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# Crystal structure of $TiBi_2$

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Black granular single crystals of monotitanium dibismuth, $TiBi_2$, were synthesized by slow cooling of a mixture of Bi and Ti from 693 K. The title compound is isostructural with $CuMg_2$ (orthorhombic *Fddd* symmetry). Ti atoms are located in square antiprisms of Bi atoms. The network of one type of Bi atom spirals along the *a*-axis direction while honeycomb layers of the other type of Bi atom spreading in the *ab* plane interlace one another.

## 1. Chemical context

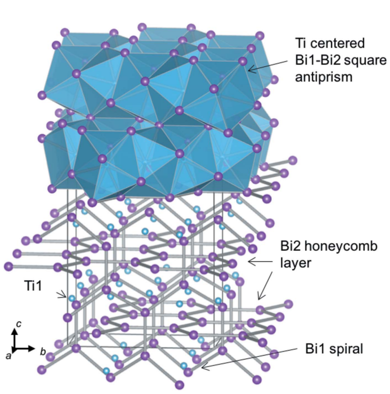
$TiBi_2$ was first reported in the study of the Ti–Bi binary phase diagram by Vassilev (2006). Maruyama *et al.* (2013) confirmed the presence of $TiBi_2$ in their phase-diagram study and showed that the powder X-ray diffraction (XRD) pattern was consistent with that of a Ti–Bi film prepared by RF sputtering (Simić & Marinković, 1990). However, the crystal system, lattice parameters and structure of $TiBi_2$ were not reported.

In the present study, we prepared single crystals of $TiBi_2$ to clarify the structure. The pellet of the starting mixture maintained the original shape after heating at 693 K. The powder XRD pattern of the sample showed that a mixture of $TiBi_2$, Bi, and Ti had been obtained. Single crystals of $TiBi_2$ approximately 120 µm in size were picked up from the fractured sample. $TiBi_2$ is unstable and decomposes in air. When the mixture was heated at 703 K, the obtained sample was a mixture of Bi and $Ti_8Bi_9$. This temperature was above the peritectic temperature of $TiBi_2$ (698 K) reported in the phase diagram by Maruyama *et al.* (2013).

## 2. Structural commentary

$TiBi_2$ is isotypic with $CuMg_2$ (Schubert & Anderko, 1951; Gingl *et al.*, 1993), $NbSn_2$, $VSn_2$, $CrSn_2$ (Wölpl & Jeitschko, 1994; Larsson & Lidin, 1995), and $IrIn_2$ (Zumdick *et al.*, 2000). TiSnSb is the only reported compound which contains Ti and crystallizes in the $CuMg_2$-type structure (Malaman & Steinmetz, 1979; Dashjav & Kleinke, 2003). The crystal structure of $TiSb_2$ adopts the $CuAl_2$ type, while that of $TiSn_2$ is not known. $TiBi_2$ is the first binary compound that is composed of Ti and a group 15 element and has the $CuMg_2$-type structure.

Fig. 1 shows the crystal structure of $TiBi_2$ while the coordination environments of the Ti1, Bi1, and Bi2 atoms are illustrated in Fig. 2. The Ti1 site is located in a square antiprism of Bi atoms. The Bi square antiprisms are aligned alternately along the $a + b$ and $a - b$ directions by sharing the square planes. Bi—Ti bond lengths in the Bi square antiprism and the Ti—Ti distance of the inter-antiprisms are 2.9382 (16)–3.0825 (6) and 2.9546 (2) Å, respectively, which are in the



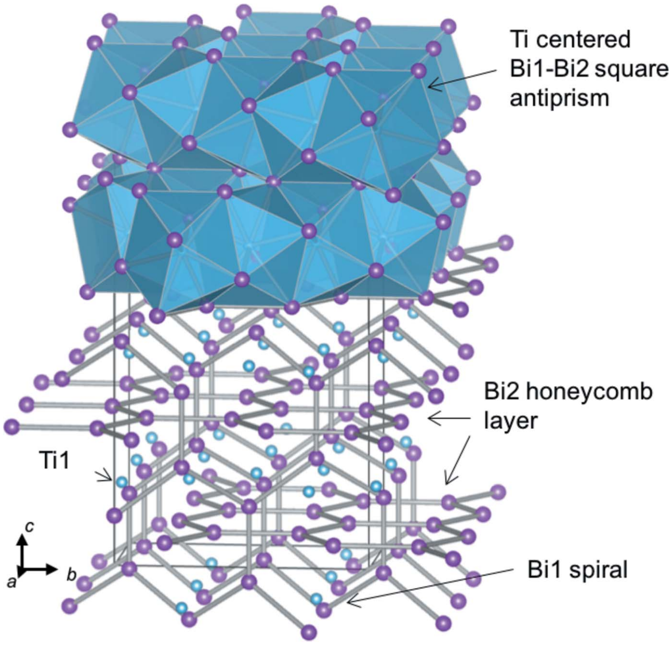



**Figure 1**
Crystal structure of $TiBi_2$ illustrated with Ti-centered Bi1–Bi2 square antiprisms and Bi1—Bi1 and Bi2—Bi2 bonds.

