Crystal Structures of $\sim[M^{I}_{5}Cl][Bi_{48}O_{59}Cl_{30}]$, M^{I} = Cu, Ag

Bengt Aurivillius

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology, P.O. Box 124, S-22100 Lund, Sweden

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Compounds of the type $[M^{I}_{5}Cl][Bi_{48}O_{59}Cl_{30}]$, M^{I} = Cu, Ag have been prepared and their structures determined from single-crystal X-ray data. Both compounds crystallize in space group $P\bar{6}2m$ and are best described by their substructures with $C = c/2$. The Cu compound has the cell dimensions a = 20.0248(13) and 3.8680(3) Å, with V = 1343.2(2) Å^3 and $Z = \frac{1}{2}$. 698 reflections with $I > 3\sigma(I)$ were registered, and the final R was 0.049. The a axes and the space group are the same for the large cell, but c = 7.7360(6) Å and Z = 1. The final R was 0.052 for 790 reflections. Reflections hkl and $hk\bar{l}$ with $I > 3\sigma(I)$ were registered for the Ag compound. The cell dimensions are a = 20.0893(12), 3.8589(3) Å, V = 1348.7(2) Å^3 and $Z = \frac{1}{2}$. The final R was 0.052 for 1111 dependent reflections. The a axes and space group are the same for the large cell, but c = 7.7178(6) Å and Z = 1. The final R was 0.058 for 1334 reflections. Disorder probably exists in the large cells. The structures are, with some approximation, formally built up from $[M^{I}_{5}Cl]$ parts and $[Bi_{48}O_{59}Cl_{30}]$ parts. The parts containing Bi, O and Cl atoms are closely related to the previously known structure of $Bi_4O_5Cl_2$. A model is presented to explain the relationship between BiOCl and the Bi,O,Cl parts of the present structures. The model is based on sharing of Bi atoms between different BiO_4 pyramids. Starting from this model the relative thermal stabilities of BiOCl, $Bi_4O_5Cl_2$, the present compounds and $Bi_{24}O_{31}Cl_{10}$ are discussed. The $[M^{I}_{5}Cl]$ parts are disordered and differ between the Cu and Ag compounds. Copper is 3-coordinated by Cl in a nearly planar fashion: Cu–3Cl≈2.3 Å. Two of the Cl atoms belong to the Bi,O,Cl part of the structure. Silver is coordinated to five Cl atoms in the form of a deformed square pyramid. Four of the Cl atoms belong to the Bi,O,Cl part of the structure. In contrast to BiOCl, $Bi_4O_5Cl_2$ and $Bi_{24}O_{31}Cl_{10}$, but like $Bi_4O_5Br_2$, the present structures belong to a non-centrosymmetric space group.

A vast number of mixed Cu,Bi and Ag,Bi sulfides are known. Aside from the superconductors based on mixed oxides of Bi, Ca, Sr and Cu, for example $Bi_2(Sr_{1-y}Ca_y)_3Cu_2O_{10-\delta}$,[1] very few mixed oxides, mixed halides or mixed oxide halides containing Cu(Ag) and Bi are known. On the other hand, a large number of mixed oxide halides of Bi^{3+} and mono- or divalent metal ions have been described, most of them crystallizing in a structure of the Nd_2O_2Se ($LiBi_3O_4Cl_2$) type. One of these compounds, $CdBiO_2Br$, exists in two closely related forms.[2] It is therefore possible that the symmetry is lower than tetragonal, and/or the real unit cell is larger. One reason for this may be that Bi and Cd in one of the forms occupy different point positions, as is the case for Pb and Sb in $PbSbO_2Cl$ of the same structure type.[2] The present investigation was started in the hope of finding compounds containing Bi^{3+}, Cu^{2+}, O^{2-} and Cl^- with a distorted or non-distorted Nd_2O_2Se type of structure. As will be seen, the result was a Cu(I) compound with a crystal structure related to those of the so-called Arppe compounds $Bi_{24}O_{31}X_{10}$ (Ref. 2).

Experimental

The compound $\sim[Cu_5Cl][Bi_{48}O_{59}Cl_{30}]$ has a formula weight of 12392 and space group $P\bar{6}2m$. Cell dimensions are a = 20.0248(23), c = 7.7360(6) Å and V = 2686.4(4) Å^3 with Z = 1. D_x = 7.65 and D_m = 7.65–7.69 g cm^{-3}. μ(Mo$K\alpha$) is 763 cm^{-1}. Corresponding values for $\sim[Ag_5Cl][Bi_{48}O_{59}Cl_{30}]$ are as follows: formula weight 12613, space group $P\bar{6}2m$, a = 20.0893(12), c = 7.7178(6) Å, V = 2697.4(3) Å^3 with Z = 1. D_x = 7.77 and D_m = 7.71–7.90 g cm^{-3}. μ(Mo$K\alpha$) = 758 cm^{-1}.

Weighed amounts of 240 mg CuO and 780 mg BiOCl, corresponding to the composition $CuBiO_2Cl$, were fused in a small, open platinum crucible for 10 min at 820 °C. Some $BiCl_3$ evaporated during the non-equilibrium fusion. The Cl content after the reaction was 10.2 % (w/w) by analysis. A very fine, nearly circular, and seemingly black needle was picked out from the reaction product. It was mounted in a Weissenberg camera and rotated around its needle axis. The photographs indicated a hexagonal unit cell with a = 20.0 and c = 3.9 Å, the c axis extending along the needle axis. No systematic extinctions were found. About 40 % of the lines in the powder photographs from the main bulk of the sample could be indexed using the cell dimensions given above. At this stage the EDAX method available at this Institute would have been of great help. However, routine methods for the simultaneous analysis of Bi,Cu and Cl had not been worked out, so other methods were used. The method of preparing the hexagonal phase could not always be reproduced, and therefore a sufficient number of single crystals for conventional analysis could

Table 1. Compositions, cell dimensions (Å) and observed densities (g cm^{-3}) for some reaction products containing the present Cu and Ag compounds.

Mol fractions (%)			Q(%)[a]	Other phases	a	c	ϱ
Cu compound							
Cu_2O	BiOCl	Bi_2O_3					
8.1	72.1	19.8	96	–	20.0248(13)	3.8680(3)	7.68
8.1	72.1	19.8	93	–	20.0308(15)	3.8681(4)	7.69
8.2	70.6	21.2	90	–	20.0237(13)	3.8673(3)	7.65
8.2	70.6	21.2	86	–	20.0227(17)	3.8678(4)	7.69
11.4	81.8	6.8	83	BiOCl	20.0227(15)	3.8678(4)	7.19
5.0	75.0	20.0	82	BiOCl	20.0249(11)	3.8679(3)	
10.0	70.0	20.0	82	$Bi_{24}O_{31}Cl_{10}$	20.0241(12)	3.8682(3)	
33.3	66.7	0	78	Cu_2O	20.0101(25)	3.8689(4)	
50.0	50.0	0	76	Cu_2O	20.0196(29)	3.8677(5)	
5.0	70.0	25.0	75	$Bi_{24}O_{31}Cl_{10}$	20.0320(15)	3.8678(3)	
Ag compound							
Ag_2O	BiOCl	Bi_2O_3					
10.0	75.0	15.0	89	?	20.0837(14)	3.8591(4)	7.71
8.1	72.1	19.8	86	?	20.0902(12)	3.8588(4)	7.79
12.5	75.0	12.5	83	?	20.0842(14)	3.8588(5)	7.69
8.2	70.6	21.2	77	$Bi_{24}O_{31}Cl_{10}$	20.0864(18)	3.8586(5)	7.90
7.1	71.4	21.4	77	$Bi_{24}O_{31}Cl_{10}$	20.0777(14)	3.8576(4)	7.84
15.0	75.0	10.0	77	$Bi_{24}O_{31}Cl_{10}$	20.0813(14)	3.8597(4)	7.65
5.4	75.5	19.2	71	BiOCl	20.0957(32)	3.8519(7)	
15.0	80.0	5.0	71	AgCl,BiOCl	20.0706(44)	3.8545(15)	

[a]See text.

not be produced. Instead the single crystal was transferred to a Nicolet *P3m* diffractometer, and data assuming Laue symmetry *6/mmm* were registered with Mo$K\alpha$ radiation. 505 independent reflections with $I > 3\sigma(I)$, corrected for Lp^{-1} but not for absorption, were used for the calculations. Standard computing programs[3] were used for this and other calculations performed in the present investigation. After some work (see below), a trial structure corresponding to an approximate composition of $Cu_3[Bi_{24}O_{30}Cl_{15}]$ with monovalent copper was first reached. To test this composition Cu_2O, BiOCl and Bi_2O_3 were mixed in different proportions similar to that shown above. The samples were transferred to glass tubes and were first preheated under evacuation to about 300 °C. The tubes were then sealed and heated to 720 °C for 1 h. They were then crushed, their contents thoroughly mixed and the same procedure repeated but with a heating time of 3 h.

