The Crystal Structure of $Bi_8(AlCl_4)_2$ and the Crystal Structure, Conductivity, and Theoretical Band Structure of Bi_6Cl_7 and Related Subvalent Bismuth Halides

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The methods of preparation for $Bi_8(AlCl_4)_2$ and Bi_6Cl_7 have been improved and the single crystal structures for these cluster compounds re-investigated and re-interpreted. In addition, conductivity measurements and band structure calculations using the tight-binding approximation have been performed on Bi_6Cl_7 and related subvalent bismuth halides. – $Bi_8(AlCl_4)_2$ consists of isolated $AlCl_4^-$ anions and rather undistorted square-antiprismatic Bi_8^{2+} clusters with an average Bi–Bi distance of 3.10 Å. Relatively short intercluster Bi–Bi contacts of 3.90 Å suggest weak bonding interactions between the Bi_8^{2+} units. In contrast, the structure determination of Bi_6Cl_7 implies that this structure should be regarded as being composed of discrete Bi_9^{5+} clusters and a *polymeric* Bi^{III}–Cl anionic lattice including infinite, distorted $^1_\infty[Bi_2Cl_2^{4+}]$ chains. According to the experimental and theoretical results, the Bi_6X_7 (X = Cl, Br) family of subvalent bismuth halide compounds are anisotropic semiconductors along the crystallographic *c* axis. The conductivity is mediated by the one-dimensional $^1_\infty[Bi_2Cl_2^{4+}]$ chains. These are interconnected with the Bi_9^{5+} clusters, which are acting as electron reservoirs. The related BiX (X = Br, I) family of subvalent bismuth halides are shown to be anisotropic semiconductors in the crystallographic *b* direction.

Subvalent bismuth chloride was at first formulated as BiCl[1,2], but was later crystallographically shown to actually have the stoichiometry Bi_6Cl_7 and to exhibit an unusually complex structure with isolated Bi_9^{5+} clusters and chlorobismuthate(III) complexes[3–6]. The authors described the structure as $(Bi_9^{5+})_2(Bi_2Cl_8^{2-})(BiCl_5^{2-})_4$, corresponding to the over-all stoichiometry Bi_6Cl_7. The 1:1 BiCl compound has so far not been synthesised, and it is interesting to note the following trend in the stoichiometry of the subvalent bismuth halides that have been isolated and characterized:

Bi_6Cl_7		
Bi_6Br_7	BiBr	
	BiI	Bi_7I_2, Bi_9I_2

All these compounds have been structurally characterised in the solid state[7–10] and the Bi_6X_7 (X = Cl or Br) pair found to be structurally analogous. There are two main reasons for our interest in the latter two compounds. First, Bi_6Cl_7 has been reported to be a metallic conductor, whereas the structural and chemical analogue Bi_6Br_7 is claimed to be an insulator[7]. Such a difference is very surprising considering the isostructurality and chemical similarity of the two compounds. Second, the previous structural characterisations of Bi_6Cl_7 are incomplete in the sense that the chloride positions were not refined anisotropically. In this work, the crystal structure of Bi_6Cl_7 has been redetermined, and the conductivity of a single crystal determined. The new results have then been rationalised using band structure calculations.

BiBr and the three different modifications of BiI are also structurally analogous and contain one-dimensional Bi_2X_4 double chains bridged by metal-metal bonded chains of interstitial, formally zero-valent Bi atoms[7,8]. The more metal-rich subvalent bismuth iodide phases are similar, but comprise metal-metal bonded networks rather than chains[8–10]. These unusual, low-dimensional chains and networks clearly have the potential to show interesting conductivity properties. Our results concerning such properties of Bi_6X_7 are therefore compared with those from similar calculations on BiBr and BiI.

Apart form the Bi_6X_7 compounds, isolated Bi_5^{3+}, Bi_8^{2+}, and Bi_9^{5+} clusters are also found in ternary compounds such as $Bi_5(MCl_4)_3$ (M = Al[11,12], Ga[13]), $Bi_8(AlCl_4)_2$[12,14], and $Bi_{10}(HfCl_6)_3$[15], which have been synthesised using regular

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high-temperature routes and structurally characterised. These compounds have also been subjected to physical chemical studies in the solid state[16] and structural studies in the liquid state[17,18]. For $Bi_8(AlCl_4)_2$ we have reported a preliminary structure determination in a short note some time ago[14]. In the meantime, in connection with subsequent investigations on $Bi_5(AlCl_4)_3$[11], we could improve the method of preparation of single crystals of $Bi_8(AlCl_4)_2$ for X-ray structure analysis. Consequently, a complete account of the final refined crystal structure of $Bi_8(AlCl_4)_2$ can now be given.

Experimental

Chemicals

Bi (Riedel-de Haën, pure grade or ALFA, 99.999% metals basis) and $SbCl_3$ (ALFA Chemicals, suprapur) were used as received. $BiCl_3$ (Riedel-de Haën; 98%, water free or J. T. Baker) was sublimed in closed glass ampoules at 220 °C priro to use. $AlCl_3$ was prepared from the elements and the crude product then sublimed twice under nitrogen. All chemicals were handled in a glovebox under dry nitrogen or by using standard vacuum techniques.

