

CdBiO₂Cl: synthesis and powder structure solution

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The title compound, cadmium bismuth dioxide chloride, CdBiO₂Cl, was obtained as a white powder by reaction of solid BiOCl with CdO at 973 K. *Ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques, including direct methods for atom location and Rietveld fitting for the final refinement. Being monoclinic, the crystal structure can be related to tetragonal Sillen layered phases. The main structural elements present are CdBiO₂⁺ pleated metal–oxygen layers alternating with Cl layers along the *c* axis, whereas along the *b* axis, all atoms are on mirror planes. The formation of a strong Cd–Cl bond draws the layers together, causing layer deformation and a monoclinic distortion in the layer arrangement.

Comment

At present, there is much information on Bi-based mixed oxides with layered structures, where infinite Bi₂O₂²⁺ charged layers alternate with slabs of other metal oxides (Alexandrov & Beznosikov, 1997). Much less attention has been paid to a related family of layered compounds known as Sillen's phases, revealed in 1939 (Sillen, 1939; Dolgih & Holodkovskaya, 1992). In these compounds, the space between the Bi₂O₂²⁺ layers is filled with halogen and metal–halogen slabs. For many members of this family, the crystal structure data were reported by Sillen and have not been revised since.

It is a characteristic of both these classes of compounds that Bi₂O₂²⁺ layers exhibit a surprising ability to complement the variety of oxygen–metal slabs, while keeping the O atoms strictly in the plane and allowing the Bi to be substituted by other metals. In particular, Sillen (1942) described three compounds, with the compositions Cd_{1.25}Bi_{1.5}O₂Cl₃, Cd_{1.1}Bi_{1.6}O₂Cl₃ and Cd_{1.03}Bi_{1.65}O₂Cl₃, and reported unit-cell constants of *a* = 3.865 and *c* = 21.08 Å, *a* = 3.862 and *c* = 21.14 Å, and *a* = 3.920 and *c* = 22.42 Å, respectively, and space group *P4/mmm* in each case. The suggested model for the crystal structure consists of two [Cd_{*x*}Bi_{2–*x*}O₂]^{(2–*x*)+} layers separated by a three-layered [Cd_{1–*y*}Cl₃] slab with the NaCl structure. Our attempt to follow the published synthesis

produced the title substance, (I), with the composition CdBiO₂Cl in the monoclinic system.

The crystal structure of (I) (Fig. 1) consists of infinite double metal–oxygen CdBiO₂²⁺ layers alternating with Cl sheets. The metal–oxygen layers in turn consist of two metal sublayers with O atoms in between. Bi and Cd atoms are located at the vertices of pyramidal BiO₄ and CdO₄ units linked by shared

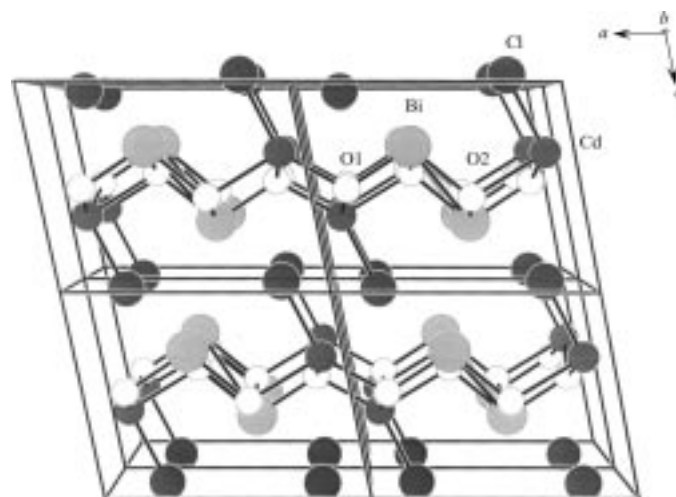


Figure 1
The crystal structure of CdBiO₂Cl.

edges. Interatomic Bi–O and Cd–O distances correspond well with literature values (Wells, 1984). It should be noted that the *M*–O distances are not equal. The Cd–O₂ bond [2.453 (14) Å] differs most from the average value (2.26 Å), but is still in the accepted range.

Distortion of the oxygen plane is a characteristic of (I) which differentiates the structure from other members of the family. The O–O distances are in the range 2.72–2.98 Å. The O₂–O₁–O₂ angle of 175° also characterizes a distortion of the oxygen plane.

Although the Bi³⁺ and Cd²⁺ cations are rather similar in size, the metal atoms in the sublayers of (I) are well ordered. Conditionally, the arrangement of the metal atoms can be regarded as a plane, with rows of Cd or Bi along the 2₁ axes. The degree of distortion of this metal-atom plane can be characterized by the Cd–Bi–Cd angle of 172°.

The nearest neighbour to Cd besides the four O atoms is the Cl atom, at a distance of 2.49 Å. This is about 1 Å less than regular *M*–halogen distances in Sillen phases. It is reasonable to suppose that Cd–Cl bonds cause the deformation of both the metal–oxygen and Cl layers, as well as the shift in the layers leading to monoclinic distortion.

The title compound differs from those described by Sillen, mainly in the structure of the halogen layer. There is a limited resemblance to the halogen layer in Bi₃O₄Cl and the series *M_x*Bi_{3–*x*}O₄Cl (Nurgaleev *et al.*, 1983; Aurivillius, 1984). However, the metal–oxygen layers in these phases are of triple thickness.

