# TlPO$_3$ and its comparison with isotypic RbPO$_3$ and CsPO$_3$

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The crystal structure of thallium(I) *catena*-polyphosphate, TlPO$_3$, contains a polyphosphate chain extending parallel to [010] with a repeating unit of two phosphate tetrahedra. The Tl$^I$ atom is located in-between the polyphosphate chains and is bonded by oxygen atoms in a distorted [6 + 1] coordination in the form of a monocapped prism, with the longest Tl—O bond to the bridging O atom of the polyphosphate chain. A quantitative structural comparison with isotypic RbPO$_3$ and CsPO$_3$ reveals that the usually pronounced stereoactivity of the 6s$^2$ lone pair at the Tl$^I$ atom is not apparent in the case of TlPO$_3$.
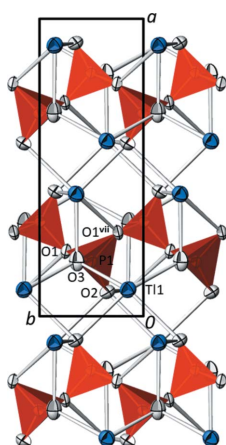
## 1. Chemical context

The crystal chemistry of inorganic thallium(I) (or thallous) compounds is dominated by the presence of the 6s$^2$ electron lone pair that, in the majority of cases, is stereochemically active (Galy *et al.*, 1975). Therefore, crystal structures comprising a Tl$^I$ atom mostly have unique structures, and isotypism with analogous phases where the Tl$^I$ site is replaced by a metal cation of comparable size or by ammonium is comparatively rare. One of these cases pertains to the *catena*-polyphosphate series $M$PO$_3$ ($M$ = Tl, Rb, Cs) for which isotypism of TlPO$_3$ with the alkali polyphosphates was reported on basis of indexed powder X-ray diffraction data (El Horr, 1991). Although single crystals were available, a refinement of the crystal structure was not performed at that time.

With the intention of obtaining detailed structure data for TlPO$_3$ for a quantitative structural comparison with isotypic RbPO$_3$ and CsPO$_3$, single crystals of the thallium polyphosphate phase were grown and the crystal structure refined using single-crystal X-ray data.

## 2. Structural commentary

The asymmetric unit of TlPO$_3$ comprises one Tl, one P and three O sites, all on general positions. The crystal structure of TlPO$_3$ is made up from a polyphosphate chain with a repeating unit of two phosphate tetrahedra propagating along the [010] direction. Two polyphosphate chains with different orientations cross the unit cell (Fig. 1). The bond-length distribution (Table 1) within a PO$_4$ tetrahedron is characteristic of a polyphosphate chain (Durif, 1995), *i.e.* two long bonds to the bridging atoms O1 and O1$^{vii}$ [mean 1.600 (8) Å; for symmetry code see Table 1] and two short bonds to the terminal O2 and O3 atoms [mean 1.483 (19) Å] are observed. The Tl$^I$ atoms are situated between the chains and are coor-

dinated to seven oxygen atoms. As has been done for thallium(I) oxoarsenates (Schroffenegger *et al.*, 2020), it is useful to classify the corresponding $Tl$—O bonds into 'short' bonds less than 3.0 Å, and 'long' bonds greater than this threshold up to the maximum bond length of 3.50 Å for the first coordination sphere. The resulting [6 + 1] polyhedron can be derived from a monocapped trigonal prism where the capping O atom is that with the longest Tl—O bond (Fig. 2). This atom (O1) represents the bridging oxygen atom of the polyphosphate chain. Next to the Tl and two P atoms, atom O1 has no further coordination partners. The terminal O2 and O3 atoms of the polyphosphate chain each are bonded to one P and to three Tl atoms in the form of a distorted tetrahedron.

