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Redetermination of the crystal structures of the 'Arppe compound' $Bi_{24}O_{31}Cl_{10}$ and the isomorphous $Bi_{24}O_{31}Br_{10}$

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The crystal structures of $Bi_{24}O_{31}X_{10}$ (X = Cl, Br; 24-bismuth 31-oxide decachloride/-bromide) have been redetermined. The structure models obtained resemble the model described in the literature about 60 years ago, but differ from it in some details of the O substructure and in the fact that the structure for X = Cl is a twofold superstructure of the literature model. A fictional mechanism is given by which the formerly described incorrect O substructure is transferred into the correct one.

1. Introduction

$Bi_{24}O_{31}Cl_{10}$ (also known as the 'Arppe compound') is a product of the thermal decomposition of BiOCl, which has been known since 1845 (Arppe, 1845). A structure model for this compound and for the isomorphous compound $Bi_{24}O_{31}Br_{10}$ has been proposed almost 60 years ago by Sillén & Edstrand (1942). Based only on the space-group symmetry and the features of the superstructure pattern obtained from Weissenberg photographs, they considered the entire structure, *i.e.* 17 atomic coordinate triplets of the asymmetric unit, to be a function of only two parameters. By comparing hand-calculated structure factors F_{h0l} with roughly estimated zero-layer Weissenberg reflection intensities they selected one of three different possible similar structure models as the correct one and determined the best values for the two parameters.

The solution obtained this way seemed to be reasonable, but had two minor drawbacks:

(i) one O—X distance turned out to be only 2.2 Å, which is much too short;

(ii) a site occupancy factor of 0.969 (31/32) had to be assigned to the $8 \times 4 = 32$ O atoms of the model to obtain the correct number of 31 O atoms per unit cell.

Within the scope of our own investigations of bismuth chalcogenide halide compounds (Ketterer *et al.*, 1985; Eggenweiler *et al.*, 1998*a*,*b*, 1999) we therefore decided to redetermine the crystal structures of the two title compounds.

2. Experimental

A mixture of 3.1 mmol Bi_2O_3 and 1 mmol $BiCl_3$ was tempered in an evacuated and sealed quartz ampoule at 723 K for 96 h. Then a temperature gradient (1113/1053 K) was applied for 48 h. During this time, pale yellow crystal needles of lengths up to 0.45 mm grew in the cooler part of the ampoule. One of these crystals (Table 1) was used for the structure analysis.

A mixture of 0.35 mmol Bi_2O_3 and 0.5 mmol BiOBr was tempered in an evacuated and sealed quartz ampoule at 723 K for 96 h. Then a temperature gradient (1143/1073 K) was applied for 8 d. During this time, pale brown–yellow narrow crystal platelets of lengths up to 2 mm grew in the cooler part of the ampoule. One of these crystals (Table 1) was used for the structure analysis.

3. Structure analysis

X-ray photographs of $Bi_{24}O_{31}Br_{10}$ showed an *A* (or *C*)-centered monoclinic cell fully compatible with the space group (*A*2/*m*) and lattice parameters described by Sillén & Edstrand (1942). However, for the 'isomorphous' $Bi_{24}O_{31}Cl_{10}$ we found a lattice parameter *b* twice as large as specified by Sillén & Edstrand (1942), corresponding to a superstructure with two subcells stacked in the **b** direction. While the substructure of this compound still could be seen to be approximately *A* (or *C*) centered, the superstructure turned out to be primitive with the *A* centering (plus *m*) having survived partially as a *c* glide of one of the space groups *Pc* or *P*2/*c*. Crystal data are given in Table 1.

Reflection intensities of crystals of both compounds were measured on a Bruker AXS SMART diffractometer with CCD detector. In each case approximately 1300 frames together covering approximately half of the available reciprocal lattice points were taken with an exposure time of 10 s per frame. Symmetry-constrained lattice parameters refined with the complete reflection data are given in Table 1,[1] together with the corresponding parameters published by Sillén & Edstrand (1942). Reflection intensities were numerically corrected for absorption by means of the program *XPREP* (*SHELXTL*; Sheldrick, 1998). All other calculations were performed with *SHELXS*97 (Sheldrick, 1990, 1997*a*) and *SHELXL*97 (Sheldrick, 1997*b*); figures have been generated with *SCHAKAL*99 (Keller, 1999).

For $Bi_{24}O_{31}Cl_{10}$, the (Bi,Cl) structure could be solved by a combination of direct and trial-and-error methods in space group *P*2/*c*; all O atoms were located on difference Fourier maps. A model (R_1 = 0.063) was obtained with all atoms having a site occupany factor of 1; while all Bi and Cl atoms and six of the O atoms occur twice, namely at similar *x*, *z* positions, but with *y* differing by approximately $\frac{1}{2}$ (*i.e.* in *both* subcells), we found four O atoms (one on a special position) which occur only in one of the two subcells; the final model is similar to Sillén & Edstrand's (1942) model, but turned out – in contrast to the latter – to be fully compatible with the supposed chemical formula.

For $Bi_{24}O_{31}Br_{10}$, after introducing and refining Sillén & Edstrand's (1942) (Bi,*X*) structure, only six O atoms (instead of 8) could be located on difference Fourier maps. However, four additional O positions could be refined successfully (*i.e.* with the isotropic displacement parameters converging at reasonable values) in space group *A*2/*m* leading to a final R_1 value of 0.064. The additional O atoms had been taken from the $Bi_{24}O_{31}Cl_{10}$ model (the four O atoms mentioned above), with half the weight.