Synthesis of $Bi_8(AlCl_4)_2$

The formation of defined phases in the system Bi-$BiCl_3$-$AlCl_3$ is especially difficult because of kinetic problems and subcooling phenomena. The synthesis of crystalline $Bi_8(AlCl_4)_2$ is achieved according to a modification of the method first given by Corbett[12,19]. For a reproducible synthesis of $Bi_8(AlCl_4)_2$ from Bi-$BiCl_3$-$AlCl_3$ melt systems as well as from solutions of these components in molten $NaAlCl_4$ the exact control and variation of the acidity of the melt by addition of $AlCl_3$ is most important. In order to optimize the conditions for the isolation of single crystals, the use of a $NaAlCl_4$ flux was avoided for the present crystallisations, although the $NaAlCl_4$-containing reaction systems show less subcooling effects. A mixture of an excess of Bi with $BiCl_3$ + 4 $AlCl_3$ (this corresponds to an excess of 33 mole-% of $AlCl_3$ compared to a "neutral" melt) was enclosed in a glass tube under vacuum and heated in a glass furnace. At about 190 °C the mixture melted to form a deep-black liquid. The reaction system was equilibrated for 7 days at 350 °C. From DTA investigations of such samples it was found that some crystallisation occurs at 130–150 °C, followed by crystallisation of the greatly sub-cooled rest of the melt at about 60 °C. Single crystals were formed if the ampoule, after an initial cooling from 350 °C to 160 °C, is cooled very slowly with 2 °C/h from 160 °C to 130 °C. At 130 °C the supernatant liquid is decanted from the resulting black $Bi_8(AlCl_4)_2$ crystals. After subliming off the excess of $AlCl_3$ the solidified remaining melt is deep-black micro-crystalline with red-brown micro-crystalline regions of a yet unidentified phase in between.

Synthesis of Bi_6Cl_7

Bi_6Cl_7 has previously been synthesised by Corbett and co-workers by reacting bismuth methal with molten bismuth trichloride[2,4] or with mixtures of bismuth trichloride and potassium chloride at temperatures above 250 °C[6]. The severe problems associated with slow equilibria and concommitant metal contamination of the final product experienced in the former synthetic route are only partially relieved by adding KCl. In this work, we have therefore used two alterations of Corbetts methods, which were found to minimize these problems.

The first method consists of a reaction between Bi and $BiCl_3$ in a 1:2 ratio (total amount 220 mg) in 20 cm glass ampoules in vacuum. The ampoule was placed asymmetrically in a horizontal tube furnace with a temperature gradient 265–240 °C. The ampoule was turned, and thereby the hot and cold sides interchanged, every day during a week. Needle like, dark green to black crystals predominantly inter-grown to bundles were formed.

In the second method, Bi_6Cl_7 was conveniently synthesized from a melt of composition 2 Bi:$BiCl_3$:4 $SbCl_3$ contained in an evacuated Pyrex container. After initial equilibration at 300 °C for several days, slow cooling (1 °C/h) to 150 °C produced well-shaped single crystals of Bi_6Cl_7, which grew at the interface between the liquid and unreacted metal. Separation of these crystals from the excess of solvent was accomplished by simply turning the container upside-down (the crystals were stuck to the bottom of the container), followed by a sublimation of the remaining traces of solvent on the crystals at 180 °C. After cracking the container in the glovebox, the crystals were separated from the metal matrix by hand picking. It should be pointed out that a previous report[2] stating that Bi_6Cl_7 reduces $SbCl_3$ is obviously in error.

Crystal Structure Determination of $Bi_8(AlCl_4)_2$[20]

The crystal structure was determined from single-crystal diffraction data and the structure was solved by direct methods in the space group $P6_3/m$. The structure model was refined with full-matrix least-squares methods[21] with all unique reflections and with anisotropic temperature factors for the bismuth atoms. The data were corrected for absorption based on ψ scans for 7 reflections. The crystal data are collected in Table 1, together with the details of data collection and refinement. Because of a suspected triplet or twin formation as indicated by the apparent disorder of the $AlCl_4^-$ groups in the cell (see below) refinements were also attempted in lower-symmetry space groups (e.g. $P6_3$ as maximal subgroup) or as triplets or twins of trigonal, orthorhombic, and monoclinic cells. None of them was successful, so the description as a disordered $P6_3/m$ cell is regarded as the most appropriate description. No signs of superstructure reflections or diffuse scattering effects were observed in the diffraction patterns. Table 2 shows the final coordinates and the isotropic temperature factors for all atoms of the unit cell.

Crystal Structure Determination of Bi_6Cl_7[20]

Single-crystal diffraction data were recorded using crystals obtained by both methods described above. The atomic coordinates given by the two data sets were identical within one σ. However, the structural refinement of the data from the specimen from the Bi-$BiCl_3$-$SbCl_3$ melt gave unsatisfactory results in the sense that one chlorine atom proved to be impossible to refine anisotropically[22]. The structural results on Bi_6Cl_7 reported hereafter are therefore those from a crystal grown in a Bi–$BiCl_3$ system.

Table 1 contains the crystal data, details of data collection and refinement, whereas the positional and thermal parameters of the atoms are found in Table 3. The crystal was sealed in a glass capillary under Ar to avoid decomposition. The structure model was solved by direct methods in the space group $Pnnm$. It was refined with full-matrix least-squares methods[21] and a numerical absorption correction was applied to the data[23]. The final model shows nearly the same positional parameters for the atoms as already published[3,4,6]. However, all atoms were possible to refine with anisotropic displacement parameters[24].

Conductivity Measurement

Crystallographic investigations revealed an appreciable stability of Bi_6Cl_7 towards moisture and oxygen, and therefore the conductivity measurements were performed in laboratory atmosphere and at room temperature by using the standard four-probe method and a Keithley Electrometer. Electric connections (gold filament) were attached under microscope to a ca. 4 mm long single crystal of

Table 1. Crystal data, details of the diffraction data collection and structure analysis for Bi_6Cl_7 and $Bi_8(AlCl_4)_2$

