

Redetermination of $K_4[Bi_2Cl_{10}] \cdot 4H_2O$

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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{Bi}-\text{Cl}) = 0.001$ Å; R factor = 0.017; wR factor = 0.017; data-to-parameter ratio = 24.6.

In comparison with the previous refinement of tetrapotassium di- μ -chlorido-bis[tetrachloridobismuthate(III)] tetrahydrate [Volkova, Udovenko, Levin & Shevchenko (1983). *Koord. Khim.* **9**, 356–360], the current redetermination reveals anisotropic displacement parameters for all non-H atoms, localization of the H atoms, and higher precision of lattice parameters and interatomic distances. The crystal structure is built up of edge-sharing $[Bi_2Cl_{10}]^{4-}$ double octahedra with the bridging Cl atoms situated on a mirror plane, three K^+ counter-cations (two of which are on mirror planes), and two water molecules that are solely coordinated to the K^+ cations. These building units are linked into a three-dimensional network structure. Additional O—H...Cl hydrogen bonds between the water molecules and the complex anions stabilize this arrangement.

Related literature

The isotopic Br compound was reported by Lazarini (1977). For related structures, see: Belkyal *et al.* (1997); Benachenhou *et al.* (1986). For general background, see: Larson (1970); Prince (1982); Watkin (1994).

Experimental

Crystal data

 $K_4[Bi_2Cl_{10}] \cdot 4H_2O$ $M_r = 1000.94$ Orthorhombic, $Pnma$ $a = 8.4310$ (1) Å $b = 21.8444$ (3) Å $c = 12.2561$ (2) Å $V = 2257.21$ (6) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 17.49$ mm⁻¹ $T = 295$ (2) K $0.28 \times 0.12 \times 0.08$ mm

Data collection

Bruker APEXII CCD diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2006)

 $T_{\min} = 0.067$, $T_{\max} = 0.247$ 26961 measured reflections
4596 independent reflections2801 reflections with $I > 3.0\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.017$ $wR(F^2) = 0.017$ $S = 1.08$

2801 reflections

114 parameters

All H-atom parameters refined

 $\Delta\rho_{\text{max}} = 1.01$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.82$ e Å⁻³

Table 1

Selected bond lengths (Å).

Bi1—Cl7 ⁱ	2.5954 (8)	Bi1—Cl6 ⁱ	2.7205 (7)
Bi1—Cl4	2.6190 (8)	Bi1—Cl5 ⁱⁱ	2.8512 (7)
Bi1—Cl2	2.6522 (8)	Bi1—Cl3	2.8724 (7)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O11—H13...Cl7 ⁱⁱⁱ	0.92 (7)	2.32 (7)	3.234 (4)	169 (7)
O11—H14...Cl4 ^{iv}	0.78 (7)	2.56 (8)	3.273 (3)	150 (9)
O12—H8...Cl7 ^v	0.79 (6)	2.78 (7)	3.497 (4)	152 (7)
O12—H15...Cl2 ^{vi}	0.81 (17)	2.81 (8)	3.514 (3)	145 (9)

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

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: CRYSTALS and publCIF (Westrip, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2201).

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supplementary materials

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Comment

Some bismuth-containing compounds (Belkhal *et al.*, 1997; Benachenhou *et al.*, 1986) exhibit phase transitions and have interesting physical properties which make them the object of an intensive research due to their potential application in catalysis.

Under investigation of a series of these materials, we have selected the $K_4[Bi_2Cl_{10}] \cdot 4H_2O$ compound and redetermined its structure. For the previous crystallographic study on this compound, see: Volkova *et al.* (1983). The isotypic Br compound was reported by Lazarini (1977).

The structure of the title compound can be described by $[Bi_2Cl_{10}]^{4-}$ pairs of octahedra, K^+ cations and water molecules (Fig. 1), forming a three-dimensional network (Fig. 2). The $[Bi_2Cl_{10}]^{4-}$ anions are formed by pairs of distorted $[BiCl_6]$ octahedra sharing an edge. The mean Bi—Cl distances range from 2.5954 (8) to 2.8724 (7) Å with the Cl—Bi—Cl angles varying between 80.58 (2) and 94.82 (3)°, likewise showing the distortions of the $BiCl_6$ octahedra. Compared to the previous study, the distortion of the $[BiCl_6]$ octahedra is relatively lower. The structure is additionally stabilized by the presence of hydrogen bonds of the type O—H...Cl between water molecules and the binuclear complex anions. For the polyhedra around the K^+ cations the coordinations are similar. Whereas two K^+ cations (K8 and K9) are located at the $4c$ sites (m symmetry), the third cation (K10) is on a general position. However, all K^+ cations are surrounded by two water O atoms and seven Cl atoms, leading to irregular $[KO_2Cl_7]$ polyhedra.

