

Tetra- μ_3 -tert-butanolato-tetrathallium(I)

Florian Blasberg, Hans-Wolfram Lerner and Michael Bolte*

Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany

Correspondence e-mail: bolte@chemie.uni-frankfurt.de

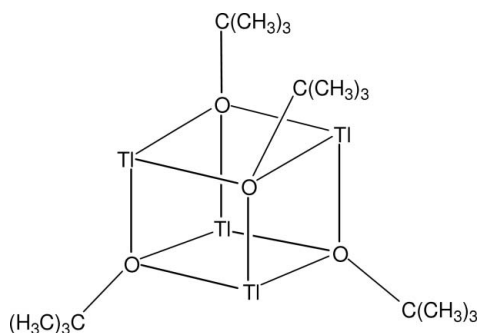
Received 2 November 2010; accepted 16 November 2010

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.030$ Å; R factor = 0.042; wR factor = 0.083; data-to-parameter ratio = 20.4.

The title compound, $[\text{Tl}_4(\text{C}_4\text{H}_9\text{O})_4]$, featuring a $(\text{Tl}-\text{O})_4$ cube, crystallizes with a quarter-molecule (located on a special position of site symmetry $\bar{4}$.) and a half-molecule (located on a special position of site symmetry 23.) in the asymmetric unit. The $\text{Tl}-\text{O}$ bond distances range from 2.463 (12) to 2.506 (12) Å. All $\text{O}-\text{Tl}-\text{O}$ bond angles are smaller than 90° whereas the $\text{Tl}-\text{O}-\text{Tl}$ angles are wider than a rectangular angle.

Related literature

For the use of bulky silyl chalcogenolate ligands of the type ESiR_3^- and alkyl chalcogenolates $E(\text{alkyl})^-$ ($E = \text{O}, \text{S}, \text{Se}, \text{Te}$) with especially bulky alkoxides to stabilize transition metal centres, see: Wolczanski (2009); Kückmann *et al.* (2005, 2008, 2010). For substitution reactions of transition metal atoms, see: Kern *et al.* (2008); Lerner *et al.* (2002, 2005). The title compound was prepared according to a slightly changed published procedure, see: Schmidbaur *et al.* (1968).



Experimental

Crystal data

$[\text{Tl}_4(\text{C}_4\text{H}_9\text{O})_4]$
 $M_r = 1109.93$
 Cubic, $P\bar{4}3n$
 $a = 17.1500$ (15) Å
 $V = 5044.2$ (8) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 25.49$ mm⁻¹
 $T = 173$ K
 $0.21 \times 0.18 \times 0.10$ mm

Data collection

Stoe IPDS II two-circle diffractometer
 Absorption correction: multi-scan (*MULABS*; Spek, 2009; Blessing, 1995)
 $T_{\min} = 0.075$, $T_{\max} = 0.185$

13612 measured reflections
 1489 independent reflections
 1226 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.084$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.083$
 $S = 1.00$
 1489 reflections
 73 parameters
 6 restraints

H-atom parameters constrained
 $\Delta\rho_{\max} = 1.77$ e Å⁻³
 $\Delta\rho_{\min} = -1.01$ e Å⁻³
 Absolute structure: Flack (1983),
 711 Friedel pairs
 Flack parameter: 0.00 (7)

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2165).

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Kern, B., Vitze, H., Bolte, M., Wagner, M. & Lerner, H.-W. (2008). *Z. Anorg. Allg. Chem.* **634**, 1830–1832.
 Kückmann, T. I., Hermsen, M., Bolte, M., Wagner, M. & Lerner, H.-W. (2005). *Inorg. Chem.* **44**, 3449–3458.
 Kückmann, T. I., Schödel, F., Sängler, I., Bolte, M., Wagner, M. & Lerner, H.-W. (2008). *Organometallics*, **27**, 3272–3278.
 Kückmann, T. I., Schödel, F., Sängler, I., Bolte, M., Wagner, M. & Lerner, H.-W. (2010). *Eur. J. Inorg. Chem.* pp. 468–475.
 Lerner, H.-W., Scholz, S. & Bolte, M. (2002). *Organometallics*, **21**, 3827–3830.
 Lerner, H.-W., Scholz, S., Wiberg, N., Polborn, K., Bolte, M. & Wagner, M. (2005). *Z. Anorg. Allg. Chem.* **631**, 1863–1870.
 Schmidbaur, H., Bergfeld, M. & Schindler, F. (1968). *Z. Anorg. Allg. Chem.* **363**, 73–83.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
 Wolczanski, P. T. (2009). *Chem. Commun.* pp. 740–757.