It should be emphasized that the idea that the structure of $Bi_{24}O_{31}Br_{10}$ is a true superposition of the two subcells of the structure of $Bi_{24}O_{31}Cl_{10}$ (see *Discussion*) is not fully compatible with the assignment of Sillén & Edstrand's (1942) space group *A*2/*m*. This is because of the two atoms O8 and O8*A* of $Bi_{24}O_{31}Cl_{10}$. The transfer of these two atoms into a truly merged $Bi_{24}O_{31}Br_{10}$ structure is only possible if the space group of the latter is reduced to *A*2; the deviations of the O8/O8*A* positions from those required for an ideal *A*2/*m* model are about 0.4 Å. However, the character of the disorder of O8/O8*A* in $Bi_{24}O_{31}Br_{10}$ is not known exactly, which means that the 'historical' space group *A*2/*m* might be the correct one as well; it has therefore been retained for this compound.

Atom numbers of all Bi, *X* atoms and of atoms O8/O8*A* were chosen according to Sillén & Edstrand (1942); for the remaining O atoms a reverse numbering scheme was adopted to have each O*n* (*n* = 1–6) of the asymmetric unit bonded to the corresponding Bi*n* of the asymmetric unit. Atoms related to each other by the pseudotranslation (0,$\frac{1}{2}$,0) have been given the same number, but with '*A*' added for the second subcell. If both atoms of a pair are addressed concurrently in the following, the letter '*N*' will be added instead.

Final atom parameters are given in Tables 2 and 3; bond lengths and some non-bonding distances are collected in Tables 4 and 5. Fig. 1 shows a [010] view of the structure model of $Bi_{24}O_{31}Cl_{10}$. The fact that the atoms of $Bi_{24}O_{31}Cl_{10}$ are shifted approximately by a vector (0, 1/8, 1/4) relative to the

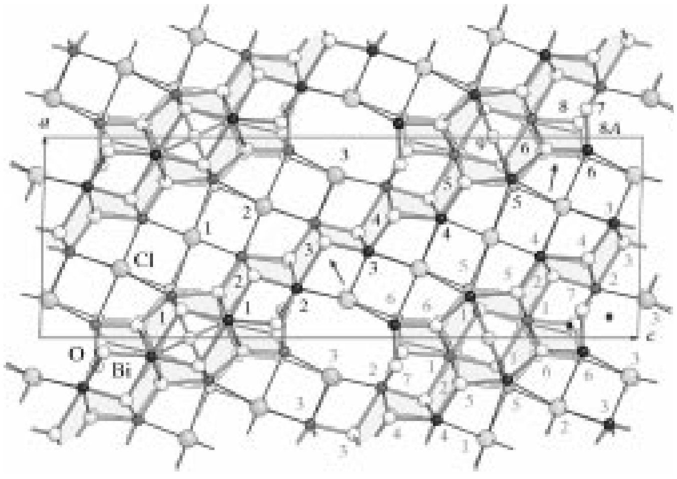

Figure 1
Crystal structure of $Bi_{24}O_{31}Cl_{10}$, as seen from [010]. Small, black spheres symbolize Bi atoms; large, grey spheres Cl; medium-sized light spheres O. Atoms with $-0.75 < y < 0.25$ are visualized. Some atoms have been labeled with the numerical parts of their names; of each pair of atoms connected by the pseudotranslation $\frac{1}{2}$**b**, only the label of the upper one is given (except for atoms O8/O8*A*). The atoms of the asymmetric unit have been labeled with black numbers; other atoms have been labeled with grey numbers. Atoms and bonds have been shaded with depth-dependent intensity. Uniformly shaded areas denote [Bi,O] 'boards'. The stars (*) near the lower-right corner of the unit cell denote the (adapted) positions of Sillén & Edstrand's (1942) atoms $O1^{SE}$ (= O7; right) and $O8^{SE}$ (= O8; left). The two arrows *within* the unit cell are explained in the captions to Figs. 2 and 3.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ0008). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	$Bi_{24}O_{31}Cl_{10}$	$Bi_{24}O_{31}Br_{10}$
Crystal data		
Chemical formula	$Bi_{24}Cl_{10}O_{31}$	$Bi_{24}Br_{10}O_{31}$
Chemical formula weight	5866.02	6310.62
Cell setting	Monoclinic	Monoclinic
Space group	$P2/c$	A_2/m
a (Å)	10.033 (2) [9.995]†	10.141 (7) [10.13]†
b (Å)	7.9745 (16) [3.969]†	4.005 (3) [4.008]†
c (Å)	29.552 (6) [29.44]†	29.977 (19) [29.97]†
β (°)	88.742 (4) [88.77]†	90.197 (12) [90.15]†
V (Å^3)	2363.8 (8)	1217.5 (14)
Z	2	1
D_x (Mg m^{-3})	8.242	8.607
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	15 924	8153
θ range (°)	1.38–28.33	1.36–28.03
μ (mm^{-1})	89.601	94.636
Temperature (K)	293 (2)	293 (2)
Crystal form	Needle	Needle
Crystal size (mm)	0.22 × 0.02 × 0.014	0.25 × 0.035 × 0.015
Crystal color	Pale green	Pale brown
Data collection		
Diffractometer	CCD area detector	CCD area detector
Data collection method	φ and ω scans	φ and ω scans
Absorption correction	Integration	Integration
$T_{\min}$	0.0293	0.0204
$T_{\max}$	0.4035	0.2685
No. of measured reflections	15 924	8153
No. of independent reflections	5546	1627
No. of observed reflections	3184	882
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.1299	0.1275
$\theta_{\max}$ (°)	28.33	28.30
Range of h, k, l	$-13 \rightarrow h \rightarrow 13$ $-10 \rightarrow k \rightarrow 0$ $0 \rightarrow l \rightarrow 39$	$-13 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 5$ $0 \rightarrow l \rightarrow 39$
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.063	0.064
$wR(F^2)$	0.146	0.186
S	0.900	0.913
No. of reflections used in refinement	5546	1627
No. of parameters used	218	84
H-atom treatment	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1089P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.000
$\Delta\rho_{\max}$ (e Å^{-3})	5.984	6.075
$\Delta\rho_{\min}$ (e Å^{-3})	−6.162	−5.916
Extinction method	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)
Extinction coefficient	0.000152 (8)	0.00025 (4)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	*SMART* (Bruker AXS, 1998)	*SMART* (Bruker AXS, 1998)
Cell refinement	*SMART* (Bruker AXS, 1998)	*SMART* (Bruker AXS, 1998)
Data reduction	*SAINT* (Bruker AXS, 1998), *SHELXTL* (Sheldrick, 1998)	*SAINT* (Bruker AXS, 1998), *SHELXTL* (Sheldrick, 1998)
Structure solution	*SHELXS*97 (Sheldrick, 1990)	*SHELXS*97 (Sheldrick, 1990)
Structure refinement	*SHELXL*97 (Sheldrick, 1997*b*)	*SHELXL*97 (Sheldrick, 1997*b*)
Preparation of material for publication	*SHELXL*97 (Sheldrick, 1997*b*), *SCHAKAL*99 (Keller, 1999)	*SHELXL*97 (Sheldrick, 1997*b*), *SCHAKAL*99 (Keller, 1999)