Powder photographs were taken of the main bulks. The samples were nearly colourless with a faint yellow tint. Single crystals in the form of needles were formed, especially inside the top and at the walls of the glass tubes. The lines of the powder photographs were indexed and the fraction, Q, of the lines that could be explained by the present unit cell were noted. Results down to $Q = 0.75$ are given in Table 1, where the measured densities, the unit-cell dimensions and the presence of other phases are also given. The densities were determined from the weight losses in benzene, and the compositions are given as mol percentages of Cu_2O, BiOCl and Bi_2O_3. The title composition is $\sim[M_3^{I}Cl][Bi_{48}O_{59}Cl_{30}]$, with Cu_2O or Ag_2O 6.00, BiOCl 74.3 and Bi_2O_3 20.4 mol %, and the calculated density is 7.65 g cm^{-3} for the Cu compound and 7.77 g cm^{-3} for the Ag compound. Since the trial structure (see above) involved Cu^+, efforts were also made to synthesize the corresponding Ag^+ compound using the same method as that described above. Ag_2O or AgCl, BiOCl and Bi_2O_3 were used as starting materials. Preliminary work showed that AgCl reacted sluggishly, so that main work was performed with Ag_2O. Here preheating under evacuation was essential, since O_2 was evolved owing to an unwanted decomposition of Ag_2O. Needle-shaped colourless crystals were formed as a result of these syntheses. Powder photographs indicated a hexagonal unit cell with dimensions differing only slightly from those of the copper compound. In Table 1 results down to $Q = 0.71$ are given in the same way as for the Cu compound. It is seen from Table 1 that the "purest" samples have higher M_2O contents and lower BiOCl contents that are valid for the finally adopted, approximated title composition. A discussion of the discrepancies is given later. The observed densities fall in the expected region.

As the compositions of the starting mixtures given in Table 1 may differ from those of the reaction products, conventional chemical analyses were made for one Cu and one Ag compound.

Result	Non-reacted mixture (mol %)	Found reacted sample (mol %)
Cu_2O	8.24	8.0
BiOCl	70.58	71.5
Bi_2O_3	21.18	20.6
Ag_2O	8.24	7.6
BiOCl	70.58	70.2
Bi_2O_3	21.18	22.2

Considering the errors in the analyses no large changes in composition have occurred on reacting the mixtures for 4 h in glass tubes at 720 °C. Efforts were also made to prepare the corresponding gold compound using Au_2O_3 as starting material. Powder photographs indicated the presence of metallic gold but not of the present phase in the reaction products.

Structure determination and refinement

Copper compound. It was mentioned above that the Weissenberg and diffractometer data were registered for a single crystal picked out from a reaction product of approximate composition $CuBiO_2Cl$. At the beginning of the single-crystal work the unit-cell content was unknown. It could, however, be assumed that the Bi atom positions should have a major influence upon the observed intensities. Diffractometer data were sampled assuming Laue symmetry *6/mmm*. Of the 00*l* reflections present, 001, 003 and 005 had $I/\sigma(I)$ values of 3.8, 2.1 and 2.3, respectively. The possibility that 00*l* reflections were systematically absent for *l* odd could therefore not be excluded. To obtain a starting point for further calculations the cell content was arbitrarily assumed to be $Cu_{12}Bi_{12}O_{18}Cl_{24}$, with calculated density 5.45 g cm^{-3}. A three-dimensional Patterson function using the diffractometer data was calculated. It was noted (i) that only two, small, maxima occurred on the lines $(u,0,0)$ and $(u,0,\frac{1}{2})$. Furthermore (ii) all high peaks on the map were situated at $w = 0$ and $\frac{1}{2}$. Space group $P6_322$ (00*l* absent for *l* odd) was first tried, but owing to observations (i) and (ii) the Patterson function could not be interpreted. Direct methods in the form of the program MULTAN80 also failed. Space groups within Laue symmetry *6/mmm* lacking systematic extinctions were then studied, taking observations (i) and (ii) into account. Space group $P\bar{6}2m$ seemed to be the only promising case. Direct methods in the form of the program MULTAN80 were applied assuming space group $P\bar{6}2m$, and a solution was obtained with 24 heavy atoms located at three- and six-fold positions with $z = 0$ or $\frac{1}{2}$. Least-squares calculations showed that one three-fold position was disordered in the *z* direction and that one six-fold position was split up into two half-occupied six-fold positions with the same *z* value. By following usual procedures, the positions of 30 oxygen atoms and 15 chlorine atoms could be ascertained. The distances to Cl and O and the coordination angles strongly indicated that the 24 heavy atom positions were occupied by Bi atoms. Further difference electron-density maps revealed three Cu atoms disordered in the *z* direction and also disordered atoms, probably Cl, at the position $\pm 00z$. The final *R* for 505 reflections was 0.06. The final thermal and positional parameters for this first refinement are not given here, but they differ very little from those given in Table 2.

A renewed inspection of the rotation photographs of the Cu compound revealed barely visible interlayer lines. New data using the larger unit cell were therefore accumulated for the Cu compound. A needle-shaped single crystal of length 220 μm and with a cross-section of about 100 μm^2 was picked out from another $CuBiO_2Cl$ melt (see above) and mounted in a Nicolet *P3m* diffracometer using Mo*K*α radiation. μ(Mo*K*α) 763 cm^{-1} was calculated from the composition finally reached (see below), and absorption and Lp^{-1} corrections were performed. The transmission factors varied between 0.32 and 0.50, and $(\sin\Theta/\lambda)_{max}$ was 0.8083. A total of 790 independent reflections with $I > 3\sigma(I)$ were measured, of which only 92 had odd *l* values. The statistically most reliable of these reflections was (461) with $I/\sigma(I) = 8.9$. None of the 00*l* reflections with *l* odd had intensities differing significantly from zero. Thus systematic absences of odd 00*l* reflections are possible. No other systematic absences were detected in the total intensity data. Space group $P6_322$ was again considered but with little success. Therefore calculations were performed for space group $P\bar{6}2m$ using the parameters obtained from the first refinement with due consideration for the doubling of the *c* axis. The Bi atoms were first considered. Because of the doubling of the *c* axis there are two possibilities for their new *z* parameters, either (i) *z*(new) (Table 3) = $\frac{1}{2}$*z*(old) (Table 2) or *z*(new) = $\frac{1}{2}[z(\text{old}) + \frac{1}{2}]$ (Table 2). With (i) the deviation of *z*[Bi(5)], Table 2, from $\frac{1}{2}$ could be explained, and the atoms Bi(4) and Bi(6) could be separated by assuming that their *z*(new) values differed by $\frac{1}{2}$ in the large unit cell (cf. Table 3). The atom Bi(3), Table 2, had to be resolved into two atoms Bi(3) and Bi(7) in Table 3, with their *z* values differing by $\frac{1}{2}$. With (ii) no splitting of Bi(3) is needed, but the atoms Bi(1), Bi(2) and Bi(5) must be split into two atoms each with $\Delta z = \frac{1}{2}$ in the large unit cell. Furthermore, disorder must be assumed for the atoms Bi(4), Bi(5) and Bi(6). Least-squares calculations favoured possibility (i). With the restrictions given above *z*(new) could be fixed arbitrarily for the pairs Bi(4)/Bi(6) and Bi(3)/Bi(7), whereafter least-squares calculations were performed. The Cu atom and the light atom positions were then split up according to the above scheme.

Final positional and thermal parameters are given in Table 3. The final *R* factor was 0.052 for all 790 reflections. R_w and *S* were 0.057 and 1.1021 for 789 reflections. ($|F_o|/|F_c|$) was >9.99 for one reflection.) Space group $P\bar{6}2m$ is acentric, but anomalous dispersion was not introduced. The separate *R* factor was 0.111 for the 92 *l* odd reflections

Table 2. Final positional and thermal parameters for the present Cu and Ag compounds, small cells, $C = 3.8680(3)$ and 3.8589(3) Å, respectively. B_{eq} is calculated as $8\pi^2/3\Sigma(\text{r.m.s.})^2$. The site in $P\bar{6}2m$ is given after the number of atoms. For the dashed lines, see the text.