Compound	Bi_6Cl_7	$Bi_8(AlCl_4)_2$
Molecular mass	1502.05	2009.43
Diffractometer	STOE Image Plate	Syntex $P2_1$
Radiation	Mo-K_α	Mo-K_α
Monochromator	Graphite	Graphite
Data collection mode	n/a	ω-2θ
Crystral size [mm]	0.38×0.076×0.076	0.02×0.01×0.02
Crystal system	orthorhombic	hexagonal
Space group	*P*nnm	$P6_3/m$
a [Å]	23.093(8)	17.854(4)
b [Å]	15.075(5)	
c [Å]	8.784(3)	12.953(3)
Z	8	6
D_{calcd} [g cm^{-3}]	6.57	5.60
μ (Mo-K_α) [cm^{-1}]	700	559
Temperature [K]	296	293
Scan range (2θ) [°]	7, 49	4, 54
hkl range	±9, ±17, ±26	±18, +18, +14
Measured reflections	17409	5399
Unique reflections	2535	1957
Data for refinement	2535	1957
Parameters refined	139	60
Absorption corr.	Numerical	ψ-scan
Transmission (max./min).	0.638/0.191	0.55/0.28
ρ[a]; max./min. [eÅ^{-3}]	+3.23/-2.01	+2.9/-1.9
$R(\lvert F\rvert)$[b]	0.065	0.079
$R(\lvert F\rvert)$,[b] $I>2\sigma(I)$	0.057	0.069
$wR(F^2)$[c]	0.108	0.062

[a] Largest final difference hole and peak. – [b] $R(|F|) = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$. – [c] $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]\}^{1/2}$.

Table 2. Final positional and thermal parameters for $Bi_8(AlCl_4)_2$

Atom	x	y	z	B[a]
Bi(1)	0.1448(2)	0.3693(2)	0.1312(3)	5.0(2)
Bi(2)	0.0400(2)	0.4640(2)	0.1304(3)	5.3(2)
Bi(3)	-0.0534(2)	0.2678(2)	0.0847(3)	5.3(2)
Bi(4)	-0.1269(3)	0.3380(4)	1/4	6.1(3)
Bi(5)	0.0216(3)	0.1992(3)	1/4	6.3(3)
Al(1)	0.056(2)	0.360(3)	3/4	7(1)
Cl(1)	-0.070(2)	0.347(2)	3/4	5(1)
Cl(2)	0.044(4)	0.250(4)	3/4	23(3)
Cl(3)	0.127(2)	0.443(2)	0.624(3)	13(1)
Al(2)	1/3	2/3	0.409(9)	14(6)
Cl(4)	1/3	2/3	1/4	23(5)
Cl(5)	0.441(1)	0.782(1)	0.486(2)	6.1(7)
Al(3)	1/3	2/3	0.534(6)	1.5(10)
Cl(6)	1/3	2/3	0.703(7)	8(3)
Al(4)	0	0	0.524(6)	1.1(10)
Cl(7)	0	0	0.664(6)	5(2)
Cl(8)	0.028(3)	0.126(3)	0.550(5)	9(2)

[a] For the Bi atoms, the B values given are B_{equiv} (1/3 of the trace of the orthogonalized B_{ij} tensor).

Bi_6Cl_7 using an electrically conducting silver-based glue. The distance between the connections was microscopically determined to 0.80 mm and the cross-sectional area of the crystal to be 0.24 mm^2.

Band Structure Calculations

All calculations performed in this work were made using the extended Hückel (eH) method[25–27]. The tested input parameters, which are shown in Table 4, have been employed in a previous work[28]. The tight-binding approximation was used for the one-dimensional systems[29].

Table 3. Final positional and thermal parameters for Bi_6Cl_7

Atom	x	y	z	B_{equiv}[a]
Bi(1)	0.04609(5)	0.22286(8)	0.1869(1)	3.58(3)
Bi(2)	0.20055(4)	0.15447(8)	0.1822(1)	3.48(3)
Bi(3)	0.41018(5)	0.45454(9)	0	2.50(3)
Bi(4)	0.09865(6)	0.0691(1)	0	3.25(3)
Bi(5)	0.07294(8)	0.3980(1)	0	4.57(4)
Bi(6)	0.41370(7)	0.1014(1)	0	3.80(4)
Bi(7)	0.85758(5)	0.30777(9)	0	2.38(3)
Bi(8)	0.23876(6)	0.3301(1)	0	3.21(3)
Bi(9)	0.15296(5)	0.34224(9)	0.2676(1)	4.03(3)
Cl(1)	0	0	0.282(1)	3.3(2)
Cl(2)	0.5486(4)	0.0831(7)	0	3.6(2)
Cl(3)	0.6099(4)	0.3751(6)	0	3.1(2)
Cl(4)	0.7650(4)	0.2098(7)	0	3.8(2)
Cl(5)	0.7893(5)	0.4458(7)	0	4.5(2)
Cl(6)	0.3134(4)	0.0135(7)	0	3.7(2)
Cl(7)	0.3384(3)	0.2143(4)	0.1928(7)	2.9(1)
Cl(8)	0.3333(3)	0.4446(5)	0.2142(8)	3.3(1)
Cl(9)	0.9327(4)	0.1629(7)	0	3.8(2)
Cl(10)	0.4432(3)	0.0832(5)	0.3053(7)	3.2(1)
Cl(11)	0.4647(4)	0.2793(7)	0	3.8(2)

[a] B_{equiv}: 1/3 of the trace of the orthogonalized B_{ij} tensor.

Table 4. Parameters used in the eH calculations

Atom	orbital	h_{ii} / eV	ζ_i
Bi	6s	-18.67	2.56
	6p	-7.81	2.07
Cl	3s	-26.30	2.18
	3p	-14.20	1.73
Br	4s	-22.07	2.59
	4p	-13.10	2.13
I	5s	-18.00	2.68
	5p	-12.70	2.32

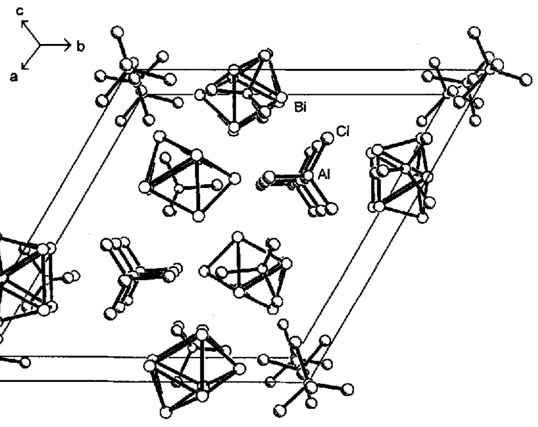
Results and Discussion

Crystal Structure of $Bi_8(AlCl_4)_2$

The structure consists of Bi_8^{2+} cluster cations and disordered, tetrahedral $AlCl_4^-$ anions. A projection of the unit cell parallel to [001] is given in Figure 1.