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $TiBi_2$ |
| $M_r$ | 465.86 |
| Crystal system, space group | Orthorhombic, *Fddd* |
| Temperature (K) | 298 |
| *a*, *b*, *c* (Å) | 5.7654 (4), 10.3155 (6), 19.4879 (12) |
| $V$ (Å$^3$) | 1159.00 (13) |
| $Z$ | 16 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 123.50 |
| Crystal size (mm) | 0.14 × 0.09 × 0.06 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 goniometer |
| Absorption correction | Numerical (*SADABS*; Bruker, 2014) |
| $T_{min}$, $T_{max}$ | 0.016, 0.102 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 3881, 339, 309 |
| $R_{int}$ | 0.048 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.649 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.024, 0.062, 1.31 |
| No. of reflections | 339 |
| No. of parameters | 17 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 2.54, −3.80 |

Computer programs: *Instrument Service*, *APEX2* and *SAINT-Plus* (Bruker, 2014), *SHELXL2014* (Sheldrick, 2015) and *VESTA* (Momma & Izumi, 2011).

ranges reported for $Ti_8Bi_9$ [Bi—Ti = 2.818 (4)–3.144 (6) Å and Ti—Ti = 2.934 (6)–3.715 (5) Å; Richter & Jeitschko, 1997].

The Bi1—Bi1 bond lengths in the Bi1 spiral-like network are 3.0730 (8) Å in the *c*-axis direction and 3.4589 (4) Å in the other direction. The Bi2—Bi2 bond lengths in the Bi2 honeycomb layers in the *ab* plane are 3.4639 (8) Å in the *b*-axis direction and 3.3435 (4) Å in the other direction. The Bi—Bi bond lengths in the spiral rings and honeycomb layers in $TiBi_2$ are in the range of those in Bi metal (3.071 and 3.529 Å; Cucka & Barrett, 1962). The interatomic distances between the Bi atoms of the spiral network and the honeycomb layers (Bi1—Bi2) are 3.6974 (3), 3.7309 (4) and 3.7546 (4) Å, which are longer than the Bi—Bi bond lengths in Bi metal.

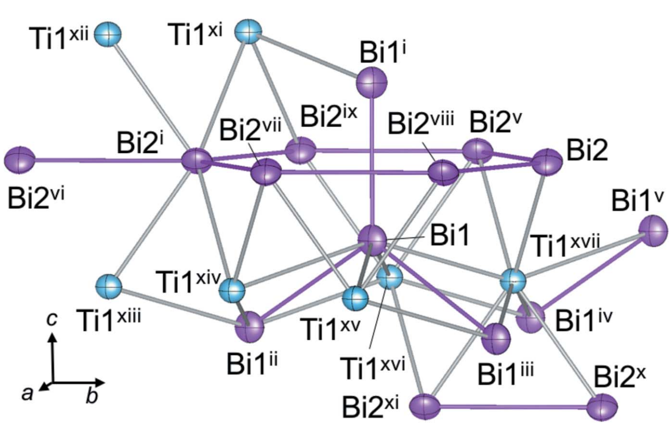



**Figure 2**
The atomic arrangement around Ti and Bi atoms in the structure of $TiBi_2$. Displacement ellipsoids are drawn at 99% probability. [Symmetry codes: (i) $x, -y + \frac{1}{4}, -z + \frac{1}{4}$; (ii) $-x, -y, -z$; (iii) $x + \frac{1}{4}, y + \frac{1}{4}, -z$; (iv) $x - \frac{3}{4}, y + \frac{1}{4}, -z$; (v) $-x - \frac{1}{4}, -y + \frac{3}{4}, z$; (vi) $x, y - 1, z$; (vii) $-x + \frac{3}{4}, y - \frac{1}{2}, -z + \frac{1}{4}$; (viii) $-x + \frac{3}{4}, -y + \frac{3}{4}, z$; (ix) $-x - \frac{1}{4}, y - \frac{1}{2}, -z + \frac{1}{4}$; (x) $-x, -y + 1, -z$; (xi) $-x, y - \frac{1}{4}, z - \frac{1}{4}$; (xii) $x, -y - \frac{1}{4}, -z + \frac{3}{4}$; (xiii) $x, y - \frac{1}{2}, z - \frac{1}{2}$; (xiv) $x + \frac{1}{4}, y - \frac{1}{4}, -z + \frac{1}{2}$; (xv) $-x + \frac{3}{4}, -y + \frac{1}{4}, z - \frac{1}{2}$; (xvi) $-x - \frac{1}{4}, -y + \frac{1}{4}, z - \frac{1}{2}$; (xvii) $-x, -y + \frac{1}{2}, -z + \frac{1}{2}$.]