Bond-valence-sum (BVS) calculations (Brown, 2002) for TlPO₃ were carried out with the values provided by Locock & Burns (2009) for $Tl^I$—O bonds, and by Brown & Altermatt

**Table 1**
Comparison of bond lengths in the isotypic $MPO_3$ polyphosphates ($M$ = Tl, Rb, Cs).

(*a*) This work; (*b*) $a$ = 12.123 (2), $b$ = 4.228 (2), $c$ = 6.479 (2) Å, $\beta$ = 96.33 (33)° (Corbridge, 1956); (*c*) $a$ = 12.6162 (11), $b$ = 4.2932 (4), $c$ = 6.7575 (6) Å, $\beta$ = 96.068 (5)° (Weil & Stöger, 2020).

|  | $M = Tl^a$ | $M = Rb^b$ | $M = Cs^c$ |
|---|---|---|---|
| $M$—O3$^i$ | 2.867 (5) | 2.920 | 3.1097 (18) |
| $M$—O3 | 2.889 (4) | 2.971 | 3.0980 (14) |
| $M$—O3$^{ii}$ | 2.935 (4) | 2.948 | 3.0983 (14) |
| $M$—O2$^{iii}$ | 2.943 (5) | 2.973 | 3.0981 (14) |
| $M$—O2$^{iv}$ | 2.963 (4) | 2.905 | 3.0431 (15) |
| $M$—O2$^v$ | 2.997 (4) | 3.024 | 3.1455 (15) |
| $M$—O1$^{vi}$ | 3.216 (4) | 3.196 | 3.3649 (14) |
| P—O2 | 1.469 (5) | 1.474 | 1.4793 (16) |
| P—O3 | 1.497(5 | 1.438 | 1.4919 (16) |
| P—O1 | 1.595 (4) | 1.621 | 1.6134 (16) |
| P—O1$^{vii}$ | 1.606 (4) | 1.624 | 1.6183 (16) |

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

(1985) for P—O bonds. The obtained BVS values (in valence units) of 0.88 for Tl1, 4.97 for P1, 2.17 for O1, 1.97 for O2 and 1.82 for O3 differ somewhat from the idealized values for atoms with a formal charge of +1, +5 and −2, respectively. In consequence, the global instability index *GII* (Salinas-Sanchez *et al.*, 1992) of 0.14 valence units is rather high and indicates a stable but strained structure (*GII* values < 0.1 valence units are typical for unstrained structures, *GII* values between 0.1 and 0.2 are characteristic of structures with lattice-induced strain, and *GII* values > 0.2 indicate unstable structures).

Apparently, the usually observed stereochemical activity of the $6s^2$ electron lone pair at the $Tl^I$ atom is not very pronounced in the case of TlPO₃, and a crystal structure isotypic with those of the room-temperature forms of RbPO₃ and CsPO₃ is realized (Table 1). This may be due to the
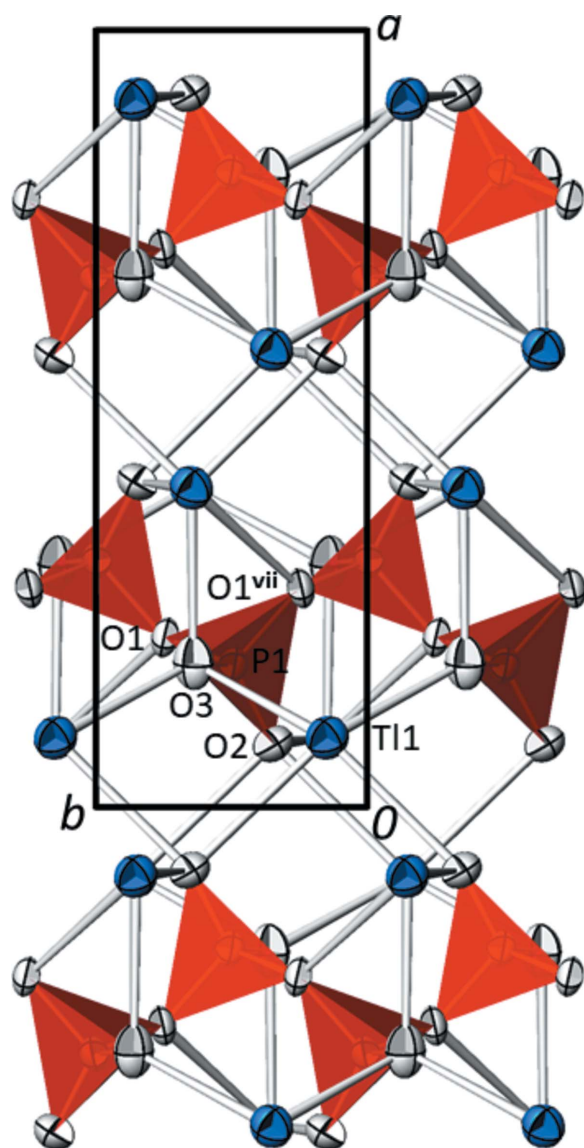


**Figure 1**
The crystal structure of TlPO₃ in a projection along [00$\bar{1}$]. Displacement ellipsoids are drawn at the 75% probability level. The symmetry code refers to Table 1.