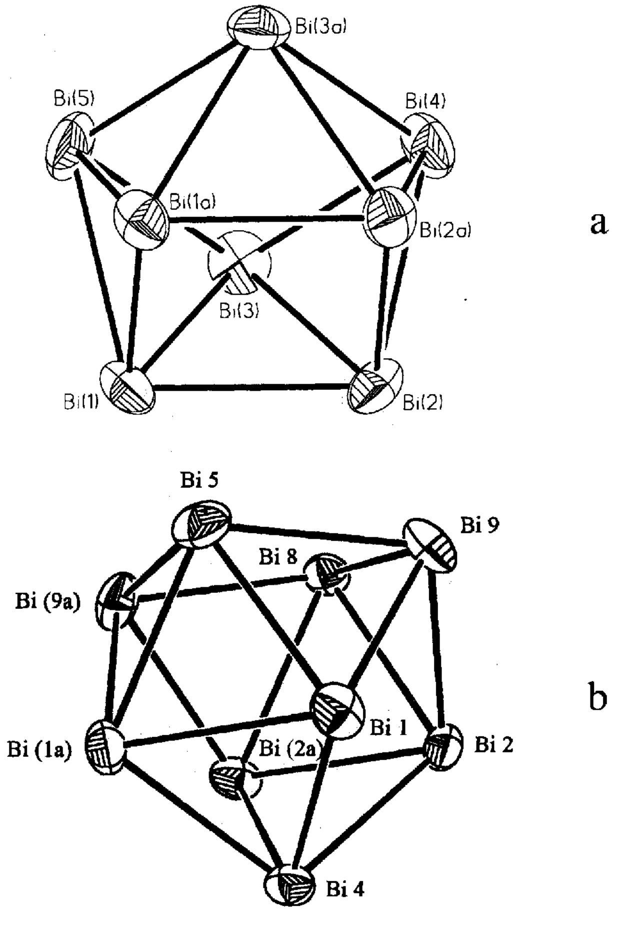
The Bi_8^{2+} clusters (Fig. 2a) have a square-antiprismatic molecular structure. They contain a crystallographic mirror

Figure 1. The unit cell of $Bi_8(AlCl_4)_2$ projected onto [001]. Only one of the two possible orientations of the disordered $AlCl_4^-$ groups centered at 0,0,z, at 1/3, 1/3, z and at 2/3, 1/3, z is shown



plane, and their deviation from an idealized D_{4h} symmetry is only very small. The average Bi–Bi distance of 3.10 Å is close to the Bi–Bi distance in elementary bismuth (3.07 Å). The geometry of the cluster cation is remarkably symmetric with rather uniform Bi–Bi bond lengths within the square faces (average 3.09 Å) and the triangular faces of the tetragonal antiprism (average 3.11 Å). The same high symmetry is observed for the Bi–Bi–Bi bond angles which vary between 88.1° and 91.8° in the square faces and between 59.3° and 60.7° in the triangular ones. The square antiprismatic structure of the Bi_8^{2+} cluster is in agreement with predictions from a qualitative MO description of this 22-electron system[12,19]. A stable cube-like (O_h) or dodecahedral (D_{2d}) cluster would require 24 or 20 valence electrons, respectively. The structural relationship to the Bi_9^{5+} cluster may give indications for possible transformation reactions. By rather small atom shifts the square antiprismatic Bi_8^{2+} is transformed into the triply capped trigonal prismatic Bi_9^{5+} unit by addition of one Bi^{3+}.

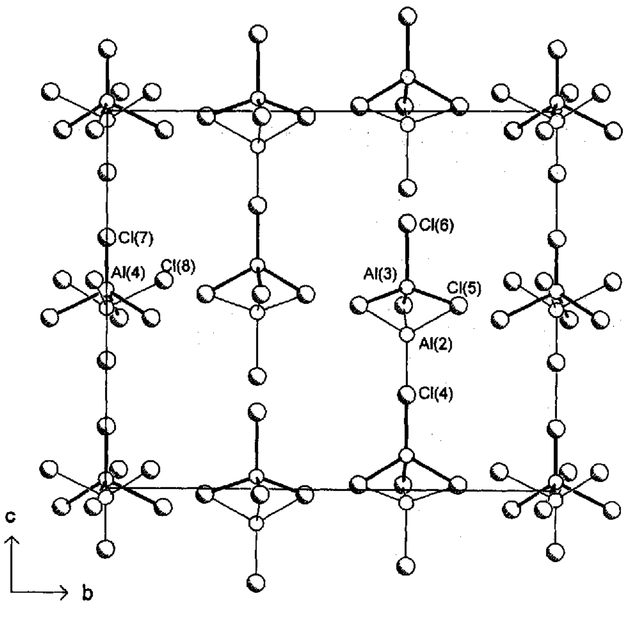
Figure 2. ORTEP representations of the crystal structures of the bismuth cluster cations in $\mathrm{Bi_8(AlCl_4)_2}$ and $\mathrm{Bi_6Cl_7}$. Thermal ellipsoids are drawn at the 50% probability level. (a) The square-antiprismatic Bi_8^{2+} cation in $\mathrm{Bi_8(AlCl_4)_2}$. Selected bond lengths [Å] and bond angles [°]: Bi(1)–Bi(2) 3.087(7), Bi(1)–Bi(3) 3.124(5), Bi(1)–Bi(5) 3.122(5), Bi(1)–Bi(1a) 3.078(9), Bi(2)–Bi(3) 3.093(5), Bi(2)–Bi(4) 3.105(5), Bi(2)–Bi(2a) 3.099(9), Bi(3)–Bi(4) 3.086(7), Bi(3)–Bi(5) 3.086(7); Bi(1a)–Bi(1)–Bi(2) 90.2(1), Bi(1)–Bi(2)–Bi(3) 60.7(1), Bi(1)–Bi(3)–Bi(4) 102.7(1). (b) The distorted, tricapped trigonal prismatic Bi_9^{5+} cation in $\mathrm{Bi_6Cl_7}$. Selected bond lengths [Å] and bond angles [°]: Bi(8)–Bi(9) 3.080(2), Bi(1)–Bi(4) 3.089(2), Bi(5)–Bi(9) 3.106(2), Bi(2)–Bi(4) 3.124(2), Bi(2)–Bi(9) 3.128(2), Bi(1)–Bi(9) 3.136(2), Bi(1)–Bi(5) 3.170(2), Bi(2)–Bi(2a) 3.201(3), Bi(2)–Bi(8) 3.217(2), Bi(1)–Bi(1a) 3.283(2); Bi(5)–Bi(1)–Bi(9) 59.02(5), Bi(1)–Bi(5)–Bi(9) 59.95(4), Bi(1)–Bi(9)–Bi(5) 61.03(5), Bi(5)–Bi(9)–Bi(8) 79.70(5), Bi(9)–Bi(5)–Bi(9a) 98.38(7), Bi(9)–Bi(8)–Bi(9a) 99.50(7), Bi(4)–Bi(2)–Bi(9) 103.37(5), Bi(4)–Bi(1)–Bi(9) 103.99(5)



