Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Bis(piperazinium) di-$\mu$-chloro-bis[tetrachlorobismuthate(III)] trihydrate

**Ping-Fan Wu,[a]* Xiao-Feng Tan,[a] Xiang-Gao Meng,[b] Dong-Sheng Li,[a] Yu-Lin Zhu[c] and Yong-Ge Wei[c]***

[a]Department of Food Sciences, College of Bioengineering, Hubei University of Technology, Wuhan 430068, People's Republic of China, [b]Department of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China, and [c]Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence e-mail:
pingfanwu_111@yahoo.com.cn,
ygwei@pku.edu.cn

Received 16 May 2005
Accepted 4 July 2005
Online 9 July 2005

The title salt, $(C_4H_{12}N_2)_2[Bi_2Cl_{10}]\cdot 3H_2O$, was prepared by reaction of bismuth trichloride and piperazine in a hydrochloric acid medium. It consists of piperazinium dications and dimeric $[Bi_2Cl_{10}]^{4-}$ tetraanions, the latter with twofold rotation symmetry, together with water of crystallization. Hydrogen-bond interactions, including N—H···O, N—H···Cl and O—H···Cl interactions, stabilize the crystal structure.

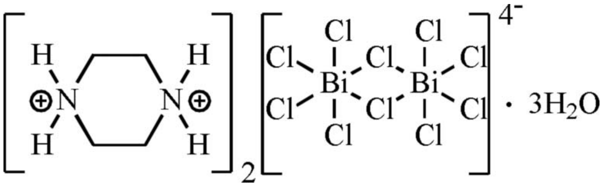
**Key indicators**

Single-crystal X-ray study
$T$ = 291 K
Mean $\sigma$(C–C) = 0.010 Å
$R$ factor = 0.036
$wR$ factor = 0.100
Data-to-parameter ratio = 26.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

There is increasing interest in halobismuthate(III) compounds, due to their anti-ulcer activity (Turel *et al.*, 1998) and their unique optical and electronic properties, including nonlinear optical activity, luminescence and semiconductivity (Goforth *et al.*, 2004). We report here the crystal structure of the title organic–inorganic hybrid complex, (I), of di-$\mu$-chlorooctachlorodibismuthate with piperazinium.



(I)

Complex (I) consists of piperazinium(2+) dications and dimeric $[Bi_2Cl_{10}]^{4-}$ tetraanions (Figs. 1 and 2), together with water molecules of crystallization. The $[Bi_2Cl_{10}]^{4-}$ anion is located on a crystallographic $C_2$ symmetric axis, with the two $[BiCl_6]$ octahedra sharing one edge formed by two bridging $Cl^-$ anions. The piperazinium cation has a chair-like conformation.

There are complicated hydrogen-bonding interactions among the $Bi_2Cl_{10}]^{4-}$ anions, piperazinium cations and water molecules of crystallization. In particular, the N—H···Cl hydrogen bonds between each of the $[Bi_2Cl_{10}]^{4-}$ anions and its four neighbouring piperazium cations result in interesting chains, formed by two parallel rows of piperazium cations sandwiched between two rows of $[Bi_2Cl_{10}]^{4-}$ anions, along the $c$ axis in the crystal structure (Fig. 3). These chains are then linked by hydrogen bonds involving the water molecules, forming an extended three-dimensional structure.

## Experimental

Colourless crystals of (I) suitable for X-ray diffraction studies were obtained by slow evaporation for about 4 d at room temperature of an aqueous solution formed by mixing aqueous solutions of $BiCl_3$

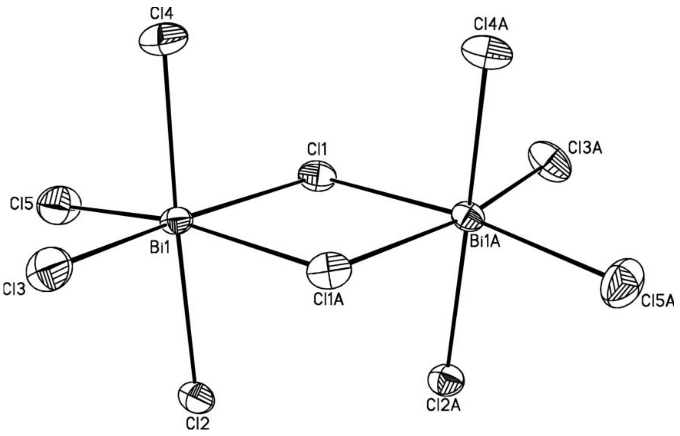


**Figure 1**
A drawing of the $[Bi_2Cl_{10}]^{4-}$ anion of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $1 - x, y, \frac{3}{2} - z$.]

