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The Crystal Structure of a Tetranuclear Bismuth(III) Complex, $(C_5H_5NH)_6Bi_4Cl_{18}$

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The crystal structure of $(C_5H_5NH)_6Bi_4Cl_{18}$ has been determined and refined from 2605 independent counter reflections (Mo$K\alpha$) to a final R-value of 0.039. The crystals are monoclinic, space group $C2/m$ with $a=17.224(3)$, $b=14.874(2)$, $c=13.043(2)$ Å, $\beta=123.94(2)°$ and $Z=2$. The structure is built up of pyridinium ions and isolated $Bi_4Cl_{18}^{6-}$ groups, the latter representing a new type of halide complex. The $Bi_4Cl_{18}^{6-}$ complex consists of two pairs of edge-sharing octahedra joined by their top ligands. Of the six Bi–Cl bonds, the three short terminals vary between 2.57 and 2.61 Å and the long bridgings are 2.83–2.94 Å.

It has long been known that the presence of a large cation in a crystal structure will promote the formation of large anion complexes. These views have been summarized by Basolo[1] in 1968 and more recently by Martinsen and Songstad.[2] Whereas comprehensive studies have been made in the solid state on complexes between Bi^{3+} and Br^- and I^- [3-5] only a few complex bismuth(III) chlorides have been investigated. We started with the pyridinium ion as cation and chose the previously known compound $(C_5H_5NH)_3Bi_2Cl_9$.[6]

EXPERIMENTAL

Crystal data. $(C_5H_5NH)_6Bi_4Cl_{18}$; F.W. 1954.73. Monoclinic, space group $C2/m$; $a=17.224(3)$ Å, $b=14.874(2)$ Å, $c=13.043(2)$ Å, $\beta=123.94(2)°$, $V=2272.2$ Å^3. $D_m=2.33$ g cm^{-3}, $Z=2$, $D_x=2.34$ g cm^{-3}, $\mu=129$ cm^{-1} (Mo$K\alpha$).

Single crystals of the title compound were prepared in the following way: 7.8 g bismuth oxide chloride was dissolved in 30 ml hot dilute (15 %) hydrochloric acid. 4.8 ml pyridine was added dropwise to the hot solution under constant stirring. The solution was then cooled very slowly and after about 30 min colourless quadratic crystals were formed. Analyses gave Bi 42.27 (42.76), Cl 32.19 (32.65), C 19.13 (18.43), N 4.17 (4.30) and H 1.90 (1.84). Calculated values are given within parentheses.

Preliminary precession photographs indicated the Laue symmetry $2/m$. The only systematic absences were $h+k+l=2n+1$, which are characteristic of the space groups Im, $I2$ and $I2/m$. Before indexing the powder photographs the body-centered cell [$\beta=103.47(2)°$] was transformed to a C-centered cell [$\beta=123.94(2)°$].

The dimensions of the single crystal used were $0.11\times0.17\times0.22$ mm^3. Intensity data were collected on a computer-controlled Enraf-Nonius CAD-4 diffractometer with Mo$K\alpha$ radiation and a graphite monochromator ($\lambda=0.70930$ Å). The $\omega-2\theta$ scan technique was used with a peak scan interval $\Delta\omega=(0.80+0.50\tan\theta)°$ and a maximum time of 4 min for each reflection. In one quadrant of reciprocal space 4195 independent reflections with $3°<\theta<30°$ were measured. Out of these, 2605 with $I>3\sigma(I)$ were used in the structure analysis. Corrections were applied for Lorentz-polarization and absorption effects. The transmission factors, evaluated by numerical integration, varied from 0.15 to 0.27.