† Cell parameters given by Sillén & Edstrand (1942).

corresponding atoms of $Bi_{24}O_{31}Br_{10}$ and of Sillén & Edstrand's (1942) model is for once due to the different positions of the twofold axis in $A2/m$ $(0,y,0)$ and $P2/c$ $(0,y,1/4)$. Furthermore, while most atoms in $Bi_{24}O_{31}Br_{10}$ are located on the mirror (*i.e.* on layers with $y = 0, \frac{1}{2}$), they happen to be approximately on layers with $y = 1/8$, $3/8$, $5/8$ and $7/8$ in $Bi_{24}O_{31}Cl_{10}$, which is to be seen in connection with the fact that the A centering plus m $(x,0,z)$ of $A2/m$ is reduced to the c $(x,0,z)$ glide of $P2/c$.

4. Discussion

Our two structure models confirm most of the features of the model which Sillén & Edstrand (1942) had derived in an admirable manner by much poorer means than are available today. With respect to the (Bi,X) structure and to six of the O positions the three models are rather similar and differ only by some relatively small positional shifts. On the other side there are also some significant differences:

(i) Two of Sillén & Edstrand's (1942) O atoms have to be replaced by four other O atoms which have lower 'overall multiplicities'. This leads to a model which is compatible with the chemical formula without the necessity of assuming chemically unreasonable partial site occupations (see *Introduction*).

(2) The structure of $Bi_{24}O_{31}Cl_{10}$ (but not that one of $Bi_{24}O_{31}Br_{10}$) is a twofold superstructure of Sillén & Edstrand's (1942) model.

It is obvious that the differences between the two structures of $Bi_{24}O_{31}Cl_{10}$ and $Bi_{24}O_{31}Br_{10}$ obtained are only a matter of order and disorder, *i.e.* one can assume that the latter structure consists of two different subcells which are following just the same construction principles as the two different subcells in the former structure. The fact that the unit cell of $Bi_{24}O_{31}Br_{10}$ obtained is actually a superposition of the two $Bi_{24}O_{31}Cl_{10}$ subcells (with Cl replaced by Br, of course) may also be seen from the fact that in $Bi_{24}O_{31}Br_{10}$ the displacement parameters of those heavy atoms are relatively large, for which the interatomic vector between the two corresponding atoms in $Bi_{24}O_{31}Cl_{10}$ differs mostly from the pseudotranslation $(0,\frac{1}{2},0)$, namely Bi1, Bi5 and Bi6 (Fig. 1). It should be noted, however, that while the relationships between U^{11} and U^{33} are as expected for these atoms, the relatively large U^{22} value especially of Bi1 (0.08 $Å^2$) cannot be explained by this model, as the y component of the pseudotranslation is almost exactly $\frac{1}{2}$ in this case. An explanation for the large U^{22} could be a deviation of this atom from the position on the mirror, which would mean that the correct space group is actually $A2$ rather than $A2/m$ (see also §3). However, U^{ij} values practically do not change when calculations are performed in space group $A2$; therefore, $A2/m$ remains the 'space group of choice'.

It is not surprising that the relationship between the two very similar structures for X = Cl and Br can be described in terms of group–subgroup relations. Two maximal subgroup transitions, one of type IIa and one of type IIc, reduce the symmetry of the disordered $Bi_{24}O_{31}Br_{10}$ to that of ordered $Bi_{24}O_{31}Cl_{10}$.

$$\mathrm{Bi_{24}O_{31}Br_{10}} : A2/m \xrightarrow[\mathrm{II}a]{k[2]} P2/c \xrightarrow[\mathrm{II}c]{i[2](\mathbf{b}'=2\mathbf{b})} P2/c : \mathrm{Bi_{24}O_{31}Cl_{10}} \qquad (1)$$

Owing to the disorder in $Bi_{24}O_{31}Br_{10}$ the results of the corresponding structure analysis are certainly less reliable than those obtained for $Bi_{24}O_{31}Cl_{10}$. This is reflected in the fact that the four missing O atoms had to be introduced compared with the $Bi_{24}O_{31}Cl_{10}$ structure and also in the remaining ambiguity with respect to the correct space group ($A2/m$ or $A2$). In the following we will therefore restrict the discussion of our results mainly to the ordered structure of $Bi_{24}O_{31}Cl_{10}$.