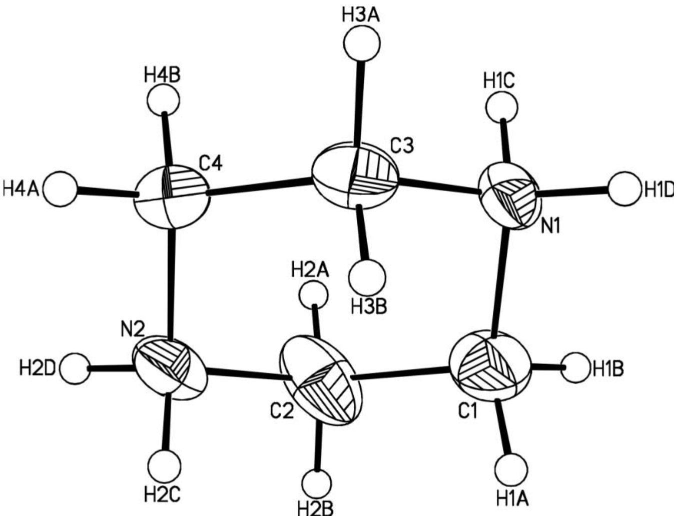


**Figure 2**
A drawing of the piperazium cation of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

(1.24 mmol, dissolved in 2 ml concentrated HCl) and piperazine hexahydrate (4.94 mmol, dissolved in 15 ml $H_2O$). Spectroscopic analysis: IR (KBr, $\nu$, $cm^{-1}$): 3546 (*m*, O—H), 3466 (*m*, O—H), 3124 (*m*, N—H), 3064 (*m*, N—H), 2810 (*m*, C—H), 2520 (*w*), 2427 (*w*), 1594 (*vs*, $H_2O$), 1444 (*vs*, $CH_2$), 1417 (*m*), 1407 (*m*), 1315 (*m*), 1201 (*w*), 1080 (*s*), 1054 (*s*), 1040 (*m*), 999 (*m*), 941 (*s*), 863 (*m*), 809 (*w*), 682 (*m*); UV (in DMSO): 256, 314 nm.

*Crystal data*

$(C_4H_{12}N_2)[Bi_2Cl_{10}]\cdot 3H_2O$
$M_r = 1002.82$
Monoclinic, $C2/c$
$a = 14.3223$ (14) Å
$b = 15.7868$ (14) Å
$c = 13.5226$ (13) Å
$\beta = 115.067$ (2)°
$V = 2769.5$ (5) Å$^3$
$Z = 4$

$D_x = 2.405$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3992 reflections
$\theta = 2.9$–28.2°
$\mu = 13.67$ mm$^{-1}$
$T = 291$ (2) K
Block, colourless
0.30 × 0.20 × 0.15 mm

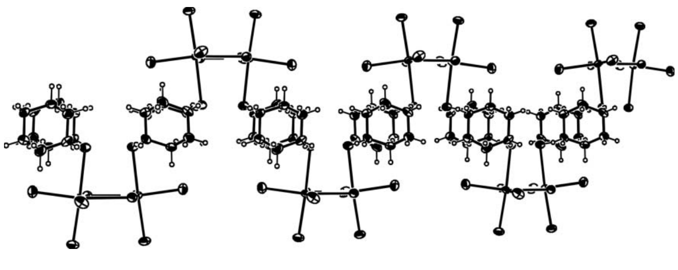


**Figure 3**
A view showing the chain formed by the $[Bi_2Cl_{10}]^{4-}$ anions and piperazium cations *via* N—H···Cl hydrogen bonds.

*Data collection*

Bruker APEX CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick 1996)
$T_{min} = 0.053$, $T_{max} = 0.132$
8270 measured reflections