## 3. Synthesis and crystallization

Starting powders of Bi (1 mmol, Mitsuwa Chemicals Co., Ltd, 99.999%) and Ti (0.5 mmol, Mitsuwa Chemicals Co., Ltd, 99.99%) were weighed, mixed in an alumina mortar with a pestle and formed into a pellet by uniaxial pressing in an Ar gas-filled glove box ($O_2$ and $H_2O$ < 1 p.p.m.). The pellet was put in a tantalum boat (Nilaco Corp., 99.95%). The boat was sealed in a stainless-steel (SUS 316) tube. The sample was heated to 693 K in an electric furnace with a heating rate of 3.5 K min$^{-1}$. This temperature was kept for 10 h, and then lowered to 473 K with a cooling rate of 5 K h$^{-1}$. After cooling to room temperature by shutting off the electrical power to the furnace, the stainless-steel tube was cut and opened in the glove box. To identify the crystalline phases, powder XRD (Cu $K\alpha$, Bruker, D2 phaser) was carried out for a portion of the sample which was ground in the alumina mortar and sealed under an Ar atmosphere in a holder with a kapton film window. The chemical compositions of $TiBi_2$ single crystals placed on a carbon tape were determined with an electron probe microanalyzer (EPMA, JEOL, JXA-8200). Bi and $TiO_2$ (Japan Electronics Co., Ltd) were used as standard samples. The analyzed composition ratio of Ti:Bi in the crystals was 1.0 (1):2.0 (1). A single crystal of $TiBi_2$ was sealed in a glass capillary with Ar gas in the glove box for the single-crystal XRD experiment.

## 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

## Acknowledgements

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# supporting information

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### Computing details

Data collection: *Instrument Service* (Bruker, 2014); cell refinement: *APEX2* (Bruker, 2014); data reduction: *SAINT-Plus* (Bruker, 2014); program(s) used to solve structure: *APEX2* (Bruker, 2014); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *VESTA* (Momma & Izumi, 2011).

### Titanium dibismuth

*Crystal data*

$TiBi_2$
$M_r = 465.86$
Orthorhombic, *Fddd*
$a = 5.7654$ (4) Å
$b = 10.3155$ (6) Å
$c = 19.4879$ (12) Å
$V = 1159.00$ (13) Å$^3$
$Z = 16$
$F(000) = 3008$
$D_x = 10.679$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4528 reflections
$\theta = 4.2$–31.4°
$\mu = 123.50$ mm$^{-1}$
$T = 298$ K
Granule, black
0.14 × 0.09 × 0.06 mm

*Data collection*

Bruker D8 goniometer diffractometer
Radiation source: micro focus sealed tube
Detector resolution: 10.4167 pixels mm$^{-1}$
$\omega$, $\varphi$ scans
Absorption correction: numerical (SADABS; Bruker, 2014)
$T_{min} = 0.016$, $T_{max} = 0.102$
3881 measured reflections
339 independent reflections
309 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 27.5°$, $\theta_{min} = 4.2°$
$h = -7 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -25 \rightarrow 25$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.31$
339 reflections
17 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 47.1241P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.54$ e Å$^{-3}$
$\Delta\rho_{min} = -3.80$ e Å$^{-3}$
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00038 (3)