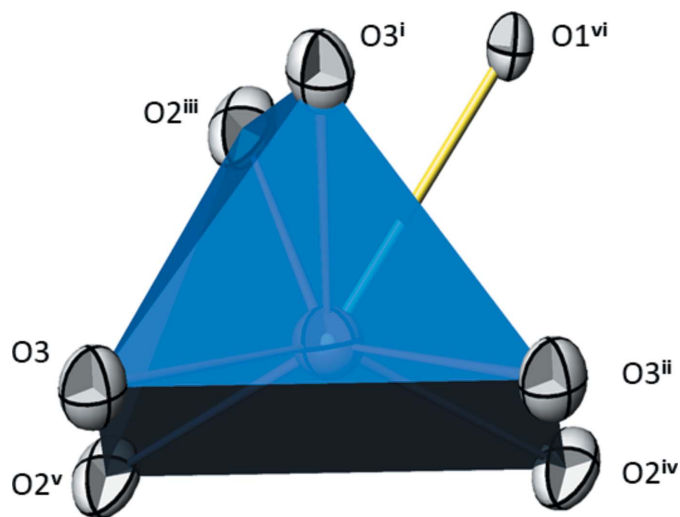**Figure 2**
The [TlO$_{6 + 1}$] monocapped prism in the crystal structure of TlPO₃, with the long Tl—O bond shown in yellow. Displacement ellipsoids are drawn at the 75% probability level. Symmetry codes refer to Table 1.

**Table 2**
Absolute atomic displacements (Å) of isotypic RbPO$_3$ and CsPO$_3$ relative to TlPO$_3$, as well as lattice distortion ($S$), arithmetic mean distance $d_{av}$ (Å) and measure of similarity ($\Delta$).

|  | Rb | Cs |
|---|---|---|
| $M1$ | 0.0656 | 0.0703 |
| P1 | 0.0505 | 0.0595 |
| O1 | 0.0421 | 0.0494 |
| O2 | 0.0996 | 0.0735 |
| O3 | 0.1332 | 0.1793 |
| $S$ | 0.0099 | 0.0245 |
| $d_{av}$ | 0.0782 | 0.0864 |
| $\Delta$ | 0.060 | 0.039 |

comparable ionic radii for monovalent Tl, Rb$^+$ and Cs$^+$ cations of 1.50, 1.52 and 1.67 Å, respectively, using a coordination number of six (Shannon, 1976; values for a coordination number of seven were not listed for Tl and Cs).

Whereas the isotypic polyphosphates RbPO$_3$ and CsPO$_3$ show structural phase transitions to two (Holst *et al.*, 1994) and to one high-temperature phases (Chudinova *et al.*, 1989), a structural phase transition at higher temperatures has not been reported for TlPO$_3$. On the contrary, the tetra-metaphosphate Tl$_4$P$_4$O$_{12}$ converts at 690 K to the title polyphosphate (Dostál *et al.*, 1969) that therefore represents the high-temperature form of a phosphate with a Tl:P ratio of 1:1.

For a quantitative structural comparison of the three isotypic $M$PO$_3$ ($M$ = Tl, Rb, Cs) structures, the program *compstru* (de la Flor *et al.*, 2016) available at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006) was used. Numerical details of the comparison with the TlPO$_3$ structure as the reference are collated in Table 2. The low values for the degree of lattice distortion ($S$), the similarity index $\Delta$ and the arithmetic mean distance of paired atoms ($d_{av}$) indicate very similar structures, with the highest absolute displacement of atom O3 in each case.

## 3. Synthesis and crystallization

A mass of 0.50 g Tl$_2$CO$_3$ was immersed in 3 ml of concentrated phosphoric acid (85%$_{wt}$) in a glass carbon crucible. The mixture was heated within six hours to 573 K, kept at that temperature for ten hours and slowly cooled to room temperature over the course of twelve hours. The obtained highly viscous phosphate flux was leached with a mixture of water and methanol ($v/v$ = 1:4). After separation of the liquid phase through suction filtration, colourless crystals of TlPO$_3$, mostly with a platy form, were obtained.

