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The crystal structure of BiOCl

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Abstract. The crystal structure of BiOCl has been redetermined with 3570 observed reflections of which 174 were unique measured on a computer controlled Philips PW 1100 single crystal diffractometer. The structure belongs to the tetragonal space group $P4/nmm$ and the cell constants, obtained by a least-squares calculation from direct θ-value measurements on the diffractometer, are $a = 3.8870(5)$ and $c = 7.3540(5)$ Å.

The positional and thermal parameters, with anisotropic temperature factors, were refined by full-matrix least-squares calculations to a final $R = 9.17\%$.

Each Bi atom is eight-coordinated by 4 O and 4 Cl atoms at distances of 2.316 Å and 3.059 Å respectively thus forming a decahedron. The faces of the decahedron are 2 rectangles (O–O–O–O and Cl–Cl–Cl–Cl) with sides 3.487 Å and 8 isosceles triangles (four O–Cl–O and four Cl–O–Cl) with sides O–Cl 3.249 Å and O–O or Cl–Cl 3.487 Å.

The decahedra are linked to each other by a common O–Cl edge along the a and b axes in infinite layers.

Introduction

The crystal structure of BiOCl has been determined within the framework of a general program for accurate structure determination of compounds with the general formula $A^{V}_{m}B^{VI}_{n}X^{VII}_{p}$ with A = As, Sb, Bi; B = O, S, Se, Te and X = Cl, Br, I. A reliable structural model was necessary for the

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Table 1. Crystal data for BiOCl.

BiOCl			
Tetragonal			
Space group:	*P4/nmm*	F.W.	= 260.432
a	3.887 Å	Z	= 2
c	7.354 Å	ϱ_{calc}	= 7.784 g · cm^{-3}
V	111.15 Å^3	ϱ_{meas}	= 7.9 g · cm^{-3}
λ(MoK_α)	0.71069 Å	μ	= 799.322 cm^{-1}

explanation of the interesting physical properties (optical, ferroelectric, etc.) of the group.

Most of the structural data for BiOCl and generally for BiOX compounds (X = Halogen) given in the literature are from the work of Bannister and Hey (1934, 1935). Their structure investigation was carried out by means of photographic methods, and none of these articles describe the structure in detail. For this reason a new structure refinement work was undertaken recently by a number of investigators and by ourselves.

Experimental

Pure, lightly transparent, faint yellow, very thin, plates of BiOCl were prepared by heating a high purity mixture of Bi_2O_3 and $BiCl_3$ in stoichiometric proportion in an evacuated (10^{-6} Torr) quartz tube to 820° C and gradually cooling to room temperature. A small single crystal, with dimensions $0.6 \times 0.6 \times 0.02$ mm, was selected and centred on a Philips PW-1100 four-cycle single crystal diffractometer in our Laboratory. The cell constants were refined by a least-squares procedure. The final values for the unit cell are given in Table 1.

Three-dimensional intensity data were measured with Mo$K\alpha$ radiation monochromated with a graphite monochromator. In view of the very large linear absorption coefficient (799.3 cm^{-1}) and the shape of the crystal (very thin plate) an exact absorption calculation was out of question. Ψ-scanning data were taken and worked out.

Determination of the structure and refinement

An approximate structural model for BiOCl, obtained from the isostructural BiOBr (Ketterer and Kramer, 1986), was used as a staring point. Each atom (Bi, O, Cl) occupies a special position with multiplicity 2.

The structure was refined using the EHELX76 program (Sheldrick, 1976).

Table 2. Fractional atomic coordinates (Å) and equivalent isotropic thermal parameters (Å^2) for BiOCl.

Name	x	y	z	B_{eq}*
Bi	1/4	1/4	0.1714(3)	0.995
O	1/4	3/4	0	2.464
Cl	1/4	1/4	0.6459(25)	1.536

* $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} \bar{a}_i \bar{a}_j a_i^* a_j^*$

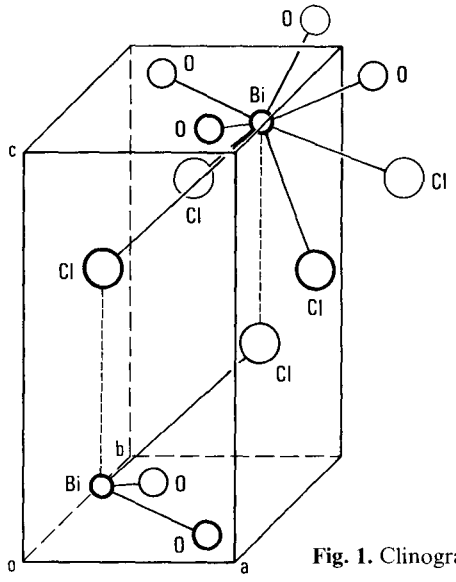

Fig. 1. Clinographic projection of the unit cell of BiOCl.

Structure factor calculation using the starting parameters with individual isotropic temperature factors gave $R = 14.35\%$.

Refinement was carried out by full-matrix least-squares, with unit weight to all reflections. The function minimised in the least-squares refinement was $\Sigma w(F_o - F_c)^2$. Final $\Delta/\sigma(I)_{max} = 0.012$ and $(\Delta(\varrho)_{max}/\Delta(\varrho)_{min} = 6.23/-13.46$ eÅ^{-3}). The atomic scattering factors were taken from the International Tables for X-ray Crystallography vol. III (1974). The final R factor with all atoms refined anisotropically was 9.17%.[1]

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 55527, the names of the authors and the title of the paper.