Atom	*x*	*y*	*z*	No. of atoms	B_{eq}	*B*
Cu compound						
Bi(1)	0.7556(2)	0	1/2	3,3 *g*	0.90(5)	
Bi(5)	0.4749(2)	0	0.541(5)	3,6 *i*	1.43(22)	
Bi(2)	0.1328(1)	0.3586(1)	1/2	6,6 *k*	0.70(5)	
Bi(3)	0.4679(1)	0.6569(1)	0	6,6 *j*	0.95(5)	
Bi(4)	0.5676(4)	0.9049(4)	0	3,6 *j*	1.99(18)	
Bi(6)	0.5804(3)	0.8880(3)	0	3,6 *j*	0.74(12)	
Cu	0.1031(9)	0	0.882(5)	2.68(18), 6 *i*		2.4(5)
Cl(1)	0.2230(9)	0.6690(9)	1/2	6,6 *k*		1.0(2)
Cl(3)	0.3318(10)	0	0	3,3 *f*		1.1(3)
Cl(5)	0.1087(10)	0.2178(8)	0	6,6 *j*		1.4(2)
O(1)	0.2478(22)	0.3589(22)	1/2	6,6 *k*		0.8(6)
O(2)	0.1376(21)	0.4694(22)	1/2	6,6 *k*		0.7(6)
O(3)	0.6946(25)	0	0	3,3 *f*		0.5(7)
O(5)	0.1886(22)	0.4153(20)	0	6,6 *j*		0.4(5)
O(7)	0.0845(20)	0.5381(19)	0	6,6 *j*		0.4(5)
O(9)	0.587(4)	0	0.587(23)	3,6 *i*		2.4(17)
Cl(6)	0	0	0.638(18)	0.75, 2 *e*		1.5(9)
O(10)	0	0	0.648(19)	1,2 *e*		−1.3(9)
Cu(2)	0	0	0.649(20)	0.16(8), 2 *e*		−1.6(16)
Ag compound						
Bi(1)	0.7529(1)	0	1/2	3,3 *g*	0.77(5)	
Bi(5)	0.4747(1)	0	1/2	3,3 *g*	1.89(6)	
Bi(2)	0.1342(1)	0.3606(1)	1/2	6,6 *k*	0.70(5)	
Bi(3)	0.4671(1)	0.6557(1)	0	6,6 *j*	0.95(6)	
Bi(4)	0.5647(3)	0.9056(3)	0	3,6 *j*	1.66(15)	
Bi(6)	0.5793(3)	0.8874(3)	0	3,6 *j*	0.59(11)	
Ag	0.1327(5)	0	1/2	2.39(9), 3 *g*	2.73(24)	
Cl(1)	0.2233(8)	0.6682(9)	1/2	6,6 *k*	0.9(4)	
Cl(3)	0.3334(12)	0	0	3,3 *f*	1.4(4)	
Cl(5)	0.1070(9)	0.2172(8)	0	6,6 *j*	1,6(4)	
O(1)	0.2488(20)	0.3590(21)	1/2	6,6 *k*		0.5(6)
O(2)	0.1426(19)	0.4715(19)	1/2	6,6 *k*		0.2(4)
O(3)	0.6928(21)	0	0	3,3 *f*		0.2(7)
O(5)	0.1911(23)	0.4153(23)	0	6,6 *j*		0.9(6)
O(7)	0.0810(23)	0.5370(22)	0	6,6 *j*		1.2(6)
O(9)	0.587(4)	0	0.590(16)	3,6 *i*		1.3(12)
Cl(6)	0	0	0.417(16)	0.70(20), 2 *e*		1.8(17)
O(10)	0	0	0.413(18)	1,2 *e*		−0.5(12)
Ag(2)	0	0	0.417(16)	0.23(6), 2 *e*		2.1(17)

and 0.048 for the 698 even ones. The results of the refinements as shown in Table 3 are hardly satisfactory. Although all the B_{eq} values of the Bi atoms are positive, one of the r.m.s. components of Bi(3) is imaginary, and the isotropic temperature factors are uneven, four of them being negative. The position of the O(2) atom oscillated during the refinements when its *z* value was varied, and *z* was finally fixed at $\frac{1}{4}$ (cf. Table 3). The occupancy number of Cl(6) could not be varied, and it had to be fixed to 1.5 atoms in the two-fold position. Finally the *R* factor for the *l* odd reflections was much larger than for the *l* even ones (see above). Other inadvertences are common to all the present refinements and will be discussed later. Many of the present discrepancies must be due to the fact that only few and weak *l* odd reflections are present. For instance, the atoms O(3) and O(4) (Table 3) at $z = \frac{1}{2}$ and 0 in three-fold positions could scarcely be expected to be properly resolved. Another effect may be that disorder can also be present in the large unit cell. Thus, for example, the atoms Bi(4) and Bi(6) may partially exchange their *z* values (cf. Table 3). In view of such possible exchanges and also of the difficulties in resolving pairs such as O(3) and O(4), it seemed appropriate to make a new refinement using the small unit cell. The same data set as before was used, but the *l* odd reflections were deleted. The results of these calculations are given in Table 2. On making this refinement it was found that *z* for Bi(5) deviated more from $\frac{1}{2}$ than could be expected from Table 3, that the splitting of

Table 3. Final positional and thermal parameters for the present Cu and Ag compounds, large cells, $c = 7.7360(6)$ and 7.7178(6) Å, respectively. B_{eq} is calculated as $8\pi^2/3\Sigma(\text{r.m.s.})^2$.

Atom	*x*	*y*	*z*	No. of atoms	B_{eq}	*B*
Cu compound						
Bi(1)	0.7557(2)	0	0.2522(15)	6	0.84(6)	
Bi(5)	0.4749(2)	0	0.2451(15)	6	2.13(9)	
Bi(2)	0.1328(1)	0.3586(1)	0.2512(10)	12	0.72(5)	
Bi(3)	0.4689(3)	0.6597(3)	1/2	6	0.84(16)	
Bi(7)	0.4669(4)	0.6545(3)	0	6	1.07(19)	
Bi(4)	0.5676(3)	0.9036(3)	1/2	6	2.03(16)	
Bi(6)	0.5812(3)	0.8887(3)	0	6	0.91(12)	
Cu	0.1051(18)	0	0.421(5)	3		2.2(7)
Cu(1)	0.1011(20)	0	0.041(6)	3		2.9(10)
Cl(1)	0.2227(9)	0.6692(9)	0.258(5)	12		0.94(24)
Cl(2)	0.337(3)	0	0	3		0.9(9)
Cl(3)	0.3269(23)	0	1/2	3		0.7(9)
Cl(4)	0.108(3)	0.2188(22)	0	6		1.8(9)
Cl(5)	0.1088(22)	0.2164(17)	1/2	6		0.9(7)
O(1)	0.2473(21)	0.3589(22)	0.231(7)	12		0.3(6)
O(2)	0.1372(22)	0.4684(23)	1/4	12		0.7(6)
O(3)	0.699(3)	0	1/2	3		−1.6(6)
O(4)	0.679(11)	0	0	3		6(6)
O(5)	0.194(3)	0.423(3)	0	6		−1.1(6)
O(6)	0.176(3)	0.402(3)	1/2	6		−0.6(7)
O(7)	0.086(4)	0.538(3)	1/2	6		−0.9(8)
O(8)	0.081(6)	0.538(7)	0	6		2(2)
O(9)	0.585(4)	0	0.289(11)	6		2(2)
Cl(6)	0	0	0.185(10)	1.5		1.8(10)
Ag compound						
Bi(1)	0.7528(1)	0	0.2530(11)	6	0.70(6)	
Bi(5)	0.4748(2)	0	0.2437(10)	6	1.87(8)	
Bi(2)	0.1341(1)	0.3606(1)	0.2528(8)	12	0.71(5)	
Bi(3)	0.4691(3)	0.6601(2)	1/2	6	0.68(12)	
Bi(7)	0.4648(3)	0.6514(2)	0	6	0.97(14)	
Bi(4)	0.5642(2)	0.9047(3)	1/2	5.83(14)	1.60(14)	
Bi(6)	0.5798(2)	0.8883(2)	0	6	0.58(10)	
Ag	0.1326(6)	0	0.248(3)	4.78(20)	2.9(3)	
Cl(1)	0.2240(9)	0.6690(9)	0.248(5)	12		1.27(24)
Cl(2)	0.338(4)	0	0	3		5(2)
Cl(3)	0.3319(11)	0	1/2	3		−0.7(3)
Cl(4)	0.1103(19)	0.2135(17)	0	6		1.8(6)
Cl(5)	0.1050(13)	0.2198(12)	1/2	6		0.5(4)
O(1)	0.2478(20)	0.3588(22)	0.260(9)	12		0.6(7)
O(2)	0.1415(19)	0.4686(19)	1/4	12		0.4(4)
O(3)	0.696(5)	0	1/2	3		0.1(16)
O(4)	0.690(4)	0	0	3		−0.7(12)
O(5)	0.196(4)	0.424(4)	0	6		0.6(12)
O(6)	0.184(3)	0.407(3)	1/2	6		−0.5(7)
O(7)	0.0916(23)	0.5474(22)	1/2	6		−1.4(4)
O(8)	0.069(3)	0.528(3)	0	6		−0.6(6)
O(9)	0.584(3)	0	0.300(8)	6		0.8(10)
Cl(6)	0	0	0.288(9)	1.5		2.9(13)

the Bi(3) atom positions into Bi(3) and Bi(7) positions resulted in higher *R* values and that the r.m.s. components of Bi(3) were now all real. All isotropic temperature factors were positive and reasonable. The occupancy factor of Cl(6) was first varied, giving 0.7(1) atoms at the site ±00*z*; it was finally fixed at 0.75 atoms. The final *R* for all 698 reflections was 0.049. R_w and *S* were 0.053 and 1.0733 for 697 reflections, respectively. Some of the data given in Table 2 require discussion. Calculations were also performed assuming one oxygen atom, O(10), or a fraction of a Cu atom, Cu(2), to occupy the Cl(6) position; see the coordinates given below the dashed line in Table 2. The *R* values were practically unchanged as a result of these substitutions. Although the occupation of the Cl(6) site by O^{2-} or Cu^{+} can not be excluded on account of both the intensity data and the observed distances (cf. Table 4), Cl atoms are

Table 4. Selected distances (Å) and angles (°) within the present Cu and Ag compounds. Because of the disorder of some atoms distances less than 2.0 Å have not been calculated. Maximum distance calculated to is 3.60 Å. Note that only three atoms occupy the O(9) site.