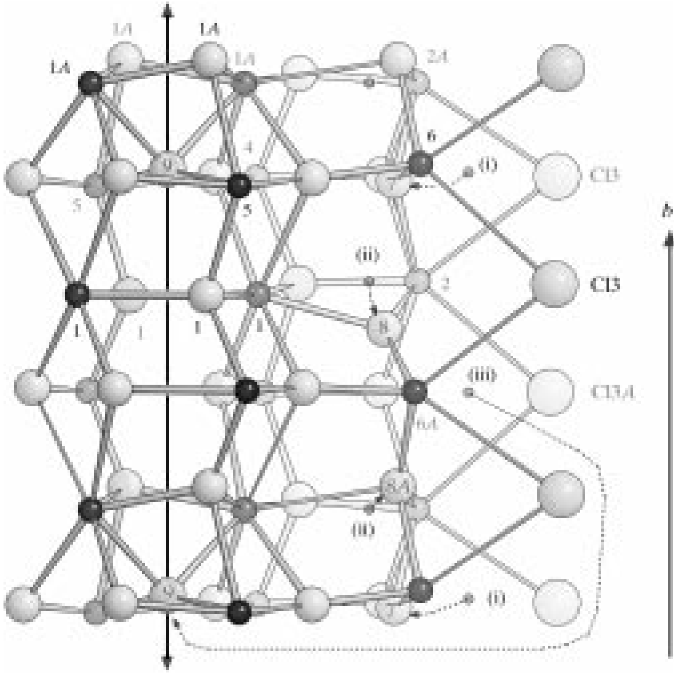

Figure 2
Part of the structure as seen from $[\overline{31},0\bar{2}]$ (indicated by the arrow in the upper right part of Fig. 1). Some Bi (small size; black) and O (medium size, light) atoms have been labeled with the numerical parts of their names. Atoms and bonds have been shaded with depth-dependent intensity. Small circles in the right part denote the positions of Sillén & Edstrand's (1942) atoms $O1^{SE}$ [labeled (i) and (iii)] and $O8^{SE}$ [labeled (ii)]. The double arrow at the left denotes a twofold axis. For arrows starting at (i), (ii) and (iii), see text.

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$).

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Bi1	0.08954 (12)	0.15098 (13)	0.31393 (4)	0.0160 (3)
Bi1*A*	0.07898 (12)	0.65569 (13)	0.30449 (3)	0.0142 (3)
Bi2	0.24586 (11)	0.11927 (12)	0.42714 (3)	0.0108 (2)
Bi2*A*	0.25409 (11)	0.65391 (13)	0.42667 (3)	0.0119 (3)
Bi3	0.42866 (11)	0.12419 (11)	0.54524 (3)	0.0091 (2)
Bi3*A*	0.43899 (11)	0.62388 (11)	0.54670 (3)	0.0092 (2)
Bi4	0.59455 (11)	0.12297 (12)	0.66644 (3)	0.0094 (2)
Bi4*A*	0.60071 (11)	0.61913 (12)	0.66265 (3)	0.0089 (2)
Bi5	0.79200 (12)	0.10376 (13)	0.78250 (3)	0.0129 (2)
Bi5*A*	0.75409 (11)	0.62361 (11)	0.78521 (3)	0.0105 (2)
Bi6	0.93266 (12)	0.15522 (12)	0.90838 (3)	0.0132 (3)
Bi6*A*	0.90338 (12)	0.62165 (11)	0.90284 (3)	0.0114 (2)
Cl1	1/2	0.1151 (13)	1/4	0.024 (2)
Cl1*A*	1/2	0.6313 (11)	1/4	0.017 (2)
Cl2	0.6551 (8)	0.1233 (8)	0.3684 (2)	0.0234 (18)
Cl2*A*	0.6619 (8)	0.6269 (8)	0.3700 (2)	0.0213 (18)
Cl3	0.8110 (9)	0.1264 (9)	0.4870 (2)	0.027 (2)
Cl3*A*	0.8037 (9)	0.6202 (8)	0.4909 (2)	0.0229 (18)
O1	0.1392 (19)	0.153 (2)	0.2342 (6)	0.011 (4)
O1*A*	0.140 (2)	0.602 (2)	0.2317 (6)	0.016 (4)
O2	0.3093 (19)	0.1240 (19)	0.3542 (5)	0.008 (4)
O2*A*	0.3074 (18)	0.6324 (18)	0.3546 (5)	0.007 (4)
O3	0.4777 (19)	0.124 (2)	0.4723 (6)	0.013 (4)
O3*A*	0.4688 (19)	0.6244 (19)	0.4718 (6)	0.010 (4)
O4	0.6054 (19)	0.130 (2)	0.5863 (6)	0.013 (4)
O4*A*	0.620 (2)	0.624 (2)	0.5881 (6)	0.014 (4)
O5	0.773 (2)	0.126 (2)	0.7046 (6)	0.016 (4)
O5*A*	0.7797 (19)	0.628 (2)	0.7017 (6)	0.013 (4)
O6	0.939 (2)	0.122 (2)	0.8389 (6)	0.015 (4)
O6*A*	0.918 (2)	0.631 (2)	0.8317 (6)	0.018 (4)
O7	1.138 (2)	0.116 (2)	0.9048 (6)	0.019 (4)
O8	1.071 (3)	0.769 (3)	0.8941 (7)	0.038 (6)
O8*A*	1.0152 (18)	0.3990 (19)	0.8992 (5)	0.009 (4)
O9	1	0.143 (3)	3/4	0.019 (6)