The Bi–Cl distances suggest only weak interactions between the cluster cations and the surrounding anions; all Bi–Cl distances are above 3.60 Å except two at 3.34(2) and 3.42(2) Å. On the other hand, there is only insufficient shielding of the Bi_8^{2+} cluster cations against each other by the AlCl_4^- ions: Some relatively short intermolecular Bi–Bi distances of 3.900(6) Å (Bi1···Bi3a) and 4.109(6) Å (Bi2···Bi2a) suggest weak bonding interactions between the Bi_8^{2+} units.

If the space group $P6_3/m$ is chosen as symmetry of the unit cell the AlCl_4^- ions in the structure of $\mathrm{Bi_8(AlCl_4)_2}$ can only be described in a disordered arrangement across the mirror planes, as shown in Figure 3. Due to large experimental errors the individual Al–Cl distances vary between 1.81(9) and 2.26(5) Å; the individual experimental Cl–Al–Cl bond angles are observed between 101(2) and 115(2)°. Within one column of AlCl_4^- tetrahedra along [001] steric requirements result in cooperative parallel alignment of the tetrahedra. No signs of complete or partial order of the columns with respect to each other is observed from the diffraction experiments.

Figure 3. The disordered structure of the AlCl_4^- ions in the unit cell of $\mathrm{Bi_8(AlCl_4)_2}$ as given by a projection parallel to *a*



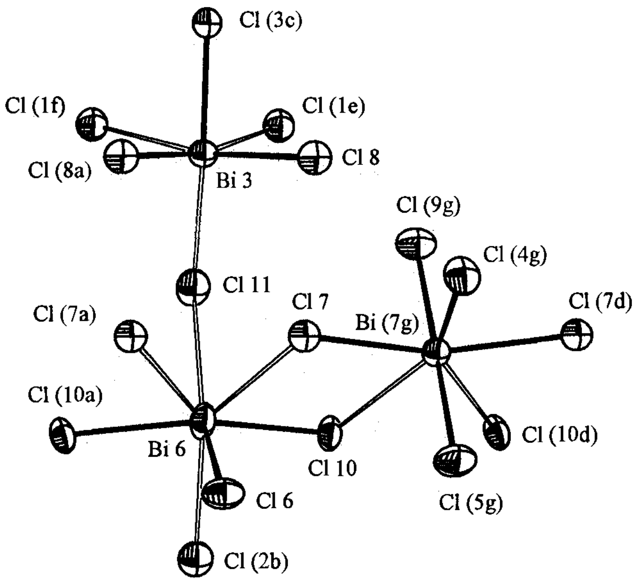
The Crystal Structure of $\mathrm{Bi_6Cl_7}$

The crystal structure consists of discrete Bi_9^{5+} cluster cations (C_s symmetry; Fig. 2b) and chlorobismuthate(III) anions. The deviations of the atomic positions from those of the most accurate of the former determinations[6] are small and the intra-cluster Bi–Bi bond distances found [3.080(2)–3.283(2) Å, average 3.15 Å] as well as the cluster geometry (distorted, tricapped trigonal prism) are in accordance with those given in the earlier reports[3–6]. The larger Bi–Bi bond lengths in Bi_9^{5+} as compared to Bi_8^{2+} in $Bi_8(AlCl_4)_2$ may be correlated to the higher valence electron concentration of 2.75 per Bi atom in Bi_8^{2+} versus 2.44 per Bi in Bi_9^{5+}. In Bi_6Cl_7, the clusters are well isolated from each other but in contact with the chlorobismuthate(III) anions via chlorides at distances between 3.209(8) and 3.451(7) Å. These Bi–Cl distances are similar to those found in $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$, but significantly shorter than those in $Bi_8(AlCl_4)_2$. The stronger interaction of the Bi_9^{5+} cluster cation with neighbouring chlorine atoms may be considered due to the larger electrostatic charge per bismuth atom on Bi_9^{5+} as compared to Bi_8^{2+}, and may also be a contributing factor to the longer average Bi-Bi distance in Bi_9^{5+}.