Bi,O,Cl parts		
Atoms	Cu	Ag
Bi(1)–2O(1)	2.26(4)	2.23(4)
Bi(1)–2O(3)	2.29(3)	2.28(2)
Bi(1)–4Cl(5)	3.16(1)	3.21(1)
Bi(2)–O(2)	2.17(4)	2.15(3)
Bi(2)–2O(5)	2.24(2)	2.23(2)
Bi(2)–O(1)	2.30(4)	2.32(3)
Bi(2)–2Cl(3)	3.11(1)	3.13(1)
Bi(2)–2Cl(5)	3.25(1)	3.28(1)
Bi(3)–O(7)	2.15(4)	2.20(4)
Bi(3)–2O(2)	2.25(2)	2.23(2)
Bi(3)–O(5)	2.33(4)	2.39(4)
Bi(3)–2Cl(1)	3.14(1)	3.11(1)
Bi(3)–2Cl(1′)	3.28(1)	3.30(1)
Bi(4)–O(3)	2.29(4)	2.31(3)
Bi(4)–O(7)	2.40(3)	2.33(4)
Bi(4)–2O(9)	2.37(7)	2.34(5)
Bi(4)–2O(1)	2.55(2)	2.58(2)
Bi(4)–O(5)	2.82(4)	2.83(4)
Bi(4)–2O(9′)	2.86(7)	2.85(5)
Bi(4)–2Cl(1)	3.16(1)	3.16(1)
Bi(5)–O(9)	2.24(9)	2.27(7)
Bi(5)–O(9′)	2.29(9)	2.27(7)
Bi(5)–2O(7)	2.34(3)	2.43(2)
Bi(5′)–2O(7)	2.58(3)	2.43(2)
Bi(5)–2O(2)	2.82(4)	2.90(3)
Bi(5)–Cl(3)	3.37(2)	3.43(2)
Bi(5′)–Cl(3)	3.55(2)	3.43(2)
Bi(6)–O(3)	2.27(3)	2.27(2)
Bi(6)–O(5)	2.34(4)	2.30(4)
Bi(6)–2O(1)	2.28(2)	2.28(2)
Bi(6)–2O(9)	2.71(6)	2.71(5)
Bi(6)–O(7)	2.86(3)	2.85(4)
Bi(6)–2Cl(1)	3.15(1)	3.16(1)
Bi(6)–2O(9′)	3.15(7)	3.16(5)
Shortest Bi–Bi distances:		
Bi(4)–Bi(4′)	3.30(1)	3.29(1)
Bi(5)–Bi(5′)	3.55(4)	–
Shortest Cl–O distances:		
Cl(3)–O(5)	3.28(4)	
Cl(1)–O(2)		3.30(4)
Shortest O–O distances:		
O(2)–O(5)	2.66(4)	2.65(4)

contd

Table 4. (contd)

Non-bismuth parts			
Cu compound		Ag compound	
Angles:		Angles:	
Cl(5)–Cu–Cl(5′)	111.2(11)	Cl(5)–Ag–Cl(5′)	2×89.0(5)
Cl(6)–Cu–Cl(5)	2×124.3(5)	Cl(5)–Ag–Cl(5″)	2×85.1(5)
		Cl(6)–Ag–Cl(5)	2×98.1(10)
		Cl(6)–Ag–Cl(5′)	2×107.9(10)
Distances:			
Cu–Cl(6)	2.27(3)		
Cu–2Cl(5)	2.28(2)	Distances:	
Cu–Cu	2.95(4)	Ag–Cl(6)	2.68(1)
Cu–2Cu	3.58(3)	Ag–4Cl(5)	2.75(1)
Cl(6)–3Cu	2.27(3)	Ag–Ag	>3.60
Cl(6)–3Cu′	2.78(5)	Ag–2Ag	>3.60
Cl(6)–3Cu″	2.88(5)	Cl(6)–3Ag	2.68(1)
Cl(6)–Cl(6)	2.80(14)	Cl(6)–Cl(6)	3.22(12)

to be preferred at these positions for electrostatic and chemical reasons. Admittedly a possible Cl–Cl distance of 2.80(14) Å is very short, even considering that only 0.75 Cl atoms occupy the disordered site. With Cl in the Cl(6) position and with the occupancies given in Table 2 the double cell content will be $[Cu_{5.37}Cl_{1.5}][Bi_{48}O_{60}Cl_{30}]$. As is seen, there is a deficit of 2.1 positive charges. To compensate for the excess negative charge vacancies in the oxygen atom, positions may be assumed giving the composition $[Cu_{5.37}Cl_{1.5}][Bi_{48}O_{58.9}Cl_{30}]$. Efforts to localize these vacancies by means of least-squares calculations failed. The mol percentages of this composition are Cu_2O 6.32, BiOCl 7.24 and Bi_2O_3 19.44. The calculated density is 7.69 g cm^{-3}. Compared to the values given in Table 1, the observed Cu_2O fractions are higher and BiOCl fractions lower than expected, whereas the observed densities are close to the expected one. The high Cu_2O contents in Table 1 may be explained by the (visual) observation that the added Cu_2O had not reacted completely, bud discrepancies still remain. The above composition obtained from the final refinement of the crystal data has been approximated to give the title composition. Table 4 shows that the Bi(4)–Bi(4) interaction is very short, a finding which will be discussed later. The coordinates of Bi(4) and Bi(6) as given in Table 2 and visualized in Fig. 1 may give the impression of a curious double atom. This is not the case, since the Bi(4) and Bi(6) positions are only half-occupied in the small cell (Table 2), and are situated at different z levels in the large cell (Table 3).

Silver compound. The single crystal of the silver compound used for the diffractometer work was a thin needle of length 260 μm. Its cross-section had the form of a nearly equilateral triangle with a side of about 30 μm. For the composition finally assumed μ(Mo$K\alpha$) was 758 cm^{-1}. Lp^{-1} and absorption corrections were performed. The transmission factors ranged between 0.19 and 0.40, and $(\sin\Theta/\lambda)_{max}$ was 0.8086. The silver compound was first assumed to be isomorphous with the copper one. Although the Weissenberg photographs indicated Laue symmetry 6/*mmm* as in the Cu case, *hkl* and *hkl̄* data were also registered to cover Laue classes $\bar{3}m1$ and $\bar{3}1m$. The reasons for this were (i) the disorder in the Cu atom positions in the Cu compound and (ii) the absence of high maxima at $u,0,0$ and $u,0,\frac{1}{2}$ in the

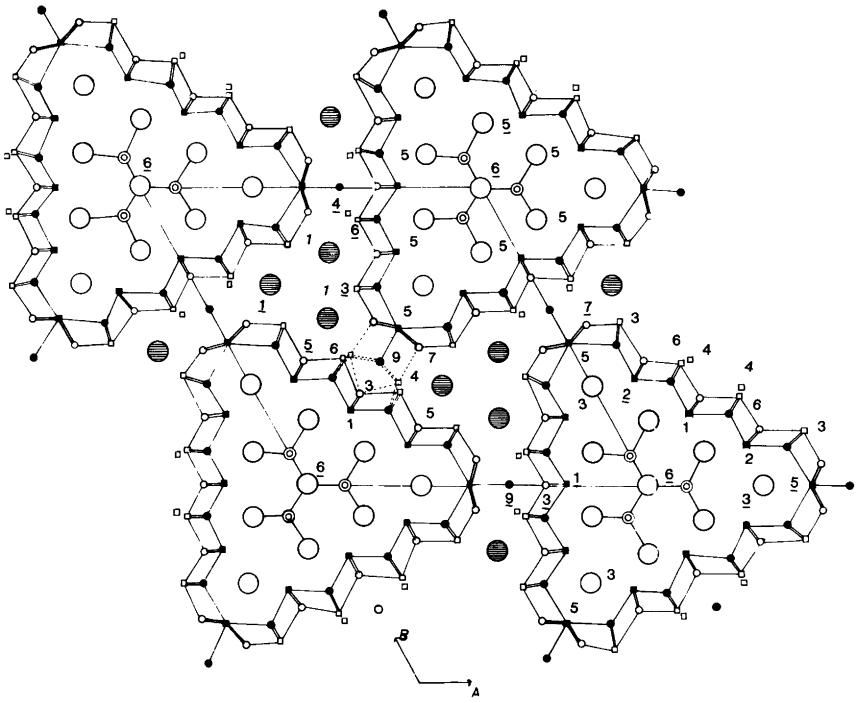

Fig. 1. Projection of the structure of the present Cu compound on the *x,y* plane. Double circles indicate Cu atoms. Large circles, empty and hatched, denote Cl atoms at $z = 0$ and $z = \frac{1}{2}$, respectively. Small circles and squares, empty and filled, denote O and Bi atoms at $z = 0$ and $\frac{1}{2}$, respectively. The Cu–Cl and Bi–O bonds are shown by solid lines except for two Bi(4) atoms, where dashed lines are used. For the numbers in the figure, see the text.