supporting information

Acta Cryst. (2010). E66, m1621 [https://doi.org/10.1107/S1600536810047550]

Tetra- μ_3 -*tert*-butanolato-tetrathallium(I)**Florian Blasberg, Hans-Wolfram Lerner and Michael Bolte****S1. Comment**

In a number of recent studies bulky silyl chalcogenolate ligands of the type ESiR_3^- and alkyl chalcogenolates $E(\text{alkyl})^-$ ($E = \text{O, S, Se, Te}$) with especially bulky alkoxides have been used to stabilize transition metal centers (Wolczanski, 2009; Kückmann *et al.* 2005, 2008, 2010). In macromolecular chemistry, these ligands have also found application. Chalcogen-based ligands offer a variety of possible binding modes. Chalcogenolates are often found bridging two or more metal ions. Normally, transition metal complexes possess 6 e^- thiolate ligands in a μ_3 -binding mode. Recently, however, we have shown that the anion of the mixed-valence Mn(I/II) complex $\text{Na}(\text{thf})_6[(\text{OC})_3\text{Mn}(\mu\text{-SSi}t\text{Bu}_3)_3\text{MnSSi}t\text{Bu}_3]$ contains a terminal thiolate ligand with a linear $\text{Mn}-\text{S}-\text{Si}$ unit (Kückmann *et al.* 2008). The prerequisite for six-electron donation (2 σ - and 4 π -electrons) comparable with Cp^- is thus fulfilled. One approach is to create such complexes by substitution reactions of transition metal halogenides with alkali metal alkoxides as $M^+[\text{OC}(\text{CH}_3)_3]^-$ or alkali metal siloxides $M^+[\text{OSiR}_3]^-$ (Kern *et al.* 2008; Lerner *et al.* 2005, 2002). In most cases the reactions that occur between alkali metal alkoxides and transition metal halides are not quantitative. Another approach to complexes with chalcogen coordination is to start from thallium alkoxides which react almost quantitatively with transition metal chlorides due to the poor solubility of TlCl . In this paper we report the synthesis and the crystal structure of $[\text{TlO}t\text{Bu}]_4$. The title compound $[\text{TlO}t\text{Bu}]_4$ was prepared according to a slightly changed published procedure (Schmidbaur *et al.* 1968), as shown in Fig. 2. The following modifications have been made in our approach: thallium ethoxide was used instead of thallium methoxide and potassium *tert*-butoxide was substituted for sodium *tert*-butoxide.

S2. Experimental

In a flame-dried vial 1.1 ml thallium ethoxide (3.77 g, 15.1 mmol) was added to 1.70 g potassium *tert*-butoxide (15.1 mmol) in 50 ml benzene. After flame-sealing, the vial was heated to 80 °C for four days. The vial was opened, the crude reaction mixture filtered hot under a nitrogen atmosphere, the solid residue was washed with 20 ml benzene and the combined filtrates evaporated to dryness. The remaining colorless solid was suspended in ether and allowed to settle. A sample of the supernatant was transferred to a flame-dried Schlenk vessel and stored at -35°C. After two days colorless crystals of the composition $[\text{TlO}t\text{Bu}]_4$ deposited and were separated from the mother liquor (Yield 15%).

S3. Refinement

H atoms were located in a difference map, but geometrically positioned and refined using a riding model with fixed individual displacement parameters [$U(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$] and with $\text{C}-\text{H} = 0.98 \text{ \AA}$.