The chloride environment around the three crystallographically unique bismuth(III) ions is depicted in Figure 4. The Bi(6) and Bi(7) ions are linked into infinite chains running along the crystallographic *c* axis by the bridging chlorides Cl(7) and Cl(10). These chains are, in turn, linked in pairs via $Bi_2Cl_{10}^{4-}$ units involving Bi(3), Cl(1), Cl(3), Cl(8), and Cl(11) to form a rather intricate, polymeric network (Fig. 5). The $Bi_2Cl_{10}^{4-}$ units can be visualised as consisting of two distorted octahedral units linked at a common edge by the chlorides Cl(1) in the same manner as in $K_4(Bi_2Cl_{10}) \cdot 4\ H_2O$[30], whereas the coordination geometries around Bi(6) and Bi(7) are more irregular. Considering the pronounced polymeric nature of the anionic part of Bi_6Cl_7 we feel that the previous[3–6] description of the structure as corresponding to $(Bi_9^{5+})_2(BiCl_5^{2-})_4\ (Bi_2Cl_8^{2-})$ with *isolated* chlorobismuthate(III) anions needs to be revised. A formulation which better describes the structural properties would be $(Bi_9^{5+})_2(Bi_3Cl_{14}^{5-})_2$, which illustrates the presence of the double $^1_\infty[Bi_3Cl_{14}^{5-}]$ strands.

Polymeric chlorobismuthate(III) structures have previously been reported in the literature. In $BiCl_3 \cdot 2$ etu (etu = ethylenethiourea)[31] and bis(piperidinium)pentabromobismutathe(III)[32] these chains are composed of BiX_6^{3-} octahedra sharing a common apex. BiX_6^{3-} octahedra linked by common edges to infinite chains are found in 2-methylpyridinium tetrabromo- and tetraiodobismuthate(III)[33]. Finally, chloride bridged infinite chains of $BiCl(Mo)_2$ units are found in $\{BiCl[Mo(CO)_3(\eta\text{-}C_5H_5)_2]\}$[34] and the electronic structure of such four-coordinate, 10-electron Bi-species has been thoroughly investigated[35].

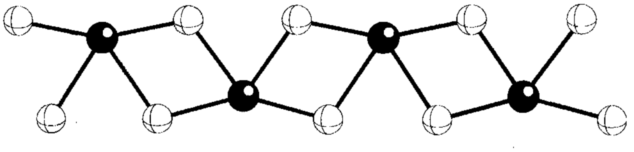
Figure 4. The chloride environment around Bi^{III} in Bi_6Cl_7. All Bi–Cl bonds shorter than 2.80 Å are drawn as solid, black lines; the non-filled sticks represent weaker Bi–Cl bonds up to 3.10 Å. Selected bond lengths [Å] and bond angles [°]: Bi(3)–Cl(8/8a) 2.591(7), Bi(3)–Cl(3c) 2.610(9), Bi(3)–Cl(1e/1f) 2.904(7), Bi(3)–Cl(11) 2.93(1), Bi(6)–Cl(6) 2.669(9), Bi(6)–Cl(10/10a) 2.780(6), Bi(6)–Cl(2b) 2.91(1), Bi(6)–Cl(11) 2.93(1), Bi(6)–Cl(7/7a) 2.964(6), Bi(7g)–Cl(4g) 2.598(9), Bi(7g)–Cl(5g) 2.61(1), Bi(7g)–Cl(7/7d) 2.755(6), Bi(7g)–Cl(9g) 2.79(1), Bi(7g)–Cl(10/10d) 3.087(6); Cl(8)–Bi(3)–Cl(8a) 93.1(3), Cl(11)–Bi(3)–Cl(3c) 164.8(3), Cl(7)–Bi(6)–Cl(10) 69.5(2), Cl(7)–Bi(6)–Cl(7a) 69.7(2), Cl(7)–Bi(7g)–Cl(10) 67.9(2)



Theoretical Band Structures of Bi_6Cl_7 and Related Compounds

The infinite chains along the *c* axis are indeed the only extended structural units in Bi_6Cl_7 with the potential to mediate conduction, even if it is obvious that no metallic conduction should be expected in such a weakly interacting extended structure. The corresponding Bi_6Br_7 structure is analogous, and can be described in terms of the same structural units with the same symmetry properties. The interaction between main-group $d^{10}s^2$ metal ions, such as Tl^+, Pb^{2+}, and Bi^{3+}, and chloride and bromide tend to be very similar both qualitatively and quantitatively[28,36,37]. It is therefore interesting to note the different conductivity properties reported for Bi_6Cl_7 and Bi_6Br_7[7]. Our conductivity study in the *c* direction of a single crystal of Bi_6Cl_7 clearly shows the compound to be semiconducting at the same order of magnitude as elemental Si. The conductivity at 25 °C amounted to $7.5 \cdot 10^{-5}\ \Omega^{-1}\ cm^{-1}$. Elemental Si has an energy gap of about 1 eV, and possibly that is what to expect for Bi_6Cl_7 as well. BiBr has also been reported to be an anisotropic semiconductor with an energy gap of at least 0.2 eV[7].

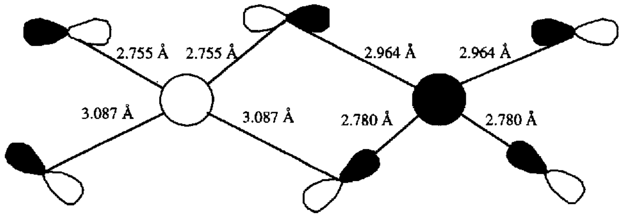
In order to gain an insight into the structure-conductivity relationship in the compounds Bi_6X_7 (X = Cl or Br) and BiX (X = Br or I), band structure calculations at the eH level were performed. As mentioned above, the only structural feature that propagates through the crystal structure in the true sense consists of the bridged $Bi_2Cl_9^{3-}$ units along the *c* axis. If the equatorial chlorides are stripped off, the conducting structural unit can be seen as a chain of distorted $Bi_2Cl_4^{2+}$ units **1**.



1

The asymmetry of the $Bi_2Cl_2^{4+}$ entity could possibly be attributed to a Jahn-Teller, or Peierls, distortion much like that in molecular cyclobutadiene, in which the degeneracy of a four-electron/four-MO scheme produced in a perfectly square configuration is removed by a distortion to form two short and two long Bi–Cl bonds. Due to the ionicity of the Bi–Cl bonds, the distortion is more likely induced by packing requirements of the surrounding structural units.