Experimental

$(BiO)_2CO_3$ was dissolved in concentrated hydrochloric acid in order to prepare a $BiCl_3$ solution. The latter was then added to an aqueous KCl solution in a molar ratio of 1:2. The resulting solution has been kept under stirring for 1 h and was allowed to stand at room temperature for some days. After this time colourless crystals of the title compound were obtained and isolated from the acid solution by filtration.

Refinement

The H atom positions were located from difference Fourier maps and were refined freely.

Figures

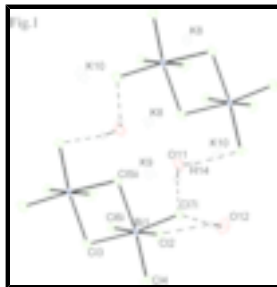


Fig. 1. Part of the crystal structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius. [Symmetry codes: (i) $x, y, z + 1$; (ii) $-x, -1/2 - y, z + 1$.]

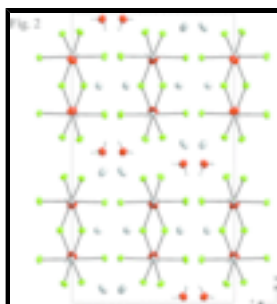


Fig. 2. Projection of the $K_4[Bi_2Cl_{10}] \cdot 4H_2O$ structure along the a axis, showing the pairs of edge-sharing $[BiCl_6]$ octahedra.

tetrapotassium di- μ -chlorido-bis[tetrachloridomuthate(III)] tetrahydrate

Crystal data



$M_r = 1000.94$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 8.43100\ (10)\ \text{\AA}$

$b = 21.8444\ (3)\ \text{\AA}$

$c = 12.2561\ (2)\ \text{\AA}$

$V = 2257.21\ (6)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1808$

$D_x = 2.945\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4596 reflections

$\theta = 1.9\text{--}34.2^\circ$

$\mu = 17.49\ \text{mm}^{-1}$

$T = 295\ (2)\ \text{K}$

Prism, colourless

$0.28 \times 0.12 \times 0.08\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Monochromator: graphite

$T = 295\ (2)\ \text{K}$

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2006)

$T_{\min} = 0.067, T_{\max} = 0.247$

26961 measured reflections

4596 independent reflections

2801 reflections with $I > 3.0\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 34.2^\circ$