Patterson function of the small cell, which excluded Laue symmetry 6/*m*. Thus for each of the Laue classes $\bar{3}m1$ and $\bar{3}1m$ some dependent reflections were registered. In this way 1334 reflections with $I > 3\sigma(I)$ were measured for the large cell. No systematic extinctions were found. In none of the least-squares calculations to be described were average values taken for symmetry-related reflections. The parameters of the Cu compound (large cell) were used in a least-squares refinement using space group $P\bar{6}2m$. Whereas the Bi,O,Cl skeleton was nearly the same for the Cu and Ag compounds, the Ag atoms were not disordered but occupied an ordered six-fold position $x0z$ with $z \approx \frac{1}{4}$ in space group $P\bar{6}2m$. Next, refinements of all atoms in space groups $P31m$ and $P321$ were tried. The results were no better than with space group $P\bar{6}2m$. All the following refinements were therefore made in $P\bar{6}2m$. With the exception of the Ag and Cl(6) atoms the result (Table 3) was similar to that for the corresponding refinement of the Cu data. However, an isotropic extinction coefficient, 185 (210), was introduced. All r.m.s. components of the Bi atoms were real. The occupancy number, *G*, for Bi(4) was varied giving a non-significant deviation from six atoms at the site. Likewise *G* for Ag was varied and gave a significant deviation from six atoms at the site. As in the Cu case, *z*[O(2)] and *G*[Cl(6)] had to be fixed. The isotropic temperature factors were uneven, and five of them were negative. *R* for 1334 reflections was 0.058, and R_w and *S* for 1333 reflections were 0.062 and 1.0961, respectively. The separate *R* values for *l* odd (223) and *l* even (1111) were 0.109 and 0.052, respectively. Lists of $|F_o|$ and $|F_c|$ values for the large cells of the Cu and Ag compounds are available on request.

As for the Cu case, it seemed that pairs such as O(3)/O(4) [and in the present case also Cl(2)/Cl(3)] could not be resolved properly. The *l* odd reflections were therefore deleted, and a refinement in the small cell was performed. The result is given in Table 2. An isotropic extinction coefficient, 250(210), was introduced. Anomalous disperson was also introduced using both *hkl* and $\bar{h}\bar{k}\bar{l}$. In both cases R_w was higher than with no correction. The result of the final calculation with no anomalous correction is given in Table 2. As for the Cu case the splitting of the atom Bi(3) into Bi(3) and Bi(7) was not supported by the data. Likewise a variation of *G*[Bi(4)] indicated a full occupation of this site. In contrast to the Cu case a variation of *z*[Bi(5)] led to the fixed value $\frac{1}{2}$. Anisotropic temperature factors were also introduced for the Cl atoms. All r.m.s. components were real, and the isotropic temperature factors positive and reasonable. *G*[Cl(6)] could be varied. The final *R* factor was 0.052 for 1111 reflections, with R_w and *S* 0.058 and 1.0761, respectively, for 1110 reflections. The distance Cl(6)–Cl(6) was 2.68(1) Å and that for Cl(6)–3Ag 3.22 (12) Å (Table 4). As in the case of Cu, calculations were performed assuming O^{2-},O(10), or a fraction of a silver atom, Ag(2), in the Cl(6) site; see Table 2 below the dashed line. The *R* values were practically unchanged as a result of these substitutions. As in the case of Cu, Cl atoms are to be prefered at the Cl(6) positions for electrostatic and chemical reasons. The internal Cl(6)–Cl(6) distance of 3.22(12) Å is not unreasonable for 0.70(20) Cl atoms at a disordered two-fold site. With the data in Table 2 the double cell content of the Ag compound would be $[Ag_{4.79}Cl_{1.4}]$ $[Bi_{48}O_{60}Cl_{30}]$, with a deficit of 2.6 positive charges. To compensate for the excess negative charge, vacancies in the

oxygen atom positions may be assumed leading to a composition $[Ag_{4.79}Cl_{1.4}][Bi_{48}O_{58.7}Cl_{30}]$. Efforts to locate the postulated defects in the oxygen atom positions by means of least-squares calculations failed. With the above composition the mol percentages would be Ag_2O 5.69, BiOCl 74.59 and Bi_2O_3 19.72, with a calculated density of 7.76 g cm^{-3}. Compared to the data in Table 1 the observed Ag_2O contents are too high and the BiOCl contents too low. Some of the discrepancies may be due to silver oxide not having reacted completely. The observed densities are somewhat high. The above composition obtained from the refinement of the crystal data has been approximated to give the title composition. Table 4 shows that the shortest Bi(4)–Bi(4) distances are 3.30(1) and 3.29(1) Å for the Cu and Ag compounds, respectively. To the author's knowledge such short Bi–Bi interactions have not previously been reported for bismuth oxide halides. Bi is (3+3) coordinated in metallic Bi, with distances 3.07 and 3.53 Å.[4] The crystal structure of $KSbO_3 \cdot \frac{1}{6}KF$[5] is closely related to that of $KBiO_3$.[6]

In these compounds the shortest Sb^{5+}–Sb^{5+} and Bi^{5+}–Bi^{5+} distances are 3.03 and 3.34 Å, respectively. Although the present Bi(4)–Bi(4) distances are very short, equally short Bi–Bi interactions occur in metallic Bi and in $KBiO_3$, in which Bi is pentavalent. Finally, it may be mentioned that for the refinements given in Tables 2 and 3 the 020 reflection, although comparatively weak, had $|F_o| \gg |F_c|$ and was not used in the calculation of R_w and S.

Description and discussion of the structures

Although the addition of Ag_2O or Cu_2O to Bi_2O_3, BiOCl mixtures are necessary for the formation of the present phases the description of their crystal structures is simplified if they are considered to be built up from a bismuth oxide chloride and a M^I,Cl part, thus $[M^I_5Cl][Bi_{48}O_{59}Cl_{30}]$ (**I**). A more approximate description is $6[(M^ICl) \cdot 2Bi_4O_5Cl_2]$ (**II**). Formally the structure **I** may be described as some kind of inclusion compound where more or less disordered (M_5Cl) units are situated in the hexagonal tunnels of a ($Bi_{48}O_{59}Cl_{30}$) skeleton.

Bismuth oxide chloride parts of the present structures

Coordination polyhedra of bismuth. Table 2 shows only minor differences in the atomic positions for the Cu and Ag compounds in their Bi,O,Cl parts, which comprise all atoms except M(I) and Cl(6). In consequence Table 4 shows that the distances within the Bi,O,Cl parts of the Cu and Ag compounds are nearly identical. The atoms Bi(1), Bi(2) and Bi(3) are eight-coordinated in the form of Archimedian antiprisms with one "square" of four Cl atoms, planar by symmetry, and one nearly planar "square" of oxygen atoms. As is seen, all distances are normal and similar to those in BiOCl: Bi–4O = 2.31 and Bi–4Cl = 3.07 Å. The Bi(6) polyhedron is best described as a monocapped Archimedian antiprism with distances to the "square" oxygen atoms O(3), O(5) and 2O(1) similar in length to those in BiOCl.

The other, larger, "square" comprises 2Cl(1) and 2O(9). The capping atom, O(7), is situated outside these atoms. The Bi(1), Bi(2), Bi(3) and Bi(6) atoms are joined in such a way that linear Bi_2O_2 rows, endless in the c direction, are formed; cf. Fig. 1 and the discussion to follow. (The numbers attached to some atoms in Fig. 1 correspond to the numbering in Table 2. The numbers are underlined if the xyz coordinates of the atom are the same as those given in Table 2.) Bi(4) has formally the same nine-coordination as Bi(6), but the distance Bi(4)–O(5), in the small "square", is long and the distance to the capping atom O(7) is short. Bi(5) is nine-coordinated in the form of a three-capped trigonal prism. The atoms in the basal planes are Cl(3) and 2O(7), and the capping atoms are 2O(2) and O(9). Bi(4) and Bi(5) in cooperation link three polyhedral rows, each consisting of fused Bi(1,2,3,6) polyhedra; see Fig. 1 and the discussion below.