As would be expected, the band structure calculations on the one-dimensional $Bi_2Cl_9^{3-}$ chain suggest a very large band gap (7.5 eV), a fact which indicates that the $Bi_2Cl_9^{3-}$ chain is an electronic insulator. The highest occupied crystal orbital (HOCO) at Γ can be visualised as **2**.



2

This band can thus be regarded as weakly Bi–Cl bonding. The lowest unoccupied crystal orbital (LUCO) at about +1.8 eV is, however, essentially Bi(p_z) non-bonding or weakly equatorially Bi–Cl antibonding. The band characters do not change much on the way from Γ to X. The bond distances indicate weak Bi–Cl bonding, in agreement with the overlap populations about 0.04 and 0.09, respectively, for the long and short bridging Bi–Cl bonds. The charge on Bi is about +1.9 and on Cl −0.8. The corresponding overlap population in $BiCl_3(s)$ is 0.14 at a Bi–Cl distance of 2.73 Å in a six-coordinate structure of C_{3v} symmetry[38].

As described above, the Cl atoms in the $Bi_2Cl_9^{3-}$ structural fragments bridge to the Bi_9^{5+} clusters at distances in the range 3.209(8)–3.451(7) Å. Such an arrangement indicates the potential for the clusters to work as electron reservoirs for the $Bi_2Cl_2^{4+}$ network. In order to study this phenomenon, one-dimensional band structure calculations along the *c* axis of the half unit cell of Bi_6Cl_7 were performed. The band structure and DOS are shown in Figure 6. The band structure reveals two pieces of information. First, the structural units are pretty isolated and only very small effects are seen going from Γ to X. Second, and more importantly, the band gap has decreased to about 0.8 eV. Such a band gap is consistent with semiconducting behavior.

The crystal orbitals (CO's) about the energy gap are very complex and any attempt to visualize them would result in a total mess. The CO's above and below the band gap all contain contributions from both $Bi_2Cl_2^{4+}$ chains and the Bi_9^{5+} clusters. The thermal excitation of electrons from the highest occupied CO to an unoccupied one above the energy gap would thus produce holes in the HOCO's and electrons in the LUCO's. Both types of charge carriers have the potential to give rise to electrical conduction since the $Bi_2Cl_2^{4+}$ chains contribute significantly to both the COs above and below the energy gap. The Bi_9^{5+} clusters thus indeed work as electron reservoirs in the Bi_6Cl_7 structure. The average Bi–Bi overlap population in the Bi_6Cl_7 structure is slightly lower than in a totally isolated cluster with the same structure: 0.40 as compared to 0.43. The average charge on Bi in Bi_9^{5+} is changed from +0.56 to +0.45 when such an isolated cluster is placed in the Bi_6Cl_7 structure, which indicates an addition of electron density to the Bi_9^{5+} clusters.

Figure 5. A section of the polymeric, anionic chlorobismuthate(III) strand in Bi_6Cl_7. Open circles: Cl; shaded circles: Bi

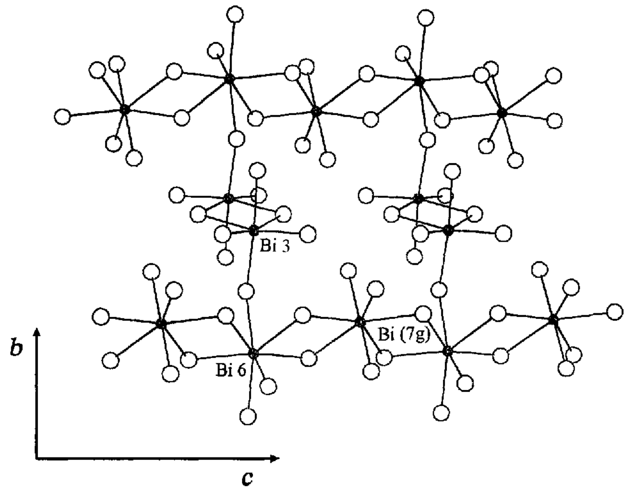
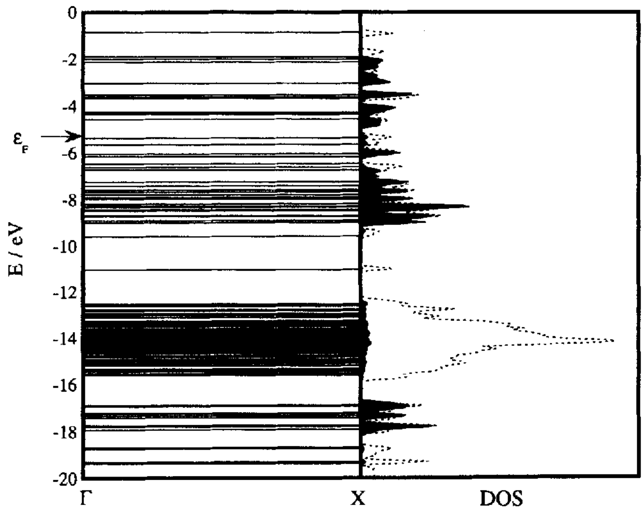


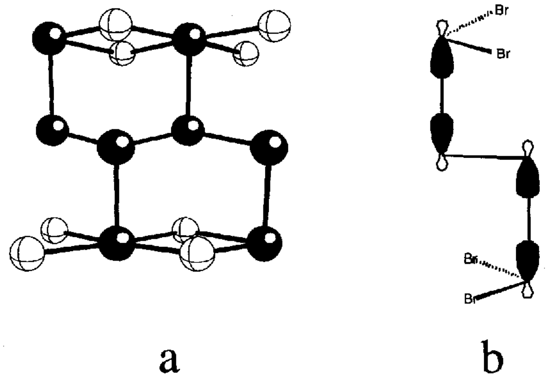
Figure 6. The band structure and DOS of a one-dimensional calculation along the crystallographic *c* axis of half of the unit cell of Bi_6Cl_7. The DOS shows the total and Bi_9^{5+} (shaded) contribution