## 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

The lattice parameters determined in the current study are in good agreement with those of the previous report [$a$ = 12.270 (7), $b$ = 4.263 (2), $c$ = 6.328 (4) Å, $\beta$ = 96.72 (3)°, $V$ = 328.7 Å$^3$; El Horr, 1991], however with higher precision.

**Table 3**
Experimental details.

| Crystal data | |
|---|---|
| Chemical formula | TlPO$_3$ |
| $M_r$ | 283.34 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 296 |
| $a$, $b$, $c$ (Å) | 12.2315 (12), 4.2432 (7), 6.3039 (1) |
| $\beta$ (°) | 96.727 (7) |
| $V$ (Å$^3$) | 324.92 (6) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 49.99 |
| Crystal size (mm) | 0.09 × 0.08 × 0.01 |
| | |
| **Data collection** | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Numerical (*HABITUS*; Herrendorf, 1997) |
| $T_{min}$, $T_{max}$ | 0.110, 0.536 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6570, 1189, 912 |
| $R_{int}$ | 0.059 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.758 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.027, 0.054, 0.99 |
| No. of reflections | 1189 |
| No. of parameters | 46 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.85, −1.64 |

Structure solution: isomorphous replacement. Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXL2018/3* (Sheldrick, 2015), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

For better comparison with the two isotypic structures of RbPO$_3$ and CsPO$_3$, the setting of the unit cell (cell choice 2 of space group No. 14), starting coordinates and atom labelling were adapted from RbPO$_3$ (Corbridge, 1956). The maximum and minimum electron densities in the final difference-Fourier synthesis are located 0.65 and 0.74 Å, respectively, from the Tl1 site.

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# TlPO₃ and its comparison with isotypic RbPO₃ and CsPO₃

## Matthias Weil

## Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: isomorphous replacement; program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

**Thallium(I) *catena*-polyphosphate**

### Crystal data

| | |
|---|---|
| TlPO₃ | $F(000) = 480$ |
| $M_r = 283.34$ | $D_x = 5.792$ Mg m⁻³ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 12.2315\,(12)$ Å | Cell parameters from 2009 reflections |
| $b = 4.2432\,(7)$ Å | $\theta = 3.4–29.2°$ |
| $c = 6.3039\,(1)$ Å | $\mu = 49.99$ mm⁻¹ |
| $\beta = 96.727\,(7)°$ | $T = 296$ K |
| $V = 324.92\,(6)$ Å³ | Plate, colourless |
| $Z = 4$ | $0.09 \times 0.08 \times 0.01$ mm |

### Data collection

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 1189 independent reflections |
| Radiation source: fine-sealed tube | 912 reflections with $I > 2\sigma(I)$ |
| $\omega-$ and $\varphi-$scans | $R_{int} = 0.059$ |
| Absorption correction: numerical (*HABITUS*; Herrendorf, 1997) | $\theta_{max} = 32.6°$, $\theta_{min} = 3.4°$ |
| | $h = -18 \rightarrow 18$ |
| | $k = -6 \rightarrow 6$ |
| $T_{min} = 0.110$, $T_{max} = 0.536$ | $l = -9 \rightarrow 9$ |
| 6570 measured reflections | |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | 0 restraints |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.0219P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.027$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.054$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 0.99$ | $\Delta\rho_{max} = 1.85$ e Å⁻³ |
| 1189 reflections | $\Delta\rho_{min} = -1.64$ e Å⁻³ |
| 46 parameters | |

*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 (Å$^2$)*

|     | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
| --- | --- | --- | --- | --- |
| Tl1 | 0.08906 (2) | 0.14776 (5) | 0.77279 (4) | 0.02917 (9) |
| P1 | 0.18222 (13) | 0.4944 (3) | 0.3224 (2) | 0.0183 (3) |
| O1 | 0.2184 (4) | 0.7447 (9) | 0.1551 (6) | 0.0202 (9) |
| O2 | 0.0814 (4) | 0.3466 (9) | 0.2180 (8) | 0.0331 (11) |
| O3 | 0.1858 (4) | 0.6404 (9) | 0.5393 (7) | 0.0316 (11) |