Relationships between the present structures and known bismuth oxide chlorides. The Bi,O,Cl parts of the present structures are strongly related to the so-called Arppe compounds[2] $Bi_{24}O_{31}Cl_{10}$,[2] $Bi_{24}O_{31}Br_{10}$,[2] $Bi_6O_7FCl_3$[7] and $Bi_4O_5Cl_2$.[8] The sub-structure of the present Cu compound is shown in Fig. 1 in projection along its short axis. Figs. 2 and 3 show the projections along their 3.8 Å axes of the structures of $Bi_{24}O_{31}Cl_{10}$ and $Bi_4O_5Cl_2$, respectively. It is seen from Figs. 1 and 3 that there is a striking resemblance

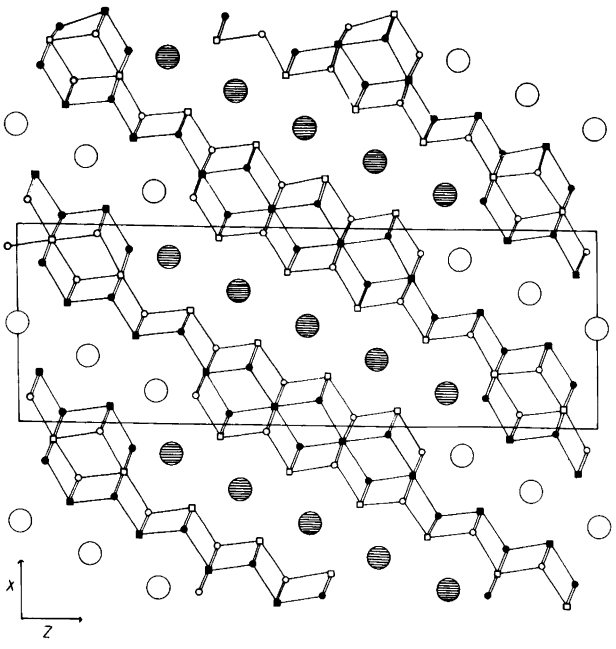

Fig. 2. Projection of the structure of $Bi_{24}O_{31}Cl_{10}$ on the x,z plane. Empty and hatched large circles indicate Cl atoms at $y = 0$ and $\frac{1}{2}$, respectively. Small circles and squares, empty and filled, denote O and Bi atoms at $y = 0$ and $\frac{1}{2}$, respectively. The Bi–O bonds are shown.

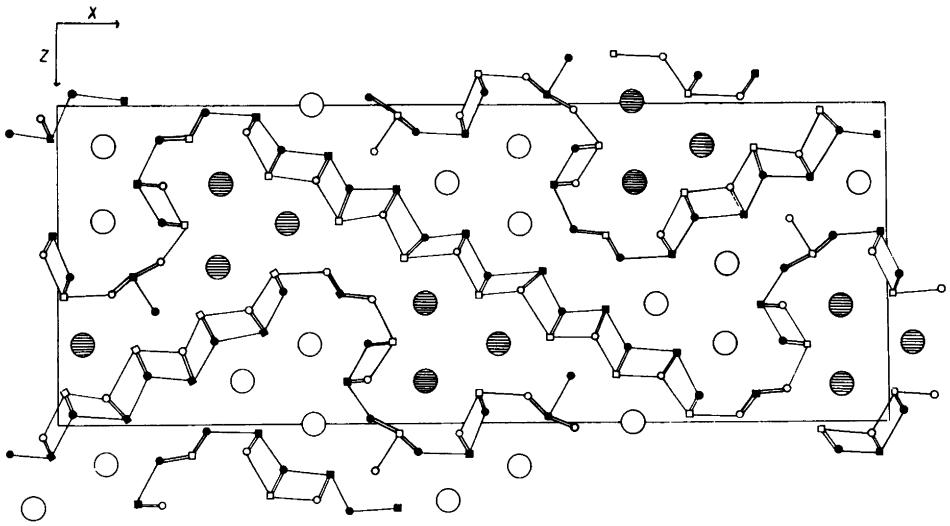

Fig. 3. Projection of the structure of $Bi_4O_5Cl_2$ on the *x,z* plane. Empty and hatched large circles indicate Cl atoms at $y = 0$ and $\frac{1}{2}$, respectively. Small circles and squares, empty and filled, denote O and Bi atoms at $y = 0$ and $\frac{1}{2}$, respectively. The Bi–O bonds are shown.

between the Bi,O,Cl part of the present structure and that of $Bi_4O_5Cl_2$. In fact the approximate formula **II** above presupposes $Bi_4O_5Cl_2$ building elements in the present Cu and Ag compounds. The structures given in Figs. 1–3 and also $Bi_6O_7FCl_3$ are all strongly related to that of BiOCl. The structures of $Bi_6O_7FCl_3$ and $Bi_4O_5Cl_2$ have been derived from a hypothetical structure $Bi_6(O,F)_{7+n}Cl_3$ by Hopfgarten[9] using the chemical twinning concept of Andersson and Hyde.[10] The parent structure consists of fused square pyramids $Bi(O,F)_4$, octahedra $Bi(O,X)_6$ (X = Cl,F) and trigonal columns of Cl_3.

Rows of different lengths of fused BiO_4 pyramids are joined by BiO_5Cl octahedra to form zig-zag rows between which trigonal prisms of Cl_3 are situated in the structure of $Bi_4O_5Cl_2$ (Fig. 3). The same type of building elements are present in the Cu and Ag compounds now discussed (cf. Fig. 1). In the present structures the fused BiO_4 pyramids of $Bi_4O_5Cl_2$ correspond to fused BiO_4 pyramids of Bi(1), Bi(2), Bi(3) and Bi(6) (see above) and the linking BiO_5Cl octahedron to the Bi(5) polyhedron. The present Bi(4) polyhedron has no counterpart in the structure of $Bi_4O_5Cl_2$, in which no more than two BiO_4 rows meet at a point. When Bi(4) and its bonds (dashed lines in Fig. 1) are removed from the figure the similarity of the present structure and that of $Bi_4O_5Cl_2$ is obvious. The basal planes of the fused BiO_4 pyramids in $Bi_4O_5Cl_2$ (Fig. 3) meet at an angle of about 60° within the BiO_5Cl octahedron, whereas the corresponding angles at the Bi(5) polyhedron in the present structures are exactly 60° by symmetry. The atom O(9) in the present structures joins three rows of fused BiO_4 pyramids. Two rows of fused O_4 "squares" have their end points at O(9) within the Bi(5) polyhedron, where they meet at 60°.

Some geometrical views on the present structures. Although the arguments[9,10] and structures[7,8] are sufficient for the description of the Bi,O,Cl parts of the present structures some other purely geometrical views will also be presented here. The structures to be discussed are BiOCl, $Bi_{24}O_{31}Cl_{10}$, $Bi_3O_5Cl_2$ and the present ones. A formal building element of all these structures are Bi_2O_2 slabs consisting of condensed BiO_4 square pyramids with the Bi atoms at their vertices. The slabs are endless in the short-axis directions. When the ratio O/Bi > 1 the Bi atom vertices must be shared if a structure based on BiO_4 fused pyramids is to result. In $Bi_{24}O_{31}Cl_{10}$ (Fig. 2) the condensed BiO_4 pyramids are ordered in linear rows, and four Bi vertices are common to two parallel rows as indicated in the figure. This linking of polyhedra by means of vertex sharing in $Bi_{24}O_{31}Cl_{10}$ has some formal similarity to edge sharing in shear structures based on ReO_3. It has been mentioned earlier that the basal O atoms in different BiO_4 rows would meet at angles of about 60° in $Bi_4O_5Cl_2$. This fact can be explained by assuming that the terminal Bi atoms of two rows are shared, thereby creating a BiO_5Cl octahedron (Fig. 3). Based on the cell dimensions of BiOCl the angles between the fused rows would be 65.4° (Fig. 4). Since there may be different numbers of BiO_4 condensed pyramids between shared Bi vertices either in linear or 60° rows a number of additional bismuth oxide chlorides and bro-

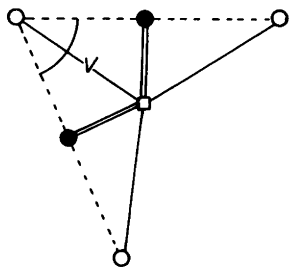

Fig. 4. One Bi atom is shared between two rows of oxygen-atom squares. The dimensions are as for BiOCl. Empty circles denote oxygen atoms at the same level as the Bi atom (empty square). Filled circles denote oxygen atoms $\frac{1}{2}a$(BiOCl) above and below the plane formed by the square and the empty circles. The Bi–O bonds are shown.

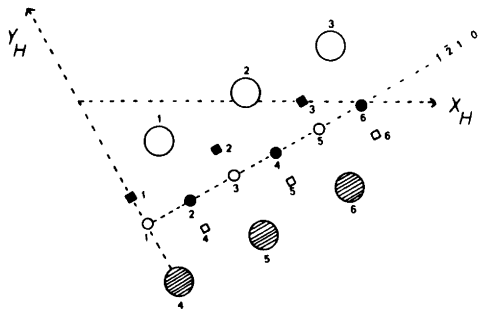

Fig. 5. Part of a BiOCl slab between $0.355 \geq z(\text{BiOCl}) \geq -0.355$, projected on the *x,z* plane of BiOCl. Six atoms each of Bi,O and Cl are shown. The unit cells of BiOCl share their *bc* planes and extend infinitely in the *b*(BiOCl) direction. Empty and hatched large circles indicate Cl at $y = 0$ and $\frac{1}{2}$, respectively. Small circles and squares, empty and filled, denote O and Bi atoms at $y = 0$ and $\frac{1}{2}$, respectively.

mides based on the sharing of Bi atoms could be foreseen. It was mentioned above that the calculated angle between two fused BiO_4 pyramidal rows is 65.4° for Bi,O,Cl. Corresponding angles for Bi,O,Br, La,O,Cl, La,O,Br and Pb,F,Cl are in turn 64.9, 60.8, 60.4 and 72.4°. $Bi_{24}O_{31}Br_{10}$ is isotypic with $Bi_{24}O_{31}Cl_{10}$,[2] and consequently contains the same building elements. A monoclinic phase $Bi_4O_5Br_2$ exists (space group *P*2 or $P2_1$),[11] but its structure is unknown. To the author's knowledge no compounds of the present type have been published in which Bi is replaced by a rare-earth metal or by Pb. In the latter case some O^{2-} ions must be replaced by F^- to achieve the desired stoichiometry.