In summary, the main structural elements of CdBiO_2Cl , *i.e.* double metal–oxygen layers alternating with Cl layers, are typical for Sillen phases. However, formation of a strong Cd–Cl bond draws the layers closer together, causing layer

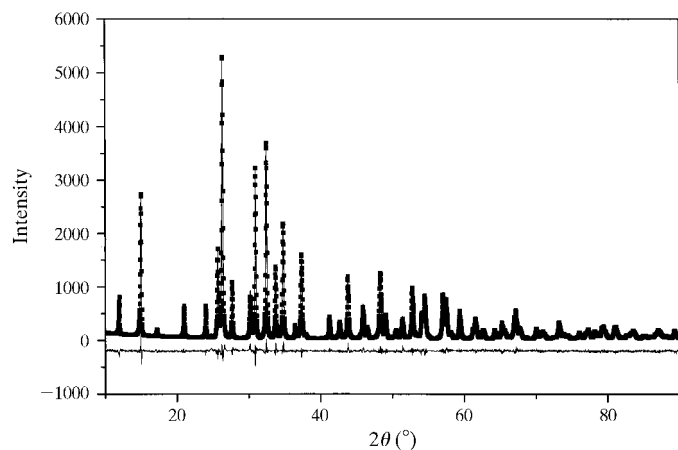


Figure 2
The Rietveld plot for CdBiO_2Cl .

deformation and distortion in the layer arrangement, from tetragonal to monoclinic.

Experimental

CdBiO_2Cl was synthesized as a white powder by the reaction of BiOCl and CdO . High purity starting materials were used as received from Reachim. BiOCl was obtained from Bi_2O_3 according to the method of Brauer (1956) and its purity was checked by X-ray diffraction. A stoichiometric mixture of BiOCl and CdO was homogenized and heated at 973 K in air for 1 h. An alternative synthesis consists of heating a stoichiometric mixture of Bi_2O_3 , CdO and CdCl_2 at 973 K.

Crystal data

CdBiO_2Cl	$D_x = 6.92 \text{ Mg m}^{-3}$
$M_r = 388.84$	Cu $K\alpha_{1,2}$ radiation
Monoclinic, $P2_1/m$	$T = 293 \text{ K}$
$a = 7.5878 (7) \text{ \AA}$	Specimen shape: circular flat plate
$b = 4.1397 (4) \text{ \AA}$	$20.0 \times 20.0 \times 0.5 \text{ mm}$
$c = 6.0594 (6) \text{ \AA}$	Specimen prepared at 973 K
$\beta = 101.529 (11)^\circ$	Particle morphology: thin powder,
$V = 186.50 (3) \text{ \AA}^3$	white
$Z = 2$	

Data collection

DRON-4 powder diffractometer at the Institute of Chemistry and Chemical Technology, Krasnoyarsk	Specimen mounted in reflection mode
Specimen mounting: packed powder pellet	$2\theta_{\min} = 10$, $2\theta_{\max} = 90^\circ$
	Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on F^2	Excluded region(s): none
$R_p = 0.076$	Profile function: Pearson VII
$R_{wp} = 0.106$	178 reflections
$R_{exp} = 0.074$	40 parameters
$R_B = 0.034$	Preferred orientation correction:
$S = 1.43$	March–Dollase correction
Wavelengths of incident radiation:	(Dollase, 1986)
1.540562 and 1.544390 \AA	

Table 1
Selected bond lengths (\AA).

Bi–O1	2.160 (14)	Cd–O1 ⁱⁱ	2.201 (16)
Bi–O2	2.298 (15)	Cd–O1	2.261 (5)
Bi–O2 ⁱ	2.223 (5)	Cd–Cl ^v	2.488 (7)
Cd–O2 ⁱ	2.453 (14)		

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, 1 - z$; (ii) $2 - x, \frac{1}{2} + y, 1 - z$.

Table 2
Contact distances (\AA).

Bi...Cl ⁱ	3.320 (6)	Bi...Cl ⁱⁱⁱ	3.408 (6)
Cd...Cl ⁱⁱ	3.220 (5)		

Symmetry codes: (i) $x, y - 1, z$; (ii) $2 - x, y - \frac{1}{2}, 1 - z$; (iii) $1 - x, y - \frac{1}{2}, -z$.

The sample was prepared by top-loading the standard quartz sample holder and removing the excess of the well grained substance. Corundum was used as the external standard. The powder pattern of CdBiO_2Cl is presented in Fig. 2. The cell parameters were obtained and refined using programs described by Kirik *et al.* (1979) and Visser (1969). Analysis of the systematic absences gave two possible space groups, $P2_1$ or $P2_1/m$; the latter was used. Errors given in the tables report primarily the precision of the measurement rather than the accuracy.

Data collection: DRON-4 data collection software; cell refinement: see above; data reduction: *XDIG* (local program); program(s) used to solve structure: *EXPO* (Altomare *et al.*, 1995); program(s) used to refine structure: local modification of *DBWM* (Wiles & Young, 1981); molecular graphics: *DIAMOND* (Brandenburg, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1340). Services for accessing these data are described at the back of the journal.

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