In Bi_6Br_7, the cell parameters are slightly larger[7], since the intermolecular Bi–Br distances are slightly longer than the corresponding Bi–Cl ones, but the space group of Bi_6Cl_7 could very well be used to describe the Bi_6Br_7 structure as well. The band structure and DOS of the $Bi_2Br_9^{3-}$ chain is also analogous to that of $Bi_2Cl_9^{3-}$. Again the band gap is rather large, 6.5 eV. The Bi–Br overlap population is 0.14 for the shorter (2.91–2.93 Å) and 0.10 for the longer (3.08–3.19 Å) Bi–Br bonds, and the charge is about +1.9 on Bi and −0.8 on Br. The results of a band structure calculation on half the Bi_6Br_7 unit cell along the *c* axis are similar to those of Bi_6Cl_7. The band gap is slightly larger, 1.5 eV. The average Bi–Bi overlap population in the Bi_9^{5+} cluster is 0.42. The contents of the CO's differ from those of Bi_6Cl_7 only in quantity. Consequently the two compounds Bi_6Cl_7 and Bi_6Br_7 are both predicted to be anisotropic (along the crystallographic c axis only) semiconductors by the structure and theoretical calculations.

The structure of BiBr is quite different from that of Bi_6Br_7[7]. It crystallizes in the monoclinic space group $C2/m$ and consists of one-dimensional double-chains of $BiBr_2$ with interstitial Bi atoms, which also are connected by direct bonds along the crystallographic b axis. Two such repeating units are shown in Figure 7a. The structure alone indicates that the BiBr compound will show anisotropy in conductivity properties. The Bi–Br distances are 2.94–2.95 Å and the directly connected Bi–Bi distances are as short as 3.02–3.04 Å. The average Bi–Br overlap population is thus about 0.10, the Bi–Bi one between the outer (connected to the bromides) and inner (interstitial) Bi atoms is 0.68 and that between inner Bi atoms is 0.61. The charge on the Br atoms is about −0.6. That on the outer Bi atoms is +1.1 and that on the inner ones is +0.1.

Figure 7. (a) Two repeating Bi_4Br_4 units in the crystal structure of BiBr. (b) The HOCO of BiBr at Γ



The results of a one-dimensional band structure calculation along the b axis are shown in Figure 8. The band gap is 3.5 eV. The HOCO at Γ consists essentially of bonding contributions between the outer and inner bismuth atoms together with a slight anti-bonding contribution between the inner Bi atoms, as shown in Figure 7b. This character changes on the way to X, where two degenerate bands of essentially Bi(outer)–Bi(inner) bonding character prevail. The LUCO remains Bi(p_x) and Br(p_x) non- or weakly antibonding in the whole Brillouin zone. It is thus likely that any semiconducting property along the crystallographic b axis in BiBr should be attributed to thermally induced holes as carries in the HOCO band. Again, the inner Bi atoms operate as electron reservoirs like in the Bi_6X_7 compounds (X = Cl or Br).

BiI exists in three different modifications[8]. Each one contains BiBr-type double-chains, and we have chosen to have a closer look at α-BiI since it is the structural analogue of BiBr. The Bi–I distances are 3.11–3.15 Å and the Bi–Bi distances are 3.04–3.06 Å. The average Bi–I overlap population is 0.10, which can be compared with 0.21 in a BiI_6^{3-} unit of C_{3v} symmetry and a Bi–I distance of 3.07 Å[38]. The overlap population between Bi(outer) and Bi(inner) is 0.67 and that between Bi(inner) and Bi(inner) is 0.61. The charges are about −0.6 on I, +1.1 on Bi(outer) and +0.1 on Bi(inner). The results of band structure calculations are very similar to that of BiBr, with a band gap of about 2.6 eV. Therefore the conductivity properties are expected to be analogous to those of BiBr.

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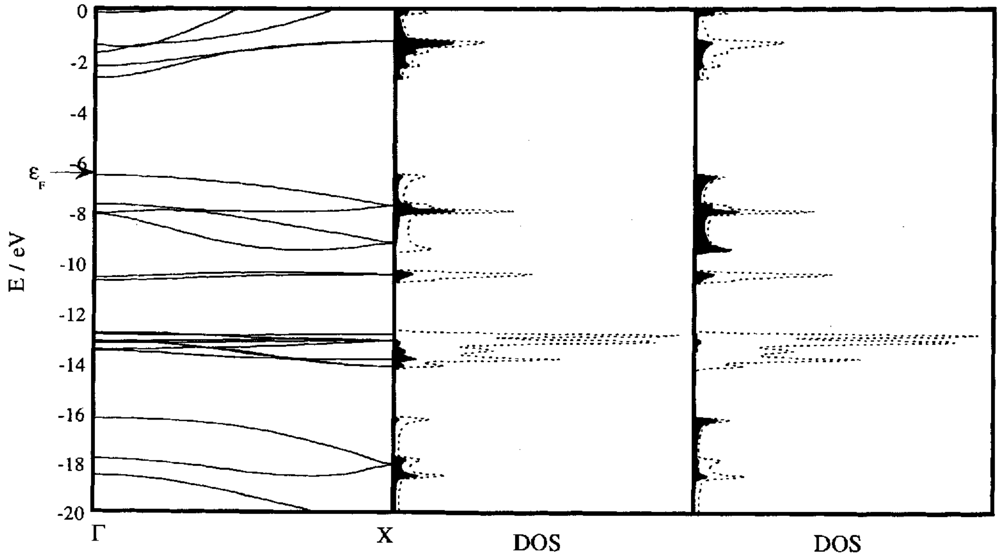
Figure 8. The band structure and DOS of the one-dimensional chain in BiBr. The DOS shows the total and outer and inner Bi (shaded) contributions, respectively



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