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Bi1 | 0.1250 | 0.1250 | 0.04615 (2) | 0.0064 (2) |
| Bi2 | 0.1250 | 0.45710 (4) | 0.1250 | 0.0066 (2) |
| Ti1 | 0.1250 | 0.1250 | 0.49898 (10) | 0.0050 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Bi1 | 0.0035 (3) | 0.0076 (3) | 0.0082 (3) | 0.00176 (15) | 0.000 | 0.000 |
| Bi2 | 0.0058 (3) | 0.0080 (3) | 0.0060 (3) | 0.000 | −0.00212 (15) | 0.000 |
| Ti1 | 0.0039 (9) | 0.0060 (9) | 0.0051 (8) | 0.0005 (8) | 0.000 | 0.000 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ti1—Bi2$^{i}$ | 2.9382 (16) | Bi1—Bi2$^{xix}$ | 3.7546 (4) |
| Ti1—Bi2$^{ii}$ | 2.9382 (16) | Bi1—Bi2 | 3.7546 (4) |
| Ti1—Bi2$^{iii}$ | 3.0051 (16) | Bi1—Ti1$^{xx}$ | 3.0257 (6) |
| Ti1—Bi2$^{iv}$ | 3.0051 (16) | Bi1—Ti1$^{xxi}$ | 3.0257 (6) |
| Ti1—Bi1$^{v}$ | 3.0257 (6) | Bi1—Ti1$^{vii}$ | 3.0825 (6) |
| Ti1—Bi1$^{vi}$ | 3.0257 (6) | Bi1—Ti1$^{i}$ | 3.0825 (6) |
| Ti1—Bi1$^{vii}$ | 3.0825 (6) | Bi1—Ti1$^{xxii}$ | 4.9243 (16) |
| Ti1—Bi1$^{i}$ | 3.0825 (6) | Bi1—Ti1$^{xxiii}$ | 4.9243 (16) |
| Ti1—Ti1$^{viii}$ | 2.9546 (2) | Bi1—Ti1$^{xxiv}$ | 4.9348 (16) |
| Ti1—Ti1$^{ix}$ | 2.9546 (2) | Bi1—Ti1$^{xxv}$ | 4.9348 (16) |
| Bi1—Bi1$^{x}$ | 3.0730 (8) | Bi1—Ti1$^{xxvi}$ | 5.1110 (4) |
| Bi1—Bi1$^{xi}$ | 3.4589 (4) | Bi2—Ti1$^{i}$ | 2.9382 (16) |
| Bi1—Bi1$^{xii}$ | 3.4589 (4) | Bi2—Ti1$^{xxiv}$ | 2.9382 (16) |
| Bi2—Bi2$^{xiii}$ | 3.3435 (4) | Bi2—Ti1$^{xxvii}$ | 3.0051 (16) |
| Bi2—Bi2$^{xiv}$ | 3.3435 (4) | Bi2—Ti1$^{xxviii}$ | 3.0051 (16) |
| Bi2—Bi2$^{xv}$ | 3.4639 (8) | Bi2—Bi1$^{xxix}$ | 3.6974 (3) |
| Bi1—Bi2$^{xiv}$ | 3.6974 (3) | Bi2—Bi1$^{xxx}$ | 3.6974 (3) |
| Bi1—Bi2$^{xvi}$ | 3.6974 (3) | Bi2—Bi1$^{xxxi}$ | 3.6974 (3) |
| Bi1—Bi2$^{xvii}$ | 3.6974 (3) | Bi2—Bi1$^{xxxii}$ | 3.6974 (3) |
| Bi1—Bi2$^{xiii}$ | 3.6974 (3) | Bi2—Bi1$^{xii}$ | 3.7310 (4) |
| Bi1—Bi2$^{xviii}$ | 3.7309 (4) | Ti1—Bi1$^{xxii}$ | 4.9242 (16) |
| Bi1—Bi2$^{xii}$ | 3.7309 (4) | Ti1—Bi1$^{xxiii}$ | 4.9242 (16) |
| | | | |
| Ti1$^{i}$—Bi2—Bi1$^{xxx}$ | 100.12 (2) | Bi2$^{xiv}$—Bi1—Ti1$^{xxiv}$ | 36.352 (10) |
| Bi1$^{xxix}$—Bi2—Bi1$^{xii}$ | 100.174 (6) | Bi2—Bi1—Ti1$^{xxiv}$ | 36.426 (10) |
| Bi2$^{xvi}$—Bi1—Bi2$^{xviii}$ | 100.175 (5) | Bi1$^{v}$—Ti1—Bi1$^{xxii}$ | 36.48 (2) |