*Atomic displacement parameters (Å$^2$)*

|     | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
| --- | --- | --- | --- | --- | --- | --- |
| Tl1 | 0.02974 (15) | 0.02897 (13) | 0.02893 (13) | −0.00135 (13) | 0.00402 (10) | 0.00170 (11) |
| P1 | 0.0196 (8) | 0.0134 (6) | 0.0227 (7) | −0.0015 (6) | 0.0060 (6) | −0.0018 (5) |
| O1 | 0.024 (2) | 0.0119 (15) | 0.025 (2) | −0.0029 (16) | 0.0039 (18) | 0.0000 (15) |
| O2 | 0.021 (2) | 0.026 (2) | 0.052 (3) | −0.004 (2) | 0.002 (2) | −0.005 (2) |
| O3 | 0.046 (3) | 0.025 (2) | 0.026 (2) | 0.001 (2) | 0.011 (2) | −0.0035 (18) |

*Geometric parameters (Å, º)*

| | | | |
| --- | --- | --- | --- |
| Tl1—O3[i] | 2.867 (5) | Tl1—O1[vi] | 3.216 (4) |
| Tl1—O3 | 2.889 (4) | P1—O2 | 1.469 (5) |
| Tl1—O3[ii] | 2.935 (4) | P1—O3 | 1.497 (5) |
| Tl1—O2[iii] | 2.943 (5) | P1—O1 | 1.595 (4) |
| Tl1—O2[iv] | 2.963 (4) | P1—O1[vii] | 1.606 (4) |
| Tl1—O2[v] | 2.997 (4) | | |
| | | | |
| O3[i]—Tl1—O3 | 77.73 (13) | Tl1[viii]—O1—Tl1[ix] | 75.05 (8) |
| O3[i]—Tl1—O3[ii] | 77.00 (13) | P1—O1—Tl1[x] | 129.7 (2) |
| O3—Tl1—O3[ii] | 93.54 (13) | P1[x]—O1—Tl1[x] | 66.97 (15) |
| O3[i]—Tl1—O2[iii] | 75.25 (13) | Tl1[viii]—O1—Tl1[x] | 79.47 (8) |
| O3—Tl1—O2[iii] | 109.83 (12) | Tl1[ix]—O1—Tl1[x] | 73.65 (7) |
| O3[ii]—Tl1—O2[iii] | 138.47 (13) | P1—O1—Tl1[v] | 69.65 (16) |
| O3[i]—Tl1—O2[iv] | 128.90 (12) | P1[x]—O1—Tl1[v] | 130.4 (2) |
| O3—Tl1—O2[iv] | 148.59 (14) | Tl1[viii]—O1—Tl1[v] | 68.02 (8) |
| O3[ii]—Tl1—O2[iv] | 79.42 (13) | Tl1[ix]—O1—Tl1[v] | 79.10 (8) |
| O2[iii]—Tl1—O2[iv] | 94.78 (12) | Tl1[x]—O1—Tl1[v] | 141.92 (11) |
| O3[i]—Tl1—O2[v] | 129.52 (12) | P1—O1—Tl1[xi] | 61.69 (14) |
| O3—Tl1—O2[v] | 79.59 (13) | P1[x]—O1—Tl1[xi] | 68.71 (14) |
| O3[ii]—Tl1—O2[v] | 149.02 (14) | Tl1[viii]—O1—Tl1[xi] | 153.65 (12) |
| O2[iii]—Tl1—O2[v] | 71.11 (16) | Tl1[ix]—O1—Tl1[xi] | 131.30 (10) |
| O2[iv]—Tl1—O2[v] | 90.79 (13) | Tl1[x]—O1—Tl1[xi] | 105.89 (10) |

