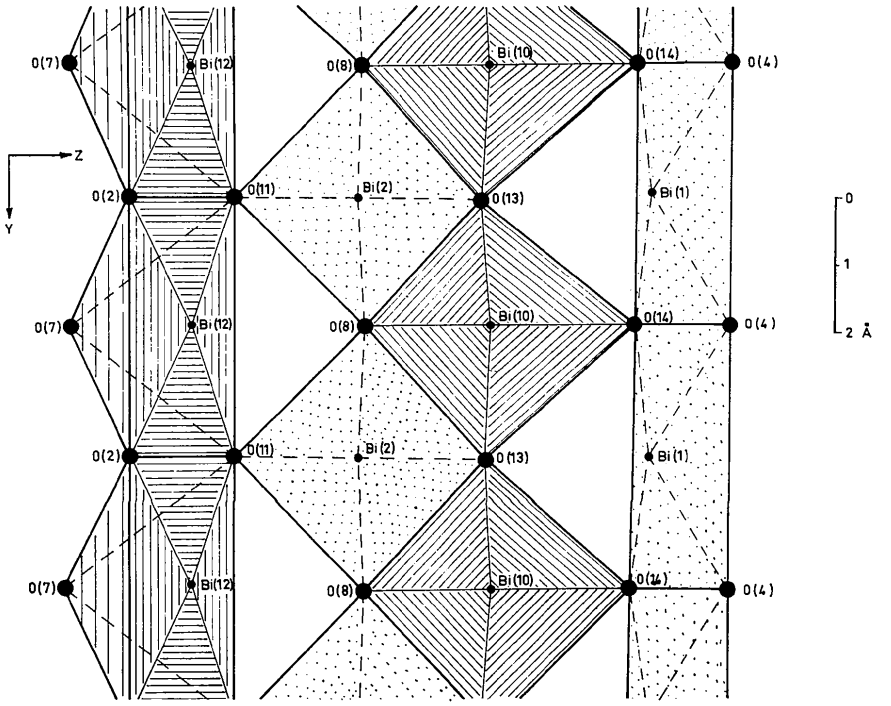


Fig. 2. The coordination polyhedra of bismuth, projected along the x axis in $Bi_{12}O_{15}Cl_6$. The atoms Bi(1), Bi(10) and Bi(2) are each surrounded by four oxygen atoms, forming approximately quadratic planes. The atom Bi(12) is coordinated to five oxygens. Including the lone electron pair of Bi, the coordination polyhedra can be described as square pyramids and as octahedra. Square pyramids around Bi(2) and Bi(10) share edges. The Bi(12) octahedron and the Bi(1) square pyramid share corners with the Bi(2) and Bi(10) polyhedra. The drawing shows part of a zigzag layer.

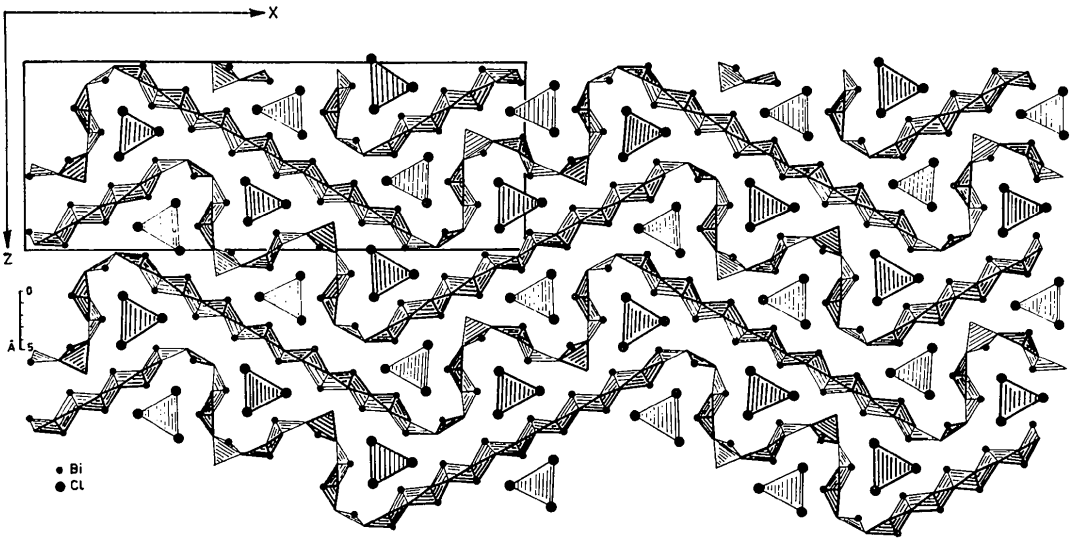


Fig. 3. The structure of $Bi_{12}O_{15}Cl_6$ projected along the y axis. The coordination polyhedra of bismuth, described as square pyramids and octahedra, are connected to form infinite zigzag layers parallel to [010]. The polyhedra drawn by heavy and thin lines are $b/2$ apart. The chloride ions form trigonal prisms, running along [010]. All atoms are at the heights $y = \pm\frac{1}{4}$.

Description and discussion of the structure

Interatomic distances and angles are given in Table 4. The values are normal compared to the structures of BiOCl (Aurivillius, 1964; Sillén, 1940) and $Bi_6O_7FCl_3$ (Hopfgarten, 1975). The coordination of Bi can be described in the following way.

Bi(1)–Bi(11) are each coordinated to four O atoms, forming a nearly quadratic plane (Fig. 2). The lone pair of electrons can be imagined to complete a square pyramid. This coordination polyhedron of Bi was found earlier in BiOCl (Bannister & Hey, 1935) and BiOF (Aurivillius, 1964). Bi(12) is, on the other hand, surrounded by five O atoms all on one side (Fig. 2). The lone pair of electrons completes a distorted octahedron. The square pyramids around Bi(2)–Bi(11) are joined by sharing edges, forming layers which are connected by corner-sharing to the square pyramids around Bi(1) and to the octahedra around Bi(12) (Fig. 2). The nets of formula $[Bi_{12}O_{15}^{6+}]_n$ run zigzag through the structure and are parallel to **b**. Between them there are trigonal-prism columns of Cl^- ions. A projection of the described layer structure is given in Fig. 3. In PbFCl and the isotypic BiOF, and $Bi_6O_7FCl_3$ (Hopfgarten, 1975) there are similar layers consisting of square pyramids. The formula $Bi_{12}O_{15}Cl_{16}$ can also be written as $(Bi_4O_5Cl_2)_3$, but the structure is quite different from that of $Sb_4O_5Cl_2$ (Edstrand, 1947).

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