$\theta_{\text{min}} = 1.9^\circ$

$h = -10 \rightarrow 12$

$k = -22 \rightarrow 33$

$l = -19 \rightarrow 17$

Refinement

Refinement on F	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
	Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982) [weight] = 1.0/[$A_0 * T_0(x) + A_1 * T_1(x) \dots + A_{n-1} * T_{n-1}(x)$]
$R[F^2 > 2\sigma(F^2)] = 0.017$	where A_i are the Chebychev coefficients listed below and $x = F / F_{\max}$ Method = Robust Weighting (Prince, 1982) $W = [\text{weight}] * [1 - (\Delta F / 6 * \sigma(F^2))^2]$ A_i are: 0.260 0.753E-01 0.968E-01
$wR(F^2) = 0.017$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 1.08$	$\Delta\rho_{\max} = 1.01 \text{ e } \text{\AA}^{-3}$
2801 reflections	$\Delta\rho_{\min} = -0.82 \text{ e } \text{\AA}^{-3}$
114 parameters	Extinction correction: Larson (1970), Equation 22
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 33.8 (8)
Secondary atom site location: difference Fourier map	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.367812 (10)	-0.349919 (4)	0.996881 (8)	0.0204
Cl2	0.49635 (11)	-0.35057 (4)	0.79938 (7)	0.0394
Cl3	0.17101 (13)	-0.2500	0.92700 (9)	0.0308
Cl4	0.15802 (11)	-0.43464 (4)	0.95182 (7)	0.0360
Cl5	0.56356 (13)	-0.2500	0.06223 (10)	0.0308
Cl6	0.24213 (9)	-0.34605 (4)	0.20120 (6)	0.0302
Cl7	0.57912 (10)	-0.42888 (4)	0.05937 (7)	0.0331
K8	0.44796 (13)	-0.2500	0.34052 (9)	0.0349
K9	0.28965 (14)	-0.2500	0.66630 (9)	0.0379
K10	0.02601 (12)	-0.54772 (5)	0.80949 (8)	0.0506
O11	0.3695 (3)	-0.16188 (16)	0.5001 (3)	0.0504
O12	0.2459 (5)	-0.47915 (15)	0.6858 (3)	0.0552
H13	0.278 (9)	-0.140 (3)	0.487 (5)	0.10 (2)*
H8	0.205 (8)	-0.481 (3)	0.629 (5)	0.09 (2)*
H14	0.428 (8)	-0.142 (3)	0.535 (5)	0.09 (2)*
H15	0.223 (5)	-0.445 (8)	0.707 (6)	0.08 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.02127 (5)	0.01939 (4)	0.02050 (4)	0.00016 (3)	0.00160 (4)	-0.00009 (4)
Cl2	0.0440 (4)	0.0469 (5)	0.0272 (3)	0.0084 (4)	0.0102 (3)	0.0035 (3)
Cl3	0.0218 (5)	0.0365 (6)	0.0342 (5)	0.0000	-0.0043 (4)	0.0000
Cl4	0.0351 (4)	0.0338 (4)	0.0392 (4)	-0.0049 (3)	-0.0057 (3)	-0.0086 (3)
Cl5	0.0228 (5)	0.0305 (5)	0.0390 (5)	0.0000	-0.0037 (4)	0.0000
Cl6	0.0316 (3)	0.0338 (4)	0.0252 (3)	-0.0039 (3)	0.0044 (3)	-0.0028 (3)

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Cl7	0.0338 (4)	0.0302 (4)	0.0354 (4)	0.0042 (3)	-0.0028 (3)	0.0025 (3)
K8	0.0329 (5)	0.0334 (5)	0.0383 (5)	0.0000	-0.0061 (4)	0.0000
K9	0.0370 (6)	0.0432 (6)	0.0335 (5)	0.0000	-0.0037 (4)	0.0000
K10	0.0460 (5)	0.0586 (5)	0.0472 (5)	-0.0134 (4)	0.0086 (4)	-0.0190 (4)
O11	0.0291 (13)	0.0507 (16)	0.071 (2)	-0.0020 (11)	-0.0121 (15)	-0.0093 (17)
O12	0.076 (2)	0.0449 (17)	0.0446 (17)	0.0092 (17)	0.0009 (17)	-0.0044 (14)

Geometric parameters (\AA , $^\circ$)

Bi1—Cl7 ⁱ	2.5954 (8)	Bi1—Cl3	2.8724 (7)
Bi1—Cl4	2.6190 (8)	O11—H13	0.92 (7)
Bi1—Cl2	2.6522 (8)	O11—H14	0.78 (7)
Bi1—Cl6 ⁱ	2.7205 (7)	O12—H8	0.79 (6)
Bi1—Cl5 ⁱⁱ	2.8512 (7)	O12—H15	0.81 (12)
Cl6 ⁱ —Bi1—Cl7 ⁱ	90.94 (3)	Cl6 ⁱ —Bi1—Cl4	87.31 (3)
Cl6 ⁱ —Bi1—Cl5 ⁱⁱ	86.74 (3)	Cl7 ⁱ —Bi1—Cl4	93.22 (3)
Cl7 ⁱ —Bi1—Cl5 ⁱⁱ	91.64 (2)	Cl5 ⁱⁱ —Bi1—Cl4	172.37 (3)
Cl6 ⁱ —Bi1—Cl2	178.11 (3)	Cl2—Bi1—Cl4	94.57 (3)
Cl7 ⁱ —Bi1—Cl2	89.16 (3)	Cl3—Bi1—Cl4	94.82 (3)
Cl5 ⁱⁱ —Bi1—Cl2	91.37 (3)	Bi1 ⁱⁱⁱ —Cl3—Bi1	98.91 (3)
Cl6 ⁱ —Bi1—Cl3	91.48 (3)	Bi1 ^{iv} —Cl5—Bi1 ^v	99.91 (3)
Cl7 ⁱ —Bi1—Cl3	171.71 (3)	H13—O11—H14	110 (6)
Cl5 ⁱⁱ —Bi1—Cl3	80.58 (2)	H8—O12—H15	103 (7)
Cl2—Bi1—Cl3	88.16 (3)		