3240 independent reflections
2631 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 28.3°$
$h = -17 \rightarrow 18$
$k = -13 \rightarrow 20$
$l = -17 \rightarrow 17$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.06$
3240 reflections
124 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 9.2258P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.20$ e Å$^{-3}$
$\Delta\rho_{min} = -3.00$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00346 (12)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Bi—Cl3 | 2.5806 (18) | N1—C3 | 1.479 (7) |
| Bi—Cl5 | 2.5828 (18) | N1—C1 | 1.481 (8) |
| Bi—Cl4 | 2.6344 (16) | N2—C4 | 1.471 (8) |
| Bi—Cl2 | 2.8034 (16) | N2—C2 | 1.475 (8) |
| Bi—Cl1 | 2.8493 (19) | C1—C2 | 1.496 (9) |
| Bi—Cl1$^i$ | 2.8652 (18) | C3—C4 | 1.488 (8) |
| Cl1—Bi$^i$ | 2.8652 (18) | | |
| | | | |
| Cl3—Bi—Cl5 | 94.08 (7) | Cl5—Bi—Cl1$^i$ | 171.53 (5) |
| Cl3—Bi—Cl4 | 93.53 (5) | Cl4—Bi—Cl1$^i$ | 98.72 (5) |
| Cl5—Bi—Cl4 | 89.74 (6) | Cl2—Bi—Cl1$^i$ | 83.54 (4) |
| Cl3—Bi—Cl2 | 92.02 (5) | Cl1—Bi—Cl1$^i$ | 83.75 (5) |
| Cl5—Bi—Cl2 | 88.00 (6) | Bi—Cl1—Bi$^i$ | 96.25 (5) |
| Cl4—Bi—Cl2 | 174.15 (4) | C3—N1—C1 | 109.4 (5) |
| Cl3—Bi—Cl1 | 169.16 (6) | C4—N2—C2 | 111.9 (5) |
| Cl5—Bi—Cl1 | 96.71 (6) | N1—C1—C2 | 112.1 (6) |
| Cl4—Bi—Cl1 | 85.54 (4) | N2—C2—C1 | 110.4 (6) |
| Cl2—Bi—Cl1 | 89.35 (4) | N1—C3—C4 | 111.8 (5) |
| Cl3—Bi—Cl1$^i$ | 85.72 (7) | N2—C4—C3 | 110.6 (5) |
| | | | |
| Cl3—Bi—Cl1—Bi$^i$ | 13.2 (3) | C4—N2—C2—C1 | 55.0 (8) |
| Cl5—Bi—Cl1—Bi$^i$ | −172.10 (5) | N1—C1—C2—N2 | −55.7 (8) |
| Cl4—Bi—Cl1—Bi$^i$ | 98.69 (5) | C1—N1—C3—C4 | −56.6 (6) |
| Cl2—Bi—Cl1—Bi$^i$ | −84.18 (4) | C2—N2—C4—C3 | −55.6 (7) |
| Cl1$^i$—Bi—Cl1—Bi$^i$ | −0.61 (5) | N1—C3—C4—N2 | 56.7 (7) |
| C3—N1—C1—C2 | 56.2 (7) | | |

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

*Acta Cryst.* (2005). E**61**, m1506–m1508 Wu *et al.* • $(C_4H_{12}N_2)[Bi_2Cl_{10}]\cdot 3H_2O$ **m1507**

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1N*B*···O1 | 0.90 | 1.92 | 2.814 (6) | 173 |
| N1—H1N*A*···Cl2 | 0.90 | 2.53 | 3.291 (5) | 143 |
| N2—H2N*A*···O2 | 0.90 | 2.16 | 3.017 (5) | 160 |
| N2—H2N*B*···Cl2$^{\rm ii}$ | 0.90 | 2.43 | 3.278 (5) | 157 |
| O1—H1···Cl4$^{\rm iii}$ | 0.85 | 2.48 | 3.318 (4) | 170 |
| O1—H2···Cl3$^{\rm i}$ | 0.85 | 2.67 | 3.407 (5) | 147 |
| O2—H3···Cl5$^{\rm iv}$ | 0.85 | 2.49 | 3.301 (5) | 159 |

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

H atoms attached to N and O atoms were located in a difference Fourier map and other H atoms were positioned geometrically. H atoms attached to N and C atoms were refined using a riding model, with C—H = 0.97 Å and N—H = 0.90 Å, and those attached to O atoms were refined in fixed positions, with O—H = 0.85 Å. For all H atoms, $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). The locations of the maximum and minimum difference density peaks are 0.95 and 0.85 Å, respectively, from Bi.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

This work was sponsored by the Natural Science Foundation of China (grant No. 20373001) and supported by funding from Hubei University of Technology.

## References

Bruker (2003). *SMART* (Version 5.628), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Goforth, A. M., Smith, M. D., Peterson, L. Jr & zur Loye, H.-C. (2004). *Inorg. Chem.* **43**, 7042–7049.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Turel, I., Golič, L., Bukovec, P. & Gubina, M. (1998). *Inorg. Biochem.* **71**, 53–60.

**m1508** Wu *et al.* • $(C_4H_{12}N_2)[Bi_2Cl_{10}]\cdot 3H_2O$ *Acta Cryst.* (2005). E**61**, m1506–m1508