Figs. 1 and 2 clearly show that the positions of the O7, O8N and O9 atoms (other than those ones of Sillén & Edstrand, 1942: atoms '$O1^{SE}$', corresponding to our O7, and '$O8^{SE}$', corresponding to our O8N) do not follow the very regular pattern defined by atoms O1–O6 and already found by Sillén & Edstrand (1942). Actually, the positions of O7, O8N and O9 seemed to be rather arbitrary on first sight. However, a closer look revealed them to be highly reasonable and allowed a straightforward fictional 'mechanism' to be set up, by which Sillén & Edstrand's (1942) incorrect positions are transferred into the correct ones observed.

Without doubt, Sillén & Edstrand's (1942) $O1^{SE}$ and O8 ^{SE} positions (symbolized by '*' in Fig. 1 and by very small spheres in Fig. 2) would have actually been occupied had not the following reason stood against it: As already mentioned in the *Introduction* and can be clearly seen from Fig. 2, Sillén &

Table 3
Selected geometric parameters (Å^2, °).

Bi1—O1	2.398 (17)	Bi4—O2^{ii}	2.270 (16)
Bi1—O1^{i}	2.726 (19)	Bi4—O2*A*^{iii}	2.266 (16)
Bi1—O2	2.538 (19)	Bi4—O4	2.368 (17)
Bi1—O5^{ii}	2.656 (17)	Bi4—O5	2.13 (2)
Bi1—O5*A*^{iii}	2.240 (17)	Bi4*A*—Cl1^{iii}	3.473 (6)
Bi1—O6^{iv}	2.741 (17)	Bi4*A*—Cl1*A*^{iii}	3.400 (5)
Bi1—O6*A*^{v}	2.492 (19)	Bi4*A*—Cl2^{iii}	3.427 (8)
Bi1—O8^{v}	2.46 (2)	Bi4*A*—Cl2*A*^{iii}	3.440 (8)
Bi1*A*—O1*A*	2.264 (17)	Bi4*A*—O2^{iii}	2.289 (16)
Bi1*A*—O1*A*^{i}	2.50 (2)	Bi4*A*—O2*A*^{iii}	2.261 (15)
Bi1*A*—O2*A*	2.763 (18)	Bi4*A*—O4*A*	2.207 (17)
Bi1*A*—O5^{iii}	2.303 (18)	Bi4*A*—O5*A*	2.16 (2)
Bi1*A*—O5*A*^{iii}	2.673 (17)	Bi5—Cl1^{ii}	3.560 (5)
Bi1*A*—O6^{v}	2.469 (17)	Bi5—Cl1*A*^{iii}	3.754 (5)
Bi1*A*—O6*A*^{v}	2.898 (18)	Bi5—Cl2^{vi}	3.385 (7)
Bi1*A*—O8*A*^{v}	2.891 (16)	Bi5—Cl2*A*^{vii}	3.586 (7)
Bi1*A*—O9^{iii}	2.419 (16)	Bi5—O1^{ii}	2.214 (16)
Bi2—Cl3^{ii}	3.247 (7)	Bi5—O1*A*^{iii}	2.479 (18)
Bi2—Cl3*A*^{iii}	3.222 (7)	Bi5—O5	2.322 (18)
Bi2—O2	2.235 (16)	Bi5—O6	2.254 (19)
Bi2—O3	2.707 (19)	Bi5—O9	2.300 (4)
Bi2—O4^{ii}	2.511 (17)	Bi5*A*—Cl1^{iii}	3.470 (6)
Bi2—O4*A*^{iii}	2.488 (17)	Bi5*A*—Cl1*A*^{iii}	3.439 (5)
Bi2—O7^{iv}	2.267 (18)	Bi5*A*—Cl2^{vii}	3.316 (7)
Bi2—O8^{v}	2.21 (2)	Bi5*A*—Cl2*A*^{vii}	3.320 (6)
Bi2*A*—Cl3^{iii}	3.152 (7)	Bi5*A*—O1^{iii}	2.149 (17)
Bi2*A*—Cl3*A*^{iii}	3.315 (7)	Bi5*A*—O1*A*^{iii}	2.142 (18)
Bi2*A*—O2*A*	2.190 (16)	Bi5*A*—O6*A*	2.17 (2)
Bi2*A*—O3*A*	2.569 (19)	Bi5*A*—O5*A*	2.476 (17)
Bi2*A*—O4^{iii}	2.256 (17)	Bi6—O6	2.070 (17)
Bi2*A*—O4*A*^{iii}	2.583 (17)	Bi6—O7	2.09 (2)
Bi2*A*—O7^{v}	2.275 (18)	Bi6—O8*A*	2.128 (16)
Bi2*A*—O8*A*^{v}	2.581 (18)	Bi6—Cl3*A*^{vii}	3.269 (7)
Bi3—Cl2^{ii}	3.320 (7)	Bi6—Cl3^{vi}	3.436 (7)
Bi3—Cl2*A*^{iii}	3.307 (6)	Bi6—Cl2*A*^{vii}	3.438 (8)
Bi3—Cl3^{ii}	3.284 (9)	Bi6—Cl2^{vi}	3.773 (8)
Bi3—Cl3*A*^{iii}	3.292 (8)	Bi6*A*—Cl2^{vii}	3.390 (8)
Bi3—O3	2.201 (17)	Bi6*A*—Cl2*A*^{vii}	3.292 (8)
Bi3—O3^{ii}	2.244 (17)	Bi6*A*—Cl3^{vii}	3.313 (7)
Bi3—O3*A*^{iii}	2.304 (16)	Bi6*A*—Cl3*A*^{vii}	3.373 (7)
Bi3—O4	2.171 (19)	Bi6*A*—O8	2.07 (2)
Bi3*A*—Cl2^{iii}	3.339 (7)	Bi6*A*—O8*A*	2.102 (16)
Bi3*A*—Cl2*A*^{iii}	3.312 (7)	Bi6*A*—O6*A*	2.107 (18)
Bi3*A*—Cl3^{iii}	3.370 (9)	O1—O6*A*^{iii}	2.67 (2)
Bi3*A*—Cl3*A*^{iii}	3.327 (8)	O1*A*—O9^{iii}	2.52 (3)
Bi3*A*—O3^{iii}	2.247 (17)	O3—O3^{ii}	2.61 (3)
Bi3*A*—O3*A*	2.227 (16)	O3—O3*A*^{iii}	2.66 (2)
Bi3*A*—O3*A*^{iii}	2.248 (16)	O4—O7^{viii}	2.59 (3)
Bi3*A*—O4*A*	2.21 (2)	O5—O9	2.68 (2)
Bi4—Cl1^{ii}	3.240 (6)	O6—O9	2.690 (17)
Bi4—Cl1*A*^{iii}	3.276 (5)	O6*A*—O8	2.66 (3)
Bi4—Cl2^{ii}	3.362 (8)	O7—O8*A*	2.58 (2)
Bi4—Cl2*A*^{iii}	3.447 (8)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x - 1, -y, z - \frac{1}{2}$; (v) $x - 1, 1 - y, z - \frac{1}{2}$; (vi) $x, -y, \frac{1}{2} + z$; (vii) $x, 1 - y, \frac{1}{2} + z$; (viii) $2 - x, y, \frac{3}{2} - z$.