Symmetry codes: (i) $x, y, z+1$; (ii) $x, -y-1/2, z+1$; (iii) $x, -y-1/2, z$; (iv) $x, y, z-1$; (v) $x, -y-1/2, z-1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H13 \cdots Cl7 ^{vi}	0.92 (7)	2.32 (7)	3.234 (4)	169 (7)
O11—H14 \cdots Cl4 ^{vii}	0.78 (7)	2.56 (8)	3.273 (3)	150 (9)
O12—H8 \cdots Cl7 ^{viii}	0.79 (6)	2.78 (7)	3.497 (4)	152 (7)
O12—H15 \cdots Cl2 ^{ix}	0.81 (17)	2.81 (8)	3.514 (3)	145 (9)

Symmetry codes: (vi) $x-1/2, -y-1/2, -z+1/2$; (vii) $x+1/2, -y-1/2, -z+3/2$; (viii) $x-1/2, y, -z+1/2$; (ix) $x-1/2, y, -z+3/2$.

Fig. 1

Fig. 1

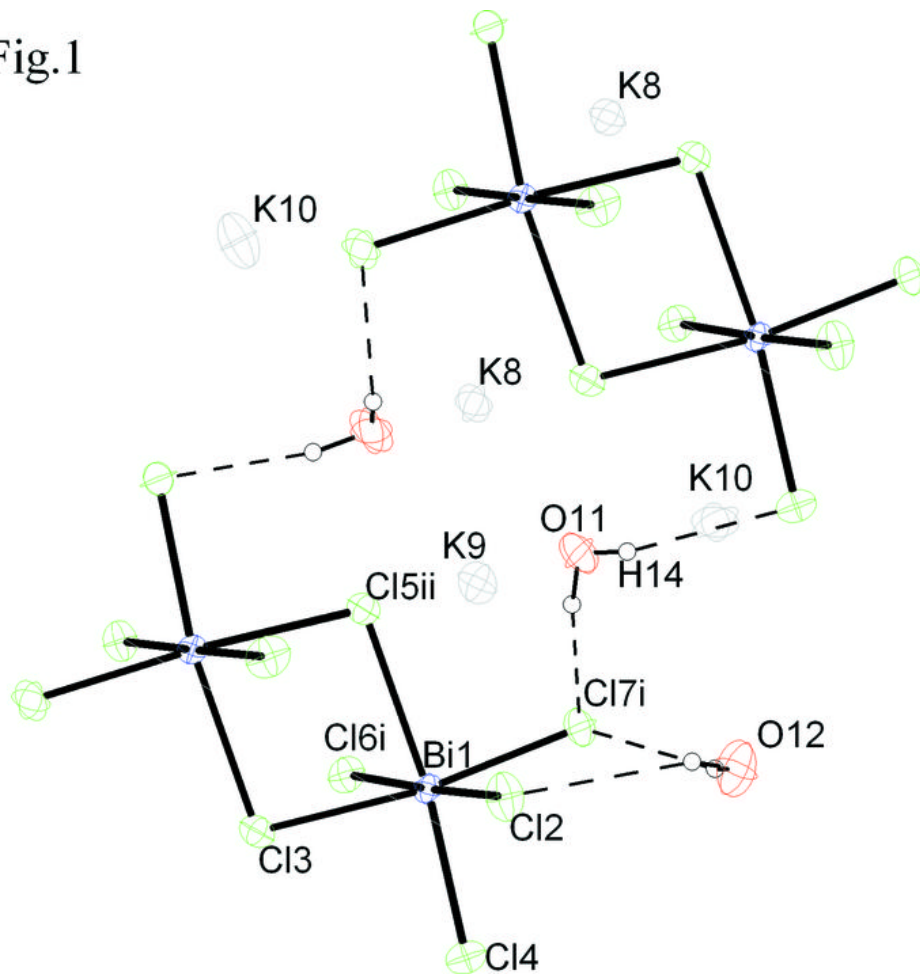


Fig. 2