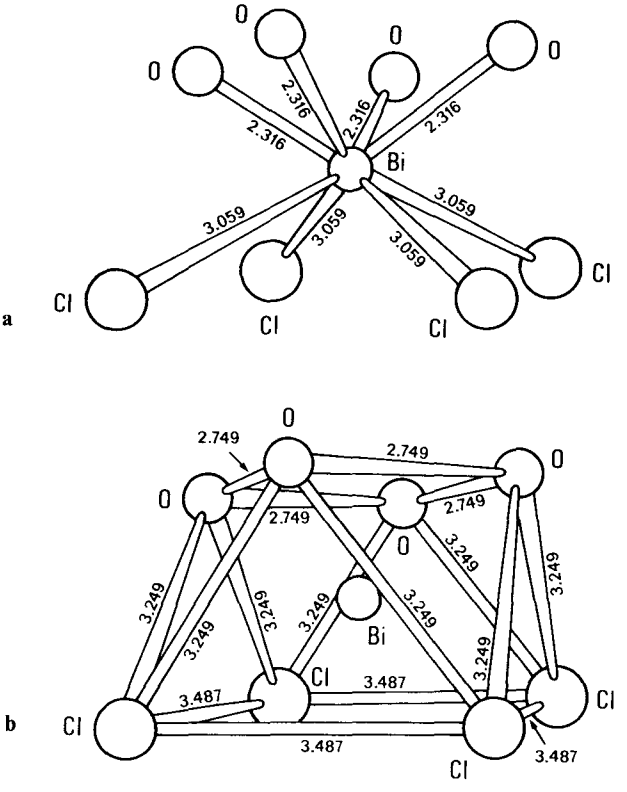

Fig. 2. (a) Interatomic distances in the coordination polyhedra around Bi. (b) Clinographic projection of the coordination polyhedron around Bi.

Description of the structure and discussion

All the atoms of the asymmetric unit lie on special positions, $4mm$ or $\bar{4}m2$ (cf. Table 2). As shown in the clinographic projection of Fig. 1, each Bi atom is eight-coordinated by four O atoms at distances of 2.316 Å and four Cl atoms at distances of 3.059 Å in the form of an asymmetric dekahedron. The faces of the dekahedron are 2 rectangles (O – O – O – O, Cl – Cl – Cl – Cl) with sides 2.749 and 3.487 Å respectively, which are parallel to the (110) plane and 8 isosceles triangles (four Cl – O – Cl, with sides O – Cl 3.249 Å and Cl – Cl 3.487 Å and four O – Cl – O with sides O – Cl 3.249 Å and O – O 2.749 Å. The decahedra are linked to each other by a common O – Cl edge along the *a* and *b* axes forming infinite layers.

Fig. 2 shows also the coordination of O and Cl. Each O atom is linked to four Bi atoms at distances 2.316 Å, forming a tetragonal pyramid with

Table 3. Selected bond lengths (Å) and angles (°) in BiOCl.

Bi – O		2.3165(12)	Bi – Cl		3.059(8)
O – Bi – Oa		114.07(9)	O – Bi – Cld		72.90(24)
O – Bi – Ob		72.78(4)	O – Bi – Cle		140.43(11)
O – Bi – Oc		72.78(4)	Cl – Bi – Cla		78.88(18)
O – Bi – Cl		72.90(24)	Cl – Bi – Cld		78.88(18)
O – Bi – Cla		140.53(11)	Cl – Bi – Cle		127.9(4)
Symmetry code					
a	x −1.000	$+y$ z	b	1.000 $-x$ 1.000	$-y$ $-z$
c	$-x$ 1.000	$-y$ $-z$	d	−1.000 $+x$	y z
e −1.000	$+x$ −1.000	$+y$ z			

the O atom at its apex (Bi – Bi 3.87 Å). Also each Cl atoms forms with the neighbouring Bi atoms (Cl – Bi 3.059 Å) A tetragonal pyramid with the Cl atom at its apex.

Neighbouring decahedra form layers along (001) which are connected by common O – Cl edges. Neighbouring layers of decahedra are connected by common O – O or Cl – Cl edges.

The coordination polyhedra in this structure are different from those found in the structures of chalcohalogenides of the same general formula $A^{V}_{m}B^{VI}_{n}X^{VII}_{p}$ with B = S, Se, TeI (Rentzeperis, 1991). In these structures the coordination polyhedra are octahedra or composite 7-coordination polyhedra, but never a decahedron. For example in BiTeI (Keramidas, Voutsas, Papazoglou and Rentzeperis, 1991), each Bi atom is octahedrally coordinated by three Te and three I atoms. The octahedra are linked to each other by a common Te – I edge along the *a* and *b* axes, forming infinite layers.

In the structure of BiSeCl (Voutsas and Rentzeperis, 1980) each Bi atom is connected to three Cl atoms which form the base of a triangular pyramid. The average Bi – Cl distance in this structure (⟨Bi – Cl⟩ = 3.147 Å) agrees well with those found in the present structure (Bi – Cl = 3.059 Å).

In the $CoSO_4$-Bi_2O_3 system (Fanariotis and Rentzeperis, 1991) the average Bi – O distance (⟨Bi – O⟩ = 2.33 Å) agrees well with the Bi – O bonds in the present structure (Bi – O = 2.3165 Å). Here four O atoms and a Bi atom form a square pyramid with the Bi atom at its apex.

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