Edstrand's (1942) O1^{SE} atom (O7 in the present work) is only 2.2 Å away from Cl3, which is much too close. O7 is therefore repelled by Cl3 and rotated about the vector Bi2 → Bi6 to a position approximately in the plane defined by Bi2N and Bi6N [arrows labeled (i) in Fig. 2], with a distance of 3.25 Å to Cl3 (sum of the ionic radii = 3.2 Å). This position is too close (2.2 Å) to Sillén & Edstrand's (1942) two atoms O8^{SE} in the neighbourhood (O8 and O8*A* in $Bi_{24}O_{31}Cl_{10}$), therefore, these atoms are themselves shifted away from O7 [*i.e.* towards each other; (ii) in Fig. 2], thus yielding distances of 2.86 (O8) and 2.62 Å (O8*A*) to O7. These latter shifts prevent the pendant of O1^{SE} in the second subcell from moving to the location 'O7*A*', *i.e.* the space between Cl3*A*, O8 and O8*A* is now too small to accommodate another O atom. Thus, 'steric hindrance' is the reason that this latter atom is missing in the structure.

Table 4
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Bi1	0.08569 (15)	0	0.05880 (6)	0.0480 (6)
Bi2	0.25344 (12)	0	0.17509 (4)	0.0228 (4)
Bi3	0.43453 (12)	0	0.29464 (4)	0.0108 (3)
Bi4	0.60015 (11)	0	0.41348 (4)	0.0114 (3)
Bi5	0.77636 (17)	0	0.53264 (5)	0.0309 (5)
Bi6	0.92640 (17)	0	0.65308 (5)	0.0317 (5)
Br1	1/2	0	0	0.0151 (10)
Br2	0.6637 (3)	0	0.11904 (11)	0.0190 (8)
Br3	0.8179 (4)	0	0.24020 (13)	0.0234 (8)
O1	0.138 (2)	0	−0.0158 (8)	0.027 (6)
O2	0.3097 (19)	0	0.1043 (7)	0.011 (4)
O3	0.478 (2)	0	0.2228 (8)	0.020 (5)
O4	0.6112 (19)	0	0.3378 (7)	0.013 (4)
O5	0.778 (2)	0	0.4542 (7)	0.019 (5)
O6	0.931 (2)	0	0.5837 (8)	0.021 (5)
O7	1.146 (4)	0	0.6472 (15)	0.024 (11)
O8	1.083 (7)	1.309 (19)	0.643 (2)	0.036 (18)
O8*A*	1.021 (5)	0.45 (2)	0.6458 (18)	0.024 (17)
O9	1	0	1/2	0.021 (14)

At this point we have a unit cell corresponding to the formula $2[Bi_{24}O_{30}Cl_{10}]^{2+}$, which can be completed to $2Bi_{24}O_{31}Cl_{10}$ by one additional O atom with multiplicity 2. In fact, there is one single region in the structure which is suited to accept additional O atoms: the twofold axis in the center of the 'tube' of face-sharing rhomb-dodecahedra formed by Bi1*N*/O1*N*/Bi5*N*/O5*N*/O6*N*. This region is completely isolated from any Cl atoms and it offers more space than the similar adjacent Bi1*N*/Bi2*N*/Bi4*N*/Bi6*N*/O4*N*–8*N* tubes. Correspond-