| | | | |
|---|---|---|---|
| Bi1$^{xii}$—Bi1—Ti1$^{xxii}$ | 100.237 (12) | Bi1$^{x}$—Bi1—Ti1$^{xxiv}$ | 36.775 (14) |
| Bi1$^{xii}$—Bi1—Bi2$^{xiii}$ | 101.056 (6) | Bi2$^{xiv}$—Bi1—Ti1$^{xxii}$ | 37.501 (10) |
| Bi1$^{xi}$—Bi1—Bi2$^{xvii}$ | 101.056 (7) | Bi2$^{iii}$—Ti1—Bi1$^{xxii}$ | 48.51 (2) |
| Bi2$^{xvi}$—Bi1—Bi2$^{xvii}$ | 102.459 (10) | Bi1$^{xxix}$—Bi2—Bi1$^{xxx}$ | 49.109 (12) |
| Bi1$^{xxix}$—Bi2—Bi1$^{xxxii}$ | 102.460 (10) | Ti1$^{vii}$—Bi1—Bi2$^{xix}$ | 49.72 (3) |
| Bi1$^{xxx}$—Bi2—Bi1$^{xxxi}$ | 102.460 (11) | Ti1$^{xx}$—Bi1—Bi2$^{xviii}$ | 50.23 (3) |
| Bi2$^{xiii}$—Bi2—Bi1$^{xii}$ | 102.596 (8) | Ti1$^{vii}$—Bi1—Bi2$^{xvii}$ | 50.37 (3) |
| Bi2$^{xv}$—Bi2—Bi1$^{xii}$ | 103.120 (6) | Ti1$^{i}$—Bi1—Bi2$^{xviii}$ | 51.27 (3) |
| Ti1$^{xxi}$—Bi1—Bi1$^{xi}$ | 103.83 (2) | Ti1$^{xxi}$—Bi1—Bi2$^{xiv}$ | 51.93 (3) |
| Bi1$^{xii}$—Bi1—Bi2$^{xvii}$ | 103.916 (6) | Ti1$^{i}$—Bi2—Bi1$^{xii}$ | 52.331 (19) |
| Bi2$^{xiv}$—Bi1—Bi2$^{xix}$ | 104.912 (8) | Ti1$^{xxvii}$—Bi2—Bi1$^{xxix}$ | 52.441 (7) |
| Ti1$^{ix}$—Ti1—Bi1$^{xxii}$ | 105.95 (7) | Ti1$^{xxviii}$—Bi2—Bi1$^{xii}$ | 53.148 (19) |
| Ti1$^{xxiv}$—Bi2—Bi2$^{xiii}$ | 106.077 (14) | Bi2$^{xviii}$—Bi1—Bi2$^{xii}$ | 53.241 (9) |
| Ti1$^{i}$—Bi1—Bi1$^{xi}$ | 106.29 (3) | Bi2$^{xvi}$—Bi1—Bi2$^{xix}$ | 53.310 (6) |
| Bi1$^{x}$—Bi1—Ti1$^{vii}$ | 106.58 (4) | Ti1$^{xxiv}$—Bi2—Bi1$^{xxix}$ | 53.901 (6) |
| Ti1$^{i}$—Bi2—Bi2$^{xv}$ | 106.753 (12) | Ti1$^{vii}$—Bi1—Bi1$^{xi}$ | 54.737 (17) |
| Ti1$^{xxvii}$—Bi2—Bi2$^{xiii}$ | 106.976 (10) | Ti1$^{xxvii}$—Bi2—Bi2$^{xv}$ | 54.81 (2) |
| Ti1$^{xx}$—Bi1—Bi1$^{x}$ | 107.69 (4) | Ti1$^{i}$—Bi2—Bi2$^{xiii}$ | 55.32 (2) |
| Bi1$^{vi}$—Ti1—Bi1$^{xxii}$ | 108.14 (5) | Bi1$^{xxx}$—Bi2—Bi1$^{xii}$ | 55.502 (6) |
| Ti1$^{xxvii}$—Bi2—Ti1$^{xxviii}$ | 109.61 (4) | Bi2$^{xiv}$—Bi1—Bi2$^{xvii}$ | 55.865 (12) |
| Ti1$^{xx}$—Bi1—Ti1$^{vii}$ | 111.026 (7) | Ti1$^{xx}$—Bi1—Bi1$^{xi}$ | 56.289 (16) |
| Bi1$^{xi}$—Bi1—Bi1$^{xii}$ | 117.32 (2) | Ti1$^{xxi}$—Bi1—Ti1$^{vii}$ | 57.847 (3) |
| Ti1$^{ix}$—Ti1—Bi1$^{v}$ | 117.43 (3) | Ti1$^{viii}$—Ti1—Bi2$^{iii}$ | 59.07 (5) |
| Ti1$^{xxiv}$—Bi2—Bi1$^{xii}$ | 118.70 (2) | Ti1$^{xxiv}$—Bi2—Ti1$^{xxvii}$ | 59.609 (4) |