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the bismuth atoms were deduced from the three-dimensional Patterson function, assuming space group $C2/m$. As the positions of all other non-hydrogen atoms could be found from three-dimensional fourier maps no other space

Table 1. Positional and thermal parameters obtained in the least-squares refinement. Estimated standard deviations are given within parentheses. The anisotropic temperature factors U_{ij} (Å^2) for the bismuth and chlorine atoms are based on the expression: $\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+2U_{23}b^*c^*kl)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	.37709(2)	.18982(2)	.31101(3)	.0300(2)	.0259(2)	.0378(2)	.0002(1)	.0173(1)	−.0012(1)
Cl(1)	.3677(4)	0	.3099(5)	.1352(50)	.0291(18)	.0959(36)	0	.0700(36)	0
Cl(2)	.3538(2)	.1778(2)	.0992(2)	.0527(13)	.0625(16)	.0425(11)	.0129(12)	.0265(10)	.0011(11)
Cl(3)	.3821(2)	.3632(2)	.3026(2)	.0442(12)	.0276(9)	.0581(14)	.0002(9)	.0299(11)	−.0005(10)
Cl(4)	.5754(2)	.1965(2)	.4346(2)	.0409(11)	.0516(14)	.0518(12)	.0102(11)	.0268(10)	.0017(11)
Cl(5)	.1990(2)	.1987(2)	.2235(3)	.0347(10)	.0547(15)	.0671(15)	−.0068(11)	.0271(11)	−.0012(13)

Atom	x	y	z	B	Atom	x	y	z	B
C(1)	.1683(13)	0	.9910(18)	5.6(4)	C(7)	.7822(10)	.0798(10)	.5212(13)	6.1(3)
C(2)	.1224(9)	.0815(9)	.9580(12)	5.5(3)	C(8)	.7378(14)	0	.5085(19)	6.0(4)
C(3)	.0261(11)	.0783(11)	.8858(14)	6.7(3)	C(9)	.6828(13)	0	.1640(17)	5.4(4)
C(4)	−.0217(15)	0	.8537(20)	6.3(4)	C(10)	.6472(8)	.0798(8)	.1690(10)	4.5(2)
C(5)	.9166(11)	0	.5620(15)	4.3(3)	C(11)	.5708(9)	.0809(9)	.1793(12)	5.3(3)
C(6)	.8729(7)	.0804(7)	.5474(9)	4.0(2)	C(12)	.5331(13)	0	.1828(18)	5.6(4)

groups were tried. The resulting atomic positions were refined by means of least-squares calculations, using anisotropic temperature factors for the bismuth and chlorine atoms and isotropic ones for the other non-hydrogen atoms. The hydrogen atoms were not included in the calculations. The nitrogen and carbon atoms in the pyridine groups could not be unequivocally distinguished and therefore all non-hydrogen atoms in the rings were treated as carbon atoms.

In the final refinement a parameter was included to correct for secondary extinction.[7] The final R-factors were $R=0.039$ and $R_w=0.049$, with the isotropic extinction parameter $g=0.33(3)$. The value of S, defined by $[\Sigma w_i(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, where m and n are the numbers of observations and parameters varied, was 1.36. The function minimized was $\Sigma w_i(|F_o|-|F_c|)^2$, with $w_i^{-1}=\sigma^2(|F_o|)+(0.025\times|F_o|)^2$. The scattering factors used were those of Doyle and Turner.[8]

The final coordinates and thermal parameters are listed in Table 1. Lists of observed and calculated structure factors are available on request from Division of Inorganic Chemistry 2.

RESULTS AND DISCUSSION

Selected distances and angles within the present structure are given in Table 2 which also includes the deviations of the atoms for their respective best planes in the pyridinium ions. For notations of the atoms and rings, *cf.* Tables 1, 2.

The pyridine rings. The carbon and nitrogen atoms of the pyridine rings could as mentioned not be distinguished with certainty. Hydrogen atom positions were geometrically deduced in order to calculate possible N−H···Cl hydrogen bonds. The numbering of the H atoms is the same as for the corresponding 'carbon' atoms. Assuming C(N)−H bonds of 0.95 Å, the two shortest Cl−H contacts, Cl(4)−H(6) and Cl(5)−H(10), were calculated to 2.52 and 2.56 Å. The distances Cl(4)−C(6) and Cl(5)−C(10) are 3.41 and 3.38 Å and the corresponding C(N)−H−Cl angles 157 and 145°. Thus if there exist N−H···Cl hydrogen bonds they are weak and it does not seem unreasonable to assume that the atoms C(6) and C(10) in the pyridinium ions II and III, respectively, stand for (0.5 C+0.5 N) each and that the pyridinium ion I is completely disordered with respect to the nitrogen atom. Similar disordering has been found in other pyridinium compounds containing anionic halide complexes where the N−H···X hydrogen bonds are weak or absent; for a survey, *cf.* Ref. 9.