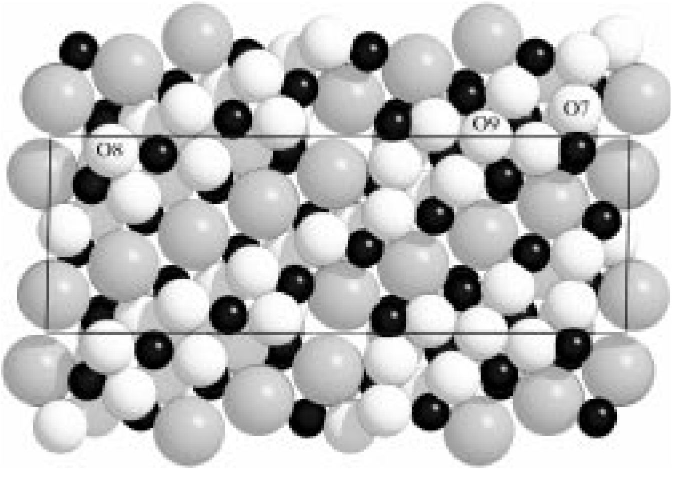

Figure 3
Ionic hard-sphere (space-filling) model of the structure displayed in Fig. 1. Small, black spheres symbolize Bi atoms; large grey spheres Cl; medium-sized light spheres O. Sphere radii are: Bi 0.97, Cl 1. 8 and O 1.38 Å.

ingly, the introduction of the missing O7*A* atom under the name O9 at the twofold axis in only one of the two subcells completes the structure (iii). To be more precise, the position of O9 is found near the center of the (distorted) rhombdodecahedron defined by Bi1*N*, O1*N*, Bi5 and O5.

The consequences of this latter operation can be seen from Figs. 1 and 2: the tetrahedron of Bi atoms around O9 (Bi1*A*/Bi5) has shrunk significantly (Fig. 1, left part) and the O1*A* atoms in the neighborhood are pushed away from O9 in the **b** direction (Fig. 2), both effects giving additional evidence to the presence of O9. The fact that O9 is not too welcome at this position can be concluded from the frequency with which this atom appears in the list of shortest O—O distances (Table 4).

However, we do not know why O9 occupies just this one of four possible similar positions in the tube (with idealized *y* parameters of 1/8 ± 0.04, 5/8 ± 0.04). It is clear that the choice of position is exclusively correlated with the arrangement of the atoms O7, O8 and O8*A*: the actual position is in the (010) atom layer which also contains O7; there is a slight out-of-plane shift (0.04 in terms of *y* if counted in relation to the closest Bi atoms) for O9 as well as for O7, but in opposite directions.

How well O7, O8 and O9 fit into their respective neighbourhoods is demonstrated by the hard-sphere model of Fig. 3 which is also well suited to illustrate the description of the overall structure of $Bi_{24}O_{31}X_{10}$: as already elaborated by Sillén & Edstrand (1942), this structure can be described as consisting of stair-like [Bi,O] layers formed parallel to (10$\bar{2}$), which are held together by layers of *X* atoms, the [Bi,O] layers themselves consisting of identical mutually connected $\{^{1}_{\infty}\}$[Bi,O] 'boards' (Sillén & Edstrand, 1942) perpendicular to (010) and making an angle of approximately 26° to **c** [*i.e.* the boards are oriented parallel to (90,$\overline{13}$)]. Such [Bi,O] boards resemble sections of $\{^{2}_{\infty}\}[BiO]^+$ layers as they are common structure elements in Bi—O—*X* compounds (*e.g.* Sillén, 1942). In Fig. 1 the boards are seen side-on (uniformly shaded areas); Fig. 4 shows a planar view of the (only) board from Figs. 1 and 3, which is contained as a whole in the displayed model. The board has a thickness of 3.0 Å (if only atom centers are accounted for) and a width of 26.5 Å. Each region II of Fig. 4 is attached to region II of an identical neighbouring board by sharing Bi atoms (and O9), thus generating a limited region with a five-atom layered structure (Bi—O—Bi—O—Bi) similar to that which can be found in the structure of Bi_3O_4Cl (Eggenweiler *et al.*, 1998*b*). Fig. 4 demonstrates how the relatively regular structure in the central strip (region I) is increasingly distorted in regions II when approaching the rims.

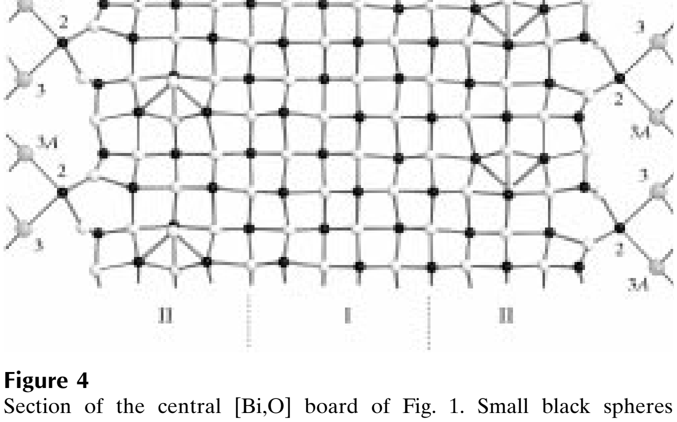

Figure 4
Section of the central [Bi,O] board of Fig. 1. Small black spheres symbolize Bi atoms; large grey spheres Cl; medium-sized light spheres O. The view direction is indicated by the arrow near the center of Fig. 1. **b** is pointing upwards. The definitions of regions I and II are given in the text.

