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Redetermination of $K_4[Bi_2Cl_{10}]\cdot4H_2O$

Mabrouk Khelifi,* Ridha Zouari and Abdelhamid Ben Salah

Faculté des Sciences de Sfax, Laboratoire de Sciences des Matériaux et d'Environnement, BP 115 Sfax 3052, Tunisia
Correspondence e-mail: mabrouk.khelifi@fss.rnu.tn

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Key indicators: single-crystal X-ray study; T = 295 K; mean σ(Bi–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 isotypic 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

$K_4[Bi_2Cl_{10}]\cdot4H_2O$
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) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 17.49 mm^{-1}
T = 295 (2) K
0.28 × 0.12 × 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 reflections
2801 reflections with $I > 3.0\sigma(I)$
R_{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
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −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···A	D—H	H···A	D···A	D—H···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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S1. Comment

Some bismuth-containing compounds (Belkyal *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 $K_4[Bi_2Cl_{10}].4H_2O$ 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 4*c* 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.

S2. 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.

S3. Refinement

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

Fig.1

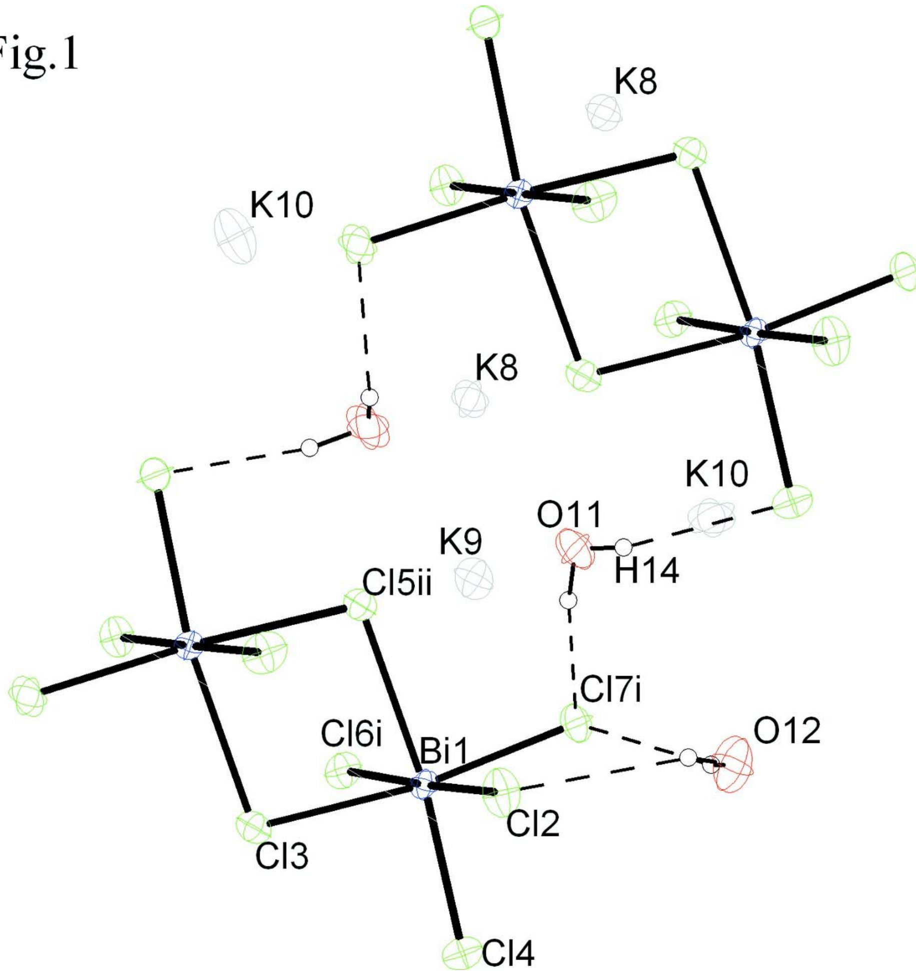

Figure 1

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 arbitary radius. [Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) -*x*, -1/2 - *y*, *z* + 1.]