The chloro bismuthate(III) complex. A stereoview of the content of one unit cell of the title compound is given in Fig. 1. It is seen that the crystal structure contains discrete $Bi_4Cl_{18}^{6-}$ groups centred about the crystallographic points $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$, which coincide with the point position 2(*d*) in the space group used,

Table 2. Selected bond distances (Å) and angles (°) in the crystal structure of $(C_5H_5NH)_6Bi_4Cl_{18}$. Distances (Å) from the best planes through the rings I – III are also given.

Within the pyridinium ions

Ring I			
C(1) – C(2)	1.38(2)	C(2) – C(1) – C(2)	123(2)
C(2) – C(3)	1.38(2)	C(1) – C(2) – C(3)	116(1)
C(4) – C(3)	1.35(2)	C(2) – C(3) – C(4)	122(2)
		C(3) – C(4) – C(3)	119(2)
Ring II			
C(5) – C(6)	1.37(1)	C(6) – C(5) – C(6)	122(1)
C(6) – C(7)	1.40(2)	C(5) – C(6) – C(7)	119(1)
C(8) – C(7)	1.37(2)	C(6) – C(7) – C(8)	120(1)
		C(7) – C(8) – C(7)	120(2)
Ring III			
C(9) – C(10)	1.35(1)	C(10) – C(9) – C(10)	122(2)
C(10) – C(11)	1.39(2)	C(9) – C(10) – C(11)	119(1)
C(12) – C(11)	1.38(2)	C(10) – C(11) – C(12)	119(1)
		C(11) – C(12) – C(11)	121(2)

Distances from the best planes through the rings

I		II		III	
C(1)	−0.001	C(5)	0.013	C(9)	−0.004
C(2)	0.006(x2)	C(6)	−0.008(x2)	C(10)	0.001(x2)
C(3)	−0.016(x2)	C(7)	−0.001(x2)	C(11)	0.005(x2)
C(4)	0.021	C(8)	0.005	C(12)	−0.008

Within the $Bi_4Cl_{18}^{6-}$ complex

Bi – Cl(2)	2.567(3)	Cl(1) – Bi – Cl(3)	177.7(1)
Cl(3)	2.585(2)	Cl(2) – Bi – Cl(4)	91.7(1)
Cl(5)	2.611(2)	Cl(4) – Bi – Cl(4)	82.5(1)
Cl(1)	2.828(1)	Cl(4) – Bi – Cl(5)	90.6(1)
Cl(4)	2.850(2)	Cl(5) – Bi – Cl(2)	95.4(1)
Cl(4)	2.941(3)		

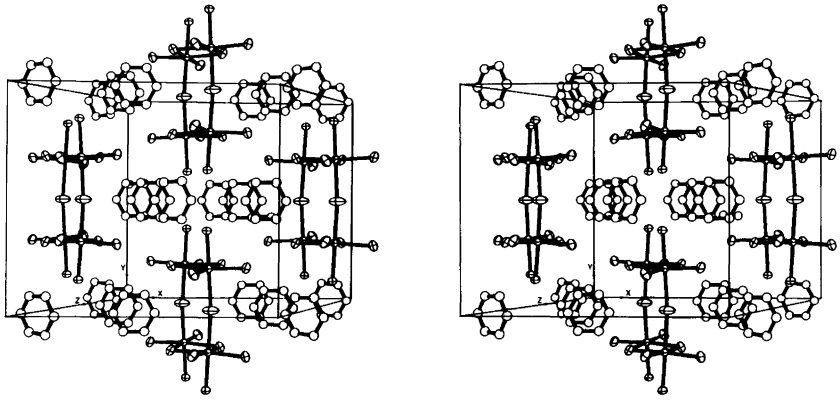

Fig. 1. A stereoview of the unit cell of $(C_5H_5NH)_6Bi_4Cl_{18}$, showing the $Bi_4Cl_{18}^{6-}$ complexes and the pyridine rings.