| Bi2$^{xiii}$—Bi2—Bi2$^{xiv}$ | 119.12 (2) | Ti1$^{ix}$—Ti1—Bi1$^{vii}$ | 60.113 (19) |
| Ti1$^{ix}$—Ti1—Bi2$^{iii}$ | 119.48 (9) | Bi2$^{ii}$—Ti1—Ti1$^{viii}$ | 61.32 (5) |
| Bi2$^{xvii}$—Bi1—Ti1$^{xxvi}$ | 119.656 (11) | Ti1$^{xxiii}$—Bi1—Ti1$^{xxiv}$ | 61.418 (6) |
| Bi2$^{xii}$—Bi1—Ti1$^{xxii}$ | 119.910 (14) | Bi1$^{xii}$—Bi1—Bi2$^{xviii}$ | 61.757 (12) |
| Bi2$^{i}$—Ti1—Ti1$^{viii}$ | 120.13 (9) | Ti1$^{viii}$—Ti1—Bi1$^{v}$ | 62.04 (2) |
| Ti1$^{i}$—Bi1—Ti1$^{xxii}$ | 120.34 (3) | Bi2$^{xv}$—Bi2—Bi1$^{xxix}$ | 62.067 (6) |
| Bi1$^{i}$—Ti1—Bi1$^{xxii}$ | 120.34 (3) | Bi2$^{xv}$—Bi2—Bi1$^{xxx}$ | 62.067 (6) |
| Ti1$^{viii}$—Ti1—Bi1$^{vii}$ | 120.39 (3) | Bi1$^{xi}$—Bi1—Bi2$^{xix}$ | 62.132 (6) |
| Bi2$^{ii}$—Ti1—Bi2$^{iii}$ | 120.391 (4) | Bi1$^{xii}$—Bi1—Bi2$^{xiv}$ | 62.742 (7) |
| Bi2$^{xiii}$—Bi2—Bi2$^{xv}$ | 120.438 (12) | Bi1$^{xi}$—Bi1—Bi2$^{xviii}$ | 62.826 (12) |
| Bi1$^{x}$—Bi1—Bi1$^{xi}$ | 121.338 (11) | Bi2$^{xiv}$—Bi2—Bi1$^{xii}$ | 63.380 (4) |
| Ti1$^{xx}$—Bi1—Ti1$^{xxiv}$ | 121.44 (3) | Bi2$^{xiv}$—Bi2—Bi1$^{xxix}$ | 64.221 (7) |
| Ti1$^{vii}$—Bi1—Ti1$^{xxiv}$ | 121.95 (3) | Bi2$^{xiii}$—Bi2—Bi1$^{xxxi}$ | 64.221 (7) |
| Bi2—Bi1—Ti1$^{xxvi}$ | 122.061 (9) | Bi1$^{x}$—Bi1—Bi2$^{xiv}$ | 65.444 (6) |
| Bi1$^{vi}$—Ti1—Bi1$^{vii}$ | 122.154 (4) | Bi1$^{x}$—Bi1—Bi2$^{xix}$ | 65.843 (6) |
| Bi1$^{xxix}$—Bi2—Bi1$^{xxxi}$ | 124.135 (12) | Bi2$^{xix}$—Bi1—Ti1$^{xxvi}$ | 67.048 (12) |
| Bi2$^{xiv}$—Bi1—Bi2$^{xviii}$ | 124.499 (6) | Ti1$^{xxv}$—Bi1—Ti1$^{xxvi}$ | 68.10 (3) |
| Bi2$^{xviii}$—Bi1—Bi2$^{xix}$ | 124.958 (7) | Bi2$^{xviii}$—Bi1—Ti1$^{xxvi}$ | 68.52 (2) |
| Ti1$^{xxii}$—Bi1—Ti1$^{xxvi}$ | 129.41 (3) | Bi1$^{v}$—Ti1—Bi1$^{vii}$ | 68.975 (7) |
| Bi1$^{xii}$—Bi1—Ti1$^{xxvi}$ | 129.73 (2) | Ti1$^{xxiii}$—Bi1—Ti1$^{xxvi}$ | 69.162 (10) |
| Ti1$^{xxiv}$—Bi1—Ti1$^{xxvi}$ | 130.440 (11) | Bi2$^{i}$—Ti1—Bi2$^{ii}$ | 69.36 (4) |
| Bi2$^{xiv}$—Bi1—Bi2$^{xvi}$ | 130.889 (12) | Bi2$^{xiii}$—Bi1—Ti1$^{xxvi}$ | 69.407 (12) |
| Bi2$^{xix}$—Bi1—Bi2 | 131.685 (13) | Bi2$^{xiii}$—Bi1—Ti1$^{xxiv}$ | 69.516 (7) |
| Bi1$^{xi}$—Bi1—Ti1$^{xxii}$ | 131.728 (9) | Bi2$^{iii}$—Ti1—Bi2$^{iv}$ | 70.39 (4) |