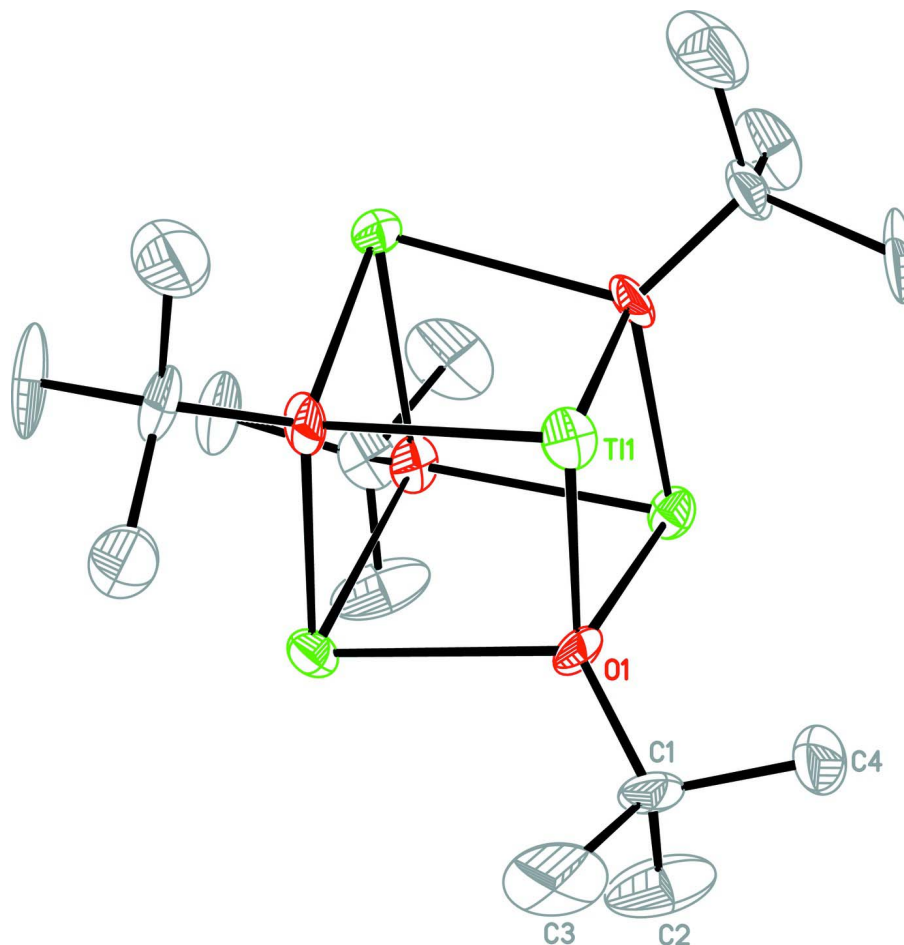


Figure 1

Perspective view of one of the two independent molecules of the title compound with the atom numbering scheme for the symmetry independent atoms; displacement ellipsoids are at the 50% probability level; H atoms are omitted for clarity.

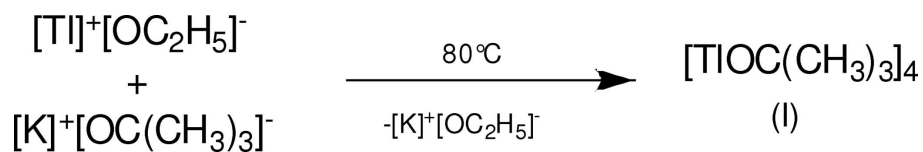


Figure 2

Preparation of the title compound.

Tetra- μ_3 -tert-butanolato-tetrathallium(I)

Crystal data

$[\text{Tl}_4(\text{C}_4\text{H}_9\text{O})_4]$

$M_r = 1109.93$

Cubic, $P43n$

Hall symbol: $P -4n 2 3$

$a = 17.1500$ (15) Å

$V = 5044.2$ (8) Å³

$Z = 8$

$F(000) = 3904$

$D_x = 2.923$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7201 reflections