Table 5
Selected geometric parameters (Å^2, °).

Bi1—O1	2.30 (3)	Bi3—O3^{ii}	2.254 (11)
Bi1—O1^{i}	2.61 (2)	Bi3—O4	2.207 (19)
Bi1—O2	2.645 (19)	Bi4—Br1^{viii}	3.4330 (180
Bi1—O5^{ii}	2.463 (13)	Bi4—Br2^{vii}	3.479 (3)
Bi1—O6^{iii}	2.654 (16)	Bi4—O2^{ii}	2.266 (10)
Bi1—O8^{iv}	2.63 (7)	Bi4—O4	2.27 (2)
Bi1—O8*A*^{v}	2.70 (6)	Bi4—O5	2.18 (2)
Bi1—O9^{iii}	2.8039 (17)	Bi5—Br1^{viii}	3.578 (2)
Bi2—Br3^{ii}	3.316 (4)	Bi5—Br2^{ix}	3.470 (4)
Bi2—O2	2.20 (2)	Bi5—O1^{ii}	2.240 (12)
Bi2—O3	2.68 (2)	Bi5—O5	2.35 (2)
Bi2—O4^{ii}	2.459 (12)	Bi5—O6	2.19 (2)
Bi2—O7^{iii}	2.43 (2)	Bi5—O9	2.473 (2)
Bi2—O8^{vi}	2.12 (7)	Bi6—Br3^{ix}	3.473 (4)
Bi2—O8*A*^{iii}	2.52 (5)	Bi6—O6	2.08 (2)
Bi3—Br2^{ii}	3.423 (3)	Bi6—O7	2.24 (5)
Bi3—Br3^{vii}	3.412 (3)	Bi6—O8^{x}	2.04 (7)
Bi3—Bi3^{vii}	3.600 (3)	Bi6—O8*A*	2.04 (8)
Bi3—O3	2.20 (2)	Bi6—O8*A*^{x}	2.43 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $x-1, y-\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-1, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $x-1, y-\frac{3}{2}, z-\frac{1}{2}$; (vii) $1-x, -\frac{1}{2}-y, \frac{1}{2}-z$; (viii) $x, y-\frac{1}{2}, \frac{1}{2}+z$; (ix) $x, \frac{1}{2}+y, \frac{1}{2}+z$; (x) $x, 1-y, z$.

In Bi—O compounds, Bi—O bond lengths cover a wide range between 2.0 Å and more than 3 Å (*cf.* Ketterer *et al.*, 1985). In $Bi_{24}O_{31}Cl_{10}$, Bi—O bond lengths range from 2.1 to 2.9 Å. The next largest Bi—O distance (Bi1—O9 3.15 Å) ought to be non-bonding [*cf.* bond lengths Bi5—O9 (2.30 Å) and Bi1*A*—O9 (2.42 Å)]. Bi—Cl bonds have lengths between 3.2 and 3.8 Å, a range which should be compared to those which can be found for BiOCl (3.1–3.5 Å; Keramidas *et al.*, 1993), Bi_3O_4Cl (3.2–3.6 Å; Eggenweiler *et al.*, 1998*b*) and $Bi_4O_5Cl_2$ (3.1–3.5 Å; Hopfgarten, 1976).

The average coordination number (c.n.) of the Bi and Cl atoms in $Bi_{24}O_{31}Cl_{10}$ is unusually high: all but three have an eight- or ninefold (Bi1*A*) coordination. The three exceptions are Bi6 (c.n. 6), Bi6*A* (7) and Cl3 (6), which are located at the edge of the [Bi,O] board. The idealized coordination of most of the remaining Bi atoms is [8ap] (Lima-de-Faria *et al.*, 1990), that of Bi1 and the remaining Cl atoms [8cb]; Bi1*A* shows an [8cb1c] coordination with O9 as the cap; the coordination polyhedra of Bi2*N* and Bi5 (c.n. 8) are irregular.

As has been observed for other Bi—O—*X* compounds (Ketterer *et al.*, 1985), the heavy atom (Bi,*X*) structure of $Bi_{24}O_{31}X_{10}$ may be seen as a superstructure of a (distorted) tetragonal body-centered subcell of roughly 4 × 4 × 5 Å. In this case, the subcell is monoclinic with $\mathbf{a}_{sub}$ = 3/17**a** + 2/17**c**, $\mathbf{b}_{sub}$ = **b**, $\mathbf{c}_{sub}$ = −7/17**a** + 1/17**c**. For *X* = Cl, this corresponds to the parameters a_{sub} = 3.94, b_{sub} = 3.99, c_{sub} = 4.45 Å, β_{sub} = 95°.

The formation of $Bi_{24}O_{31}X_{10}$ (X = Cl, Br) can be expressed by (2); it would be most interesting to compare their structures to the hitherto unknown structure of $Bi_7O_9I_3$ (Klimakov *et al.*, 1974; Krämer, 1979) which is formed due to the formal equation (3).

$$3.1Bi_2O_3 + BiX_3 \longrightarrow Bi_{7.2}O_{9.3}X_3 \quad (= 0.3Bi_{24}O_{31}X_{10}) \qquad (2)$$

$$3Bi_2O_3 + BiI_3 \longrightarrow Bi_7O_9I_3 \qquad (3)$$

Work is in progress with the aim of making such a comparison possible.

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