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|---|---|---|---|
| Bi2$^{xviii}$—Bi1—Ti1$^{xxiv}$ | 135.259 (12) | Bi2$^{xix}$—Bi1—Ti1$^{xxii}$ | 70.622 (7) |
| Bi2$^{iii}$—Ti1—Bi1$^{vii}$ | 135.68 (5) | Bi2$^{xvii}$—Bi1—Ti1$^{xxiv}$ | 71.591 (8) |
| Bi2$^{i}$—Ti1—Bi1$^{v}$ | 135.83 (5) | Ti1$^{xxii}$—Bi1—Ti1$^{xxiii}$ | 71.66 (3) |
| Bi2$^{xii}$—Bi1—Ti1$^{xxiv}$ | 136.209 (11) | Bi1$^{xxii}$—Ti1—Bi1$^{xxiii}$ | 71.66 (3) |
| Ti1$^{xxi}$—Bi1—Ti1$^{xxvi}$ | 138.917 (11) | Ti1$^{xxi}$—Bi1—Ti1$^{xxii}$ | 71.85 (5) |
| Bi1$^{xxxii}$—Bi2—Bi1$^{xii}$ | 141.173 (9) | Ti1$^{viii}$—Ti1—Bi1$^{xxii}$ | 72.76 (6) |
| Bi2$^{xvii}$—Bi1—Bi2$^{xviii}$ | 141.174 (9) | Ti1$^{xxiv}$—Bi1—Ti1$^{xxv}$ | 73.55 (3) |
| Ti1$^{xx}$—Bi1—Ti1$^{xxii}$ | 143.52 (2) | Bi2$^{iv}$—Ti1—Bi1$^{vii}$ | 75.584 (18) |
| Bi1$^{v}$—Ti1—Bi1$^{vi}$ | 144.62 (7) | Bi2$^{iii}$—Ti1—Bi1$^{v}$ | 75.62 (3) |
| Ti1$^{xx}$—Bi1—Ti1$^{xxi}$ | 144.63 (7) | Bi2$^{i}$—Ti1—Bi1$^{vii}$ | 75.73 (3) |
| Ti1$^{i}$—Bi2—Ti1$^{xxiv}$ | 146.49 (2) | Bi2$^{ii}$—Ti1—Bi1$^{vii}$ | 77.12 (3) |
| Ti1$^{vii}$—Bi1—Ti1$^{i}$ | 146.84 (7) | Bi2$^{ii}$—Ti1—Bi1$^{v}$ | 77.437 (16) |
| Bi1$^{vii}$—Ti1—Bi1$^{i}$ | 146.84 (7) | Bi1$^{xii}$—Bi1—Ti1$^{xxiv}$ | 84.563 (17) |
| Ti1$^{i}$—Bi2—Ti1$^{xxvii}$ | 146.946 (8) | Ti1$^{vii}$—Bi1—Ti1$^{xxvi}$ | 85.661 (13) |
| Bi2$^{i}$—Ti1—Bi2$^{iii}$ | 146.946 (8) | Ti1$^{i}$—Bi1—Ti1$^{xxiv}$ | 85.87 (4) |
| Ti1$^{i}$—Bi2—Bi1$^{xxix}$ | 149.23 (2) | Ti1$^{vii}$—Bi1—Ti1$^{xxii}$ | 87.57 (2) |
| Ti1$^{xxvii}$—Bi2—Bi1$^{xii}$ | 149.475 (16) | Bi1$^{vii}$—Ti1—Bi1$^{xxii}$ | 87.57 (2) |
| Ti1$^{xx}$—Bi1—Bi2$^{xiv}$ | 150.350 (13) | Bi2$^{xiii}$—Bi1—Bi2$^{xviii}$ | 87.936 (5) |
| Ti1$^{i}$—Bi1—Bi2$^{xvii}$ | 151.051 (14) | Ti1$^{xxi}$—Bi1—Ti1$^{xxiv}$ | 88.00 (2) |
| Ti1$^{i}$—Bi1—Bi2$^{xix}$ | 151.659 (13) | Ti1$^{i}$—Bi1—Ti1$^{xxvi}$ | 88.706 (13) |
| Bi1$^{xi}$—Bi1—Bi2$^{xiv}$ | 152.907 (6) | Bi1$^{xxxi}$—Bi2—Bi1$^{xii}$ | 92.064 (5) |
| Bi1$^{xii}$—Bi1—Bi2$^{xix}$ | 153.267 (4) | Bi2$^{xii}$—Bi1—Ti1$^{xxvi}$ | 93.35 (2) |
| Bi1$^{x}$—Bi1—Bi2$^{xviii}$ | 153.380 (4) | Ti1$^{xxviii}$—Bi2—Bi1$^{xxix}$ | 93.992 (16) |
| Bi2$^{xiii}$—Bi2—Bi1$^{xxix}$ | 155.439 (6) | Ti1$^{i}$—Bi1—Bi2$^{xiv}$ | 95.236 (16) |
| Bi1$^{xi}$—Bi1—Ti1$^{xxiv}$ | 158.113 (19) | Ti1$^{xxiv}$—Bi2—Bi1$^{xxx}$ | 95.410 (14) |
| Bi2$^{xviii}$—Bi1—Ti1$^{xxii}$ | 161.981 (11) | Ti1$^{xxi}$—Bi1—Bi2$^{xviii}$ | 95.54 (4) |
| Bi2$^{i}$—Ti1—Bi1$^{xxii}$ | 162.533 (7) | Ti1$^{vii}$—Bi1—Bi2$^{xviii}$ | 96.63 (4) |
| Bi2$^{xiv}$—Bi1—Ti1$^{xxvi}$ | 165.35 (2) | Bi2$^{xvi}$—Bi1—Ti1$^{xxii}$ | 96.863 (15) |
| Ti1$^{viii}$—Ti1—Ti1$^{ix}$ | 178.47 (15) | Ti1$^{xx}$—Bi1—Bi2$^{xix}$ | 97.142 (14) |
| Ti1$^{xx}$—Bi1—Ti1$^{xxvi}$ | 30.870 (13) | Bi2$^{xvi}$—Bi1—Ti1$^{xxiv}$ | 98.027 (15) |
| Bi2$^{xvi}$—Bi1—Ti1$^{xxvi}$ | 34.47 (2) | Ti1$^{vii}$—Bi1—Bi2$^{xiv}$ | 98.391 (15) |
| Ti1$^{xxii}$—Bi1—Ti1$^{xxiv}$ | 34.877 (3) | Bi2$^{xix}$—Bi1—Ti1$^{xxiv}$ | 98.570 (15) |
| Bi1$^{xi}$—Bi1—Ti1$^{xxvi}$ | 35.089 (15) | Bi2$^{xii}$—Bi1—Bi2$^{xix}$ | 99.134 (9) |
| Bi1$^{x}$—Bi1—Ti1$^{xxii}$ | 35.832 (14) | Bi1$^{x}$—Bi1—Ti1$^{xxvi}$ | 99.91 (2) |