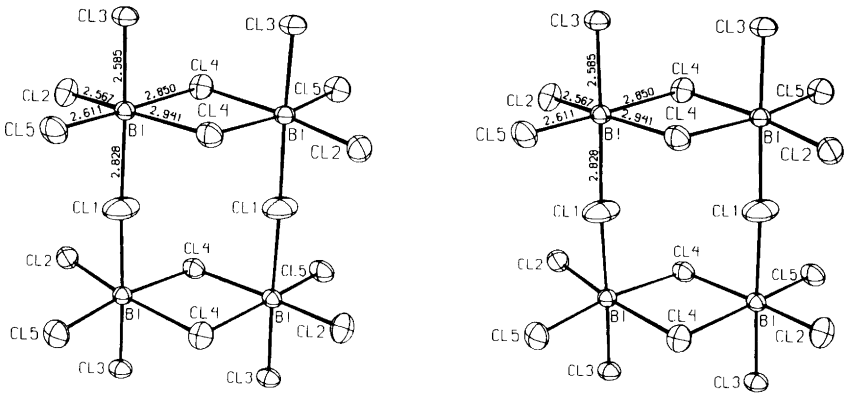

Fig. 2. A stereoview showing the discrete $Bi_4Cl_{18}^{6-}$ complex. The bond distances Bi–Cl are given.

$C2/m$. The complex thus as a whole has the symmetry $2/m$. The independent Bi–Bi distances within the complex are 4.35, 5.65 and 7.13 Å and the next nearest distance (to another complex) is 6.97 Å. The longest Bi–Cl bond distance within the complex is 2.941 Å and the shortest Bi–Cl distance between two complexes is slightly less than 5 Å. Thus the complexes are isolated. The complex $Bi_4Cl_{18}^{6-}$ consists of two pairs of edge-sharing octahedra joined by their top ligands (Fig. 2). The terminal chlorine atoms Cl(5) and the bridging Cl(4) may be joined by weak hydrogen bonds to pyridinium ions II and III respectively.

The short terminal Bi–Cl bonds to the atoms Cl(2), Cl(3) and Cl(5) are 2.567(3)–2.611(2) Å and the long bridging to Cl(4)(× 2) and Cl(1) are 2.828(1) –2.941(3) Å (Fig. 2). The short bonds observed in the present structure are longer than the corresponding ones in $BiCl_3$[10] [2.468(4)–2.518(7) Å]. The bismuth atoms of the present compound are thus (3+3)-coordinated but have a larger tendency towards 6-coordination than is found for solid $BiCl_3$. In $Cs_2NaBiCl_6$[11] the bismuth atom with the site symmetry $m3m$ is strictly octahedrally coordinated with the Bi–Cl distance 2.66(2) Å, which falls between the long and the short Bi–Cl bonds in the present structure.

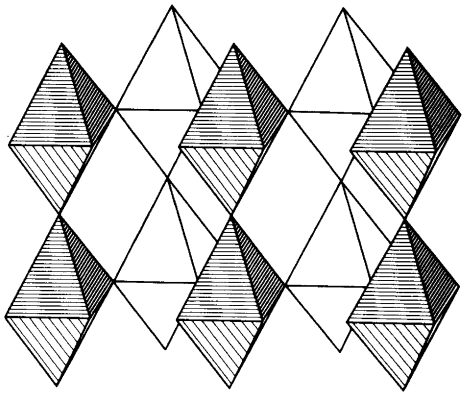

Fig. 3. A perspective view of part of the endless double chain, formed from linked $BiCl_6$ octahedra in $Cs_3Bi_2Cl_9$.[12]

A compound closely related to the present one is $Cs_3Bi_2Cl_9$,[12] in which the octahedra of the ion $Bi_2Cl_9^{3-}$ are joined to an endless double chain extending along the crystallographic a-axis. An idealized picture of part of this chain is given in Fig. 3. The authors of Ref. 12 have, however, chosen to give another description of the coordination of bismuth in this compound. They depict $BiCl_3$ molecules and this formulation is based on the fairly short three nearest Bi–Cl bonds of 2.48(5)–2.56(5) Å.

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