| | | | |
|---|---|---|---|
| O3<sup>i</sup>—Tl1—O1<sup>vi</sup> | 47.18 (11) | Tl1<sup>v</sup>—O1—Tl1<sup>xi</sup> | 112.06 (10) |
| O3—Tl1—O1<sup>vi</sup> | 124.87 (13) | P1—O2—Tl1<sup>ix</sup> | 115.5 (3) |
| O3<sup>ii</sup>—Tl1—O1<sup>vi</sup> | 78.11 (12) | P1—O2—Tl1<sup>iv</sup> | 148.1 (3) |
| O2<sup>iii</sup>—Tl1—O1<sup>vi</sup> | 60.37 (11) | Tl1<sup>ix</sup>—O2—Tl1<sup>iv</sup> | 85.22 (12) |
| O2<sup>iv</sup>—Tl1—O1<sup>vi</sup> | 83.93 (12) | P1—O2—Tl1<sup>v</sup> | 103.6 (2) |
| O2<sup>v</sup>—Tl1—O1<sup>vi</sup> | 130.42 (13) | Tl1<sup>ix</sup>—O2—Tl1<sup>v</sup> | 108.89 (16) |
| O3<sup>i</sup>—Tl1—P1 | 87.23 (9) | Tl1<sup>iv</sup>—O2—Tl1<sup>v</sup> | 90.79 (13) |
| O3—Tl1—P1 | 24.76 (9) | P1—O2—Tl1 | 74.9 (2) |
| O3<sup>ii</sup>—Tl1—P1 | 73.32 (9) | Tl1<sup>ix</sup>—O2—Tl1 | 149.54 (14) |
| O2<sup>iii</sup>—Tl1—P1 | 134.59 (9) | Tl1<sup>iv</sup>—O2—Tl1 | 75.68 (11) |
| O2<sup>iv</sup>—Tl1—P1 | 127.54 (11) | Tl1<sup>v</sup>—O2—Tl1 | 95.07 (13) |
| O2<sup>v</sup>—Tl1—P1 | 90.46 (10) | P1—O2—Tl1<sup>viii</sup> | 82.93 (19) |
| O1<sup>vi</sup>—Tl1—P1 | 130.72 (8) | Tl1<sup>ix</sup>—O2—Tl1<sup>viii</sup> | 66.99 (9) |
| O3<sup>i</sup>—Tl1—O2 | 108.64 (12) | Tl1<sup>iv</sup>—O2—Tl1<sup>viii</sup> | 128.67 (15) |
| O3—Tl1—O2 | 45.47 (11) | Tl1<sup>v</sup>—O2—Tl1<sup>viii</sup> | 61.83 (8) |
| O3<sup>ii</sup>—Tl1—O2 | 69.49 (11) | Tl1—O2—Tl1<sup>viii</sup> | 143.17 (12) |
| O2<sup>iii</sup>—Tl1—O2 | 149.54 (14) | P1—O3—Tl1<sup>xi</sup> | 107.8 (3) |
| O2<sup>iv</sup>—Tl1—O2 | 104.32 (11) | P1—O3—Tl1 | 101.3 (2) |
| O2<sup>v</sup>—Tl1—O2 | 84.93 (13) | Tl1<sup>xi</sup>—O3—Tl1 | 103.19 (15) |
| O1<sup>vi</sup>—Tl1—O2 | 144.09 (10) | P1—O3—Tl1<sup>xii</sup> | 142.3 (3) |
| P1—Tl1—O2 | 23.87 (8) | Tl1<sup>xi</sup>—O3—Tl1<sup>xii</sup> | 102.06 (14) |
| O2—P1—O3 | 121.3 (3) | Tl1—O3—Tl1<sup>xii</sup> | 93.54 (13) |
| O2—P1—O1 | 105.7 (3) | P1—O3—Tl1<sup>v</sup> | 72.3 (2) |
| O3—P1—O1 | 110.3 (2) | Tl1<sup>xi</sup>—O3—Tl1<sup>v</sup> | 163.77 (15) |
| O2—P1—O1<sup>vii</sup> | 110.2 (2) | Tl1—O3—Tl1<sup>v</sup> | 92.54 (13) |
| O3—P1—O1<sup>vii</sup> | 104.6 (3) | Tl1<sup>xii</sup>—O3—Tl1<sup>v</sup> | 72.64 (11) |
| O1—P1—O1<sup>vii</sup> | 103.41 (12) | | |

Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+3/2; (ii) *x*, *y*−1, *z*; (iii) *x*, *y*, *z*+1; (iv) −*x*, −*y*, −*z*+1; (v) −*x*, −*y*+1, −*z*+1; (vi) *x*, *y*−1, *z*+1; (vii) −*x*+1/2, *y*−1/2, −*z*+1/2; (viii) *x*, *y*+1, *z*−1; (ix) *x*, *y*, *z*−1; (x) −*x*+1/2, *y*+1/2, −*z*+1/2; (xi) −*x*+1/2, *y*+1/2, −*z*+3/2; (xii) *x*, *y*+1, *z*.