Symmetry codes: (i) −*x*, −*y*+1/2, −*z*+1/2; (ii) *x*+1/4, *y*−1/4, −*z*+1/2; (iii) −*x*+1/4, −*y*+3/4, *z*+1/2; (iv) *x*, *y*−1/2, *z*+1/2; (v) *x*+1/2, *y*, *z*+1/2; (vi) *x*−1/2, *y*, *z*+1/2; (vii) −*x*+1/2, −*y*, −*z*+1/2; (viii) −*x*+1/2, −*y*+1/2, −*z*+1; (ix) −*x*, −*y*, −*z*+1; (x) −*x*+1/4, *y*, −*z*+1/4; (xi) −*x*, −*y*, −*z*; (xii) −*x*+1/2, −*y*+1/2, −*z*; (xiii) −*x*−1/4, −*y*+3/4, *z*; (xiv) −*x*+3/4, −*y*+3/4, *z*; (xv) −*x*+1/4, −*y*+5/4, *z*; (xvi) *x*−1/2, *y*−1/2, *z*; (xvii) *x*+1/2, *y*−1/2, *z*; (xviii) *x*−1/4, *y*−1/4, −*z*; (xix) −*x*+1/4, −*y*+1/4, *z*; (xx) *x*−1/2, *y*, *z*−1/2; (xxi) *x*+1/2, *y*, *z*−1/2; (xxii) −*x*+3/4, *y*, −*z*+3/4; (xxiii) −*x*−1/4, *y*, −*z*+3/4; (xxiv) *x*+1/4, −*y*+1/2, *z*−1/4; (xxv) *x*−1/4, −*y*, *z*−1/4; (xxvi) −*x*−1/2, −*y*, −*z*+1/2; (xxvii) −*x*+1/4, *y*+1/2, −*z*+3/4; (xxviii) *x*, *y*+1/2, *z*−1/2; (xxix) −*x*+3/4, *y*+1/2, −*z*+1/4; (xxx) *x*+1/2, *y*+1/2, *z*; (xxxi) *x*−1/2, *y*+1/2, *z*; (xxxii) −*x*−1/4, *y*+1/2, −*z*+1/4.