"Construction" of the present Bi,O,Cl parts from BiOCl. In view of the similarity of the Bi,O,Cl parts of the present structures to the structure of BiOCl an effort was made to construct the Bi,O,Cl skeleton from the known distances within BiOCl. Some presuppositions had to be made; space group $P\bar{6}2m$ was assumed, and the basal planes of the pyramids (their O atoms) corresponding to five unit cells of BiOCl were assumed to be situated in a plane parallel to the $1\bar{2}10$ crystal plane and its equivalents, at a distance of $(5\times\sqrt{3}/6)$ *a*(BiOCl) from the origin of the new, hypothetic unit cell (cf. Figs. 1, 5 and 6).

The *a* axis of this new unit cell, a_h, was supposed to have the length $(5\times\sqrt{3}/2)$ *a*(BiOCl) + $[1-z(\text{Cl})]c(\text{BiOCl})$ Å (cf. Figs. 1, 5 and 6). The new *c* axis, c_h, was supposed to be the same as *a*(BiOCl). The values used for BiOCl were a = 3.8910, c = 7.3698 Å, z(Bi) = 0.170 and z(Cl) = 0.645. Using these presuppositions the coordinates in $P\bar{6}2m$ were calculated for the atoms Bi(1–6), O(1–6) and Cl(1–6) in Fig. 5. The atoms in this figure correspond to three unit cells of BiOCl, sharing their *bc* planes and within the limits $0.355 \geq z \geq -0.355$. The BiOCl slab in Fig. 5 is placed in the hypothetical unit cell with a_h = 19.49 and c_h = 3.89 Å, space group $P\bar{6}2m$, so that the plane defined by O(1–6) coincides with the crystal plane $1\bar{2}10$ and so that O(1) is situated at the b_h axis with $z_h = 0$ and O(6) at the a_h axis with $z_h = \frac{1}{2}$ (cf. Figs. 1, 5 and 6). The result is shown in Table 5, where the primarily obtained parameters refer to point positions in $P\bar{6}2m$ and versions within these point positions as close to those given in Table 2 as possible were chosen. It is seen from Table 5 that the atoms O(6) and Cl(4) (Fig. 5) have identical positions. This is a consequence of the choice of the length of the a_h axis made above. It is also seen that the atoms Cl(5) and Cl(6) have positions close to each other. If Cl(5) and Cl(6) are fused into one atom, if Cl(3) is omitted and if Cl(4) and O(6) are regarded as one chlorine atom (all atoms in Fig. 5) an electrically neutral skeleton of composition $Bi_{24}O_{27}Cl_{18}$ or $3\times(6\text{BiOCl}\cdot Bi_2O_3)$ would constitute the hypothetical hexagonal unit cell. However, no such compound is known. Fig. 6 shows a projection onto the a_hc_h plane of the structure resulting from the atomic positions given in Table 5. In this figure Cl(4) and O(6) (Fig. 5) are regarded as one oxygen

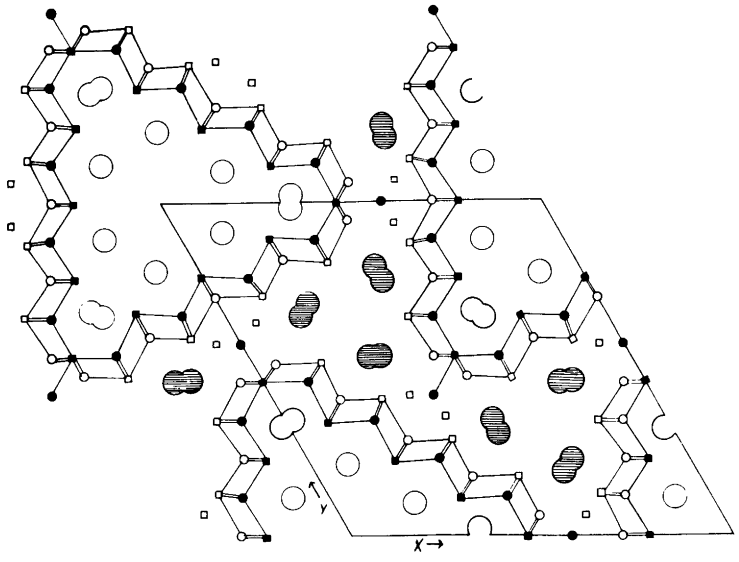

Fig. 6. Projection of a hypothetical structure for the Bi,O,Cl parts of the present structures on its x_h,y_h plane. The coordinates have been derived from the structure of BiOCl (see the text). Large circles, empty and hatched, denote Cl atoms at $z_h = 0$ and $\frac{1}{2}$, respectively. Small circles and squares, empty and filled, represent O and Bi atoms at $z_h = 0$ and $\frac{1}{2}$, respectively. The Bi–O bonds, except for those of Bi(4) (Table 2), are shown.

Table 5. Derivation of the present structures from that of BiOCl. Coordinates of the "BiOCl" atoms of Fig. 5 are given in a unit cell, space group $P\bar{6}2m$, with $a = 19.49$, $c = 3.89$ Å together with the corresponding Bi,O,Cl sites (Table 2) in the present structures.

"BiOCl" atom	x	y	z	Atom in Table 2
Bi(1)	0.7761	0	½	Bi(1)
Bi(2)	0.1086	0.3391	½	Bi(2)
Bi(3)	0.4610	0	½	Bi(5)
Bi(4)	0.5899	0.8747	0	Bi(6)
Bi(5)	0.4747	0.6542	0	Bi(3)
Bi(6)	0.5743	0.9357	0	Bi(4)
Cl(1)	0.0963	0.2116	0	Cl(5)
Cl(2)	0.3458	0.0189	0	Cl(3)
Cl(3)	0.5763	0.1342	0	–
Cl(4)	0.5763	0	½	O(9)
Cl(5)	0.2305	0.6929	½	Cl(1)
Cl(6)	0.1919	0.6529	½	
O(1)	0.7119	0	0	O(3)
O(2)	0.2305	0.3458	½	O(1)
O(3)	0.1729	0.4034	0	O(5)
O(4)	0.1153	0.4611	½	O(2)
O(5)	0.0576	0.5186	0	O(7)
O(6)	0.5763	0	½	O(9)

atom and Cl(3) (Fig. 5) is omitted since it has no counterpart in the present Cu and Ag compounds (cf. Table 5).

On comparing Figs. 2 and 6 some conclusions may be drawn. There is a certain misfit in the hypothetical structure; thus the Cl(1) and Cl(3) atoms (Table 2 and Fig. 1) are split up. There is disorder in the substructures of the Cu and Ag compounds where the Bi vertices are shared between different rows of condensed BiO_4 square pyramids. The shared Bi(5) atom (Table 2) is disordered with $z \neq \frac{1}{2}$ in the Cu compound. The atoms Bi(4) and Bi(6) are more separated in the hypothetical structure than in the present Cu and Ag compounds. In $Bi_{24}O_{31}Cl_{10}$[2] the oxygen-atom positions at the end of the "shear" regions (Fig. 2) are half-occupied, and their distance to the nearest Cl atom is only 2.2 Å. Disorder is reported in $Bi_4O_5Cl_2$, but special regions of the structure are not identified.[8]

Thermal behaviour of some bismuth oxide chlorides. The thermal behaviour of $Bi_4O_5Cl_2$ is complicated. Nurgaliev *et al.*[11,12] have studied the system $BiCl_3$–Bi_2O_3. They, like Hopfgarten,[8] state that the compound is formed at 860 °C. On melting and remelting $Bi_4O_5Cl_2$ several times they found that it decomposed to (BiOCl+$Bi_{24}O_{31}Cl_{10}$), an observation which may undermine their published phase diagram. Kodama *et al.*[13] have prepared $Bi_4O_5Cl_2$ hydrothermally. They state that $Bi_4O_5Cl_2$, once formed, is stable up to 800 °C but that it is partially decomposed to (BiOCl+$Bi_{24}O_{31}Cl_{10}$) above 840 °C. On the other hand, mixtures of 22BiOCl and Bi_2O_3 give only (BiOCl+$Bi_{24}O_{31}Cl_{10}$) at temperatures lower than 840 °C. At temperatures above 860 °C mixtures of BiOCl, $Bi_4O_5Cl_2$ and $Bi_{24}O_{31}Cl_{10}$ are obtained. It seems clear from the above data that BiOCl and $Bi_{24}O_{31}Cl_{10}$ have special stabilities in comparison to the intermediate phase $Bi_4O_5Cl_2$. This extra stability may be due to endless layers of Bi_2O_2 in BiOCl and due to linear rows of fused BiO_4 square pyramids sharing Bi vertices in $Bi_{24}O_{31}Cl_{10}$. In $Bi_4O_5Cl_2$ the Bi_4O_5 skeleton is built up from rows of BiO_4 fused square pyramids which meet at 60° to form zig-zag bands through the structure.[8,9]

It is at least possible that the repeated joining through vertex sharing at about 60° destabilizes the structure with respect to BiOCl and $Bi_{24}O_{31}Cl_{10}$, where the linking of BiO_4 pyramids is simpler. The present Cu and Ag compounds have Bi,O,Cl skeletons strongly resembling the structure of $Bi_4O_5Cl_2$. They are, however, easily formed at 720 °C. It may be that these phases are stabilized by the presence of Cu^+ and Ag^+ and by the Cl atoms at the line 00*z* in the hexagonal unit cells.