Fig. 2

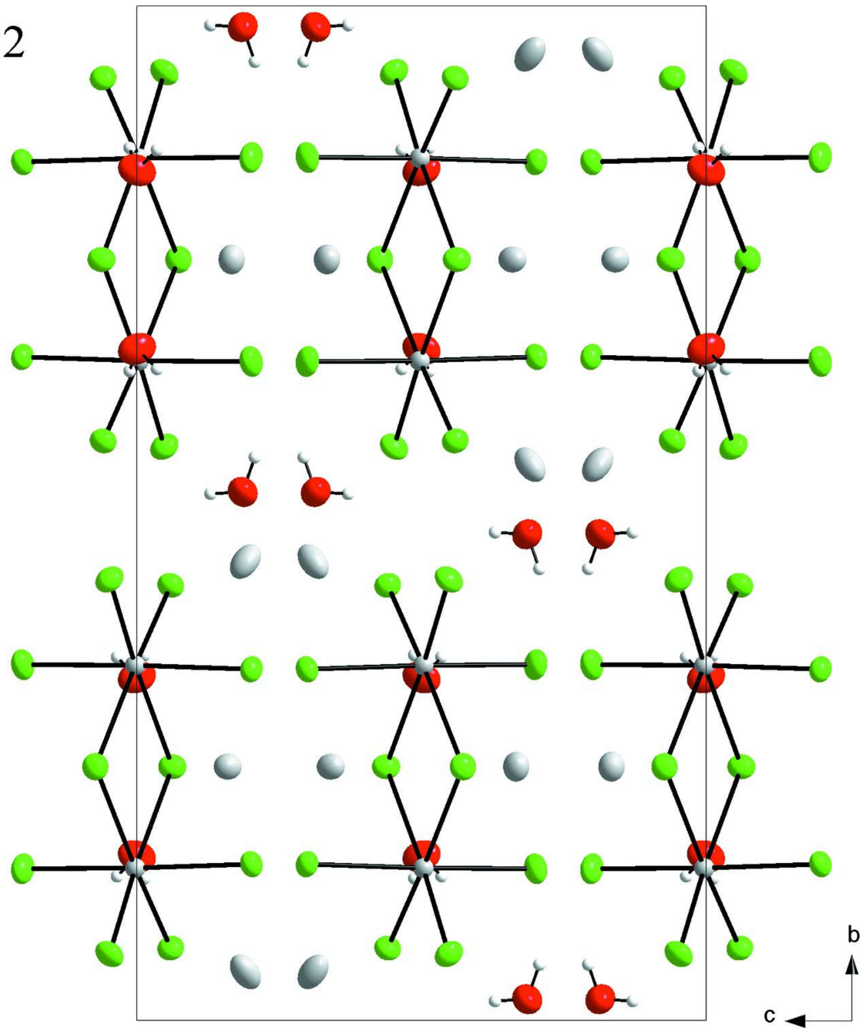

Figure 2

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

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

Crystal data

$K_4[Bi_2Cl_{10}]\cdot 4H_2O$
M_r = 1000.94
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 8.4310 (1) Å
b = 21.8444 (3) Å
c = 12.2561 (2) Å
V = 2257.21 (6) Å^3
Z = 4

F(000) = 1808
D_x = 2.945 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 4596 reflections
θ = 1.9–34.2°
μ = 17.49 mm^{-1}
T = 295 K
Prism, colourless
0.28 × 0.12 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator

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_{int} = 0.034
θ_{max} = 34.2°, θ_{min} = 1.9°
$h = -10 \rightarrow 12$
$k = -22 \rightarrow 33$
$l = -19 \rightarrow 17$

Refinement

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

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

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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)

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 (Å, º)

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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H13···Cl7^{vi}	0.92 (7)	2.32 (7)	3.234 (4)	169 (7)
O11—H14···Cl4^{vii}	0.78 (7)	2.56 (8)	3.273 (3)	150 (9)
O12—H8···Cl7^{viii}	0.79 (6)	2.78 (7)	3.497 (4)	152 (7)
O12—H15···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.