Silver and copper parts of the present structures

The possibilities that the Cl(6) positions within the Ag and Cu parts are occupied by O^{2-} or M^+ have been discussed above. In the following the Cl(6) positions are assumed to be occupied by Cl^-. Strictly speaking the Ag and Cu parts consist of $[Ag_{2.39}Cl_{0.70}]^{1.69+}$ and $[Cu_{2.68}Cl0_{.75}]^{1.93+}$ (cf. Table 2), respectively, but the total coordinations are, of course, also discussed, since both Ag and Cu have strong bonds to the Cl(5) atoms of the Bi,O,Cl parts (Table 4). There is no indication in the intensity calculations and in the observed M–O and M–Cl distances that M(I) is substituted for Bi in the Bi,O,Cl parts of the present structures. Instead Ag^+ and Cu^+ are "pushed away" to the regions around 00*z* in the hexagonal unit cells, with the consequence that they are only coordinated to Cl atoms. It is known[14] that Cu^+ and Ag^+ prefer Cl^- to F^- in solution, and the same may be true for Cl^- and O^{2-} in the solid state.

Silver compound. Ag^+ is situated at an only partially occupied three-fold position in the subcell (Table 2). The Cl(6) atoms are disordered and partially occupy the two-fold position ±00*z* with $z = 0.42$. The shortest Ag–Ag distance is the axis, 3.86 Å. The $[Ag_{2.39}Cl_{0.70}]$ unit, idealized as $ClAg_3$, is slightly pyramidal with Cl–3Ag distances of 2.68 Å (Table 4). The height of the pyramid is 0.32(6) Å. Because of the disorder of the Cl(6) atoms, Cl atoms can occupy positions both above and below the Ag triangle. Each Ag atom is coordinated to four Cl(5) atoms and one Cl(6) atom at distances 4×2.75 and 2.68 Å in the form of a slightly deformed square pyramid (cf. Table 4). The present Ag–Cl distances do not differ very much from those in AgCl, 2.78 Å, taking its cell edge as 5.55 Å. Another example of similar Ag–Cl distances is furnished by the structure of $Ag_2Al_4Cl_{10}O_2$,[15] where Ag is coordinated solely to Cl with distances ranging between 2.631 and 2.855 Å. Ag is five-coordinated in the form of a slightly deformed trigonal bipyramid. One example of a five-coordination of Ag in the form of a distorted square pyramid is reported in the structure of β-$AgCuPO_4$.[16] The Ag–O distances range be-

tween 2.33 and 2.61 Å. (There is also an additional interaction at 2.84 Å.) Considering the vacancies in the Ag and Cl(6) positions and the disorder of the latter ones it seems possible that ionic conduction exists in the Ag compound along its axis (needle directions in the single crystals). No measurements have been made.

Copper compound. In the Cu–Cl(6) part of the Cu structure (Tables 2 and 4) 2.68 Cu atoms occupy position 6(i), $x0z$, in space group $P\bar{6}2m$, and are consequently disordered. 0.75 Cl(6) atoms are situated at position 2(e) $00z,00\bar{z}$. When z(Cu) and z[Cl(6)] are chosen so as to give minimum Cu–Cl distances the unit $[Cu_{2.68}Cl_{0.75}]$, idealized as $ClCu_3$ with Cl–3Cu distances of 2.27(3) Å, will be pyramidal with a height of 0.9(7) Å. Thus the $ClCu_3$ and $ClAg_3$ complexes differ considerably. With other combinations of z(Cu) and z[Cl(6)], Cl–3Cu distances of less than 3.5 Å are 2.78 and 2.85 Å (Table 4). Thus the data do not support a switching of the Cl(6) atoms between mirror-related positions above and below the M_3 triangles, as might be the case in the Ag compound. With a combination of parameters $\pm z$(Cu) = 0.12, z[Cl(6)] = 0.36 the Cu atoms will be coordinated by three Cl atoms at the distances 2×2.28 and 1×2.27 Å. The Cl–Cu–Cl angles will be 2×124 and 1.111° (Table 4). The height of the flat pyramid will be 0.05 Å. If z(Cu) and z[Cl(6)] as above have the same signs, Cu will always be nearly planarly coordinated to three Cl atoms except for the regions where the preceeding (+) or (−) signs above are reversed. Irrespective of the disorder, Cu will always be coordinated to two Cl(5) atoms at distances 2.29 Å. Owing to the disorder, more or less pyramidal three-coordinations of Cu may arise with height 0.05 (as above), 0.36 or 0.90 Å. Severely deformed tetrahedral coordinations may also arise, but in these cases the Cu atom will have a maximum distance to a tetrahedral face of 0.36 Å. Cu is tetrahedrally coordinated to Cl in the room-temperature modification of CuCl. Taking a(CuCl) as 5.41(5) Å the Cu–Cl distance, not corrected for thermal movements, is 2.34 Å. Andersson and Jagner have made extensive studies on chlorocuprates(I).[17] Three-coordinated Cu exists in the anions $[Cu_7Cl_{10}^{3-}]_\infty$ and $[Cu_2Cl_3^-]_\infty$. Discrete, almost planar, $CuCl_3^{2-}$ ions exist in $[P(CH_3)_4]_2CuCl_3$ with Cu–Cl distances of 2.232(3) and 2×2.215(2) Å. The angles Cl–Cu–Cl are 121.94(10) and 2×118.90(5)°. The complex ion $[Cu_5Cl_{16}^{11-}]$[18] may be described as built up from a central, regular $CuCl_4$ tetrahedron, with Cu–Cl = 2,278 Å, which shares all its Cl atoms with four equal (by symmetry) subsidiary Cu–Cl tetrahedra. The distance of the shared Cl atoms to the respective subsidiary Cu atom is 2.495 Å, whereas the remaining Cu–Cl distances are 3×2.323 Å. The subsidiary Cu atoms may thus also be regarded as three-coordinate, forming apexes in pyramids with height 0.36 Å. In these cases the shared Cl atom is omitted. Cu(I) is coordinated to three Cl atoms in a nearly planar trigonal fashion in $Cu_2Mo_6Cl_{14}$.[19] No positional parameters are, however, given in the paper. The present Cu compound may be an electric conductor. No measurements were made.

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References

1. v. Schnering, H. G., Walz, L., Schwarz, M., Becker, V., Hartweg, M., Popp, T., Hettig, B., Müller, P. and Kämpf, G. *Angew. Chem. 27* (1988) 574.
2. Sillén, L. G. *Naturwiss. 30* (1942) 318.
3. Lundgren, J.-O. *Crystallographic Computer Programs*, Report No. UUIC-B13-4-05, University of Uppsala, Uppsala 1983.
4. Cucka, P. and Barret, C. S. *Acta Crystallogr. 15* (1962) 865.
5. Goodenough, J. B., Hong, H. Y.-P. and Kafalas, J. A. *Mater. Res. Bull. 11* (1976) 203.
6. Zeman, J. *Anzeiger der Österr. Akad. Wiss. 85* (1948) 85.
7. Hopfgarten, F. *Acta Crystallogr., Sect. B 31* (1975) 1087.
8. Hopfgarten, F. *Acta Crystallogr., Sect. B 32* (1976) 2570.
9. Hopfgarten, F. *Acta Crystallogr., Sect. B 33* (1977) 952.
10. Andersson, S. and Hyde, B. G. *J. Solid State Chem. 9* (1974) 92.
11. Nurgaliev, B. Z., Popovkin, B. A. and Stefanovich, S. Yu. *Russ. J. Inorg. Chem. 28* (1983) 1252.
12. Nurgaliev, B. Z., Vasekina, T. F., Baron, A. E., Popovkin, B. A. and Novoselova, A. V. *Russ. J. Inorg. Chem. 28* (1983) 415.
13. Kodema, H., Horiuchi, S. and Watanabe, A. *J. Solid State Chem. 75* (1988) 279.
14. Ahrland, S. *Acta Chem. Scand. 10* (1956) 723.
15. Jentsch, D., Jones, P. G., Schwarzmann, E. and Sheldrick, G. M. *Acta Crystallogr., Sect. C 39* (1983) 1173.
16. Quarton, M. and Oumba, B. T. *Mater Res. Bull. 18* (1983) 1967.
17. Andersson, S. and Jagner, S. *Acta Chem. Scand., Ser. A 42* (1988) 691.
18. Murray-Rust, P. *Acta Crystallogr., Sect. B 29* (1973) 2559.
19. Potel, M., Perrin, C., Perrin, A. and Sergel, M. *Mater. Res. Bull. 21* (1986) 1239.

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