$\theta = 3.4\text{--}25.9^\circ$

$\mu = 25.49$ mm⁻¹

$T = 173$ K

Plate, colourless

$0.21 \times 0.18 \times 0.10$ mm

Data collection

| | |
|--|--|
| Stoe IPDS II two-circle diffractometer | 13612 measured reflections |
| Radiation source: fine-focus sealed tube | 1489 independent reflections |
| Graphite monochromator | 1226 reflections with $I > 2\sigma(I)$ |
| ω scans | $R_{\text{int}} = 0.084$ |
| Absorption correction: multi-scan (<i>MULABS</i> ; Spek, 2009; Blessing, 1995) | $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.4^\circ$ |
| $T_{\text{min}} = 0.075$, $T_{\text{max}} = 0.185$ | $h = -18 \rightarrow 20$ |
| | $k = -19 \rightarrow 20$ |
| | $l = -20 \rightarrow 18$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | $w = 1/[\sigma^2(F_o^2) + (0.037P)^2]$ |
| $wR(F^2) = 0.083$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.00$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 1489 reflections | $\Delta\rho_{\text{max}} = 1.77 \text{ e } \text{\AA}^{-3}$ |
| 73 parameters | $\Delta\rho_{\text{min}} = -1.01 \text{ e } \text{\AA}^{-3}$ |
| 6 restraints | Absolute structure: Flack (1983), 711 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Absolute structure parameter: 0.00 (7) |
| Secondary atom site location: difference Fourier map | |

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|-------------|----------------------------------|
| Tl1 | 0.66760 (4) | 0.91953 (4) | 0.57229 (3) | 0.02168 (17) |
| O1 | 0.8130 (7) | 0.9310 (7) | 0.5635 (7) | 0.022 (2) |
| C1 | 0.8550 (13) | 0.8777 (10) | 0.6115 (13) | 0.029 (4) |
| C2 | 0.9386 (12) | 0.8950 (18) | 0.6078 (19) | 0.059 (8) |
| H2A | 0.9478 | 0.9485 | 0.6256 | 0.088* |
| H2B | 0.9569 | 0.8895 | 0.5539 | 0.088* |
| H2C | 0.9671 | 0.8586 | 0.6414 | 0.088* |
| C3 | 0.8400 (19) | 0.7958 (10) | 0.583 (2) | 0.059 (7) |
| H3A | 0.7839 | 0.7853 | 0.5844 | 0.089* |
| H3B | 0.8669 | 0.7588 | 0.6177 | 0.089* |
| H3C | 0.8596 | 0.7901 | 0.5301 | 0.089* |
| C4 | 0.8261 (16) | 0.8852 (14) | 0.6961 (12) | 0.041 (6) |
| H4A | 0.8368 | 0.9380 | 0.7153 | 0.061* |
| H4B | 0.8533 | 0.8472 | 0.7290 | 0.061* |
| H4C | 0.7698 | 0.8753 | 0.6980 | 0.061* |

| | | | | |
|------|-------------|-------------|-------------|------------|
| Tl1A | 0.42129 (4) | 0.42129 (4) | 0.42129 (4) | 0.0223 (2) |
| O1A | 0.5652 (6) | 0.4348 (6) | 0.4348 (6) | 0.020 (4) |
| C1A | 0.6118 (13) | 0.3882 (13) | 0.3882 (13) | 0.020 (7) |
| C2A | 0.6960 (12) | 0.3942 (13) | 0.4110 (14) | 0.035 (5) |
| H2A1 | 0.7125 | 0.4488 | 0.4086 | 0.053* |
| H2A2 | 0.7277 | 0.3631 | 0.3751 | 0.053* |
| H2A3 | 0.7027 | 0.3746 | 0.4643 | 0.053* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|------------|------------|------------|-------------|-------------|-------------|
| Tl1 | 0.0231 (3) | 0.0211 (3) | 0.0208 (3) | -0.0047 (3) | 0.0036 (3) | 0.0011 (3) |
| O1 | 0.031 (6) | 0.020 (6) | 0.015 (6) | 0.005 (5) | -0.005 (5) | 0.009 (5) |
| C1 | 0.036 (10) | 0.016 (9) | 0.034 (12) | 0.012 (8) | -0.009 (9) | 0.003 (8) |
| C2 | 0.023 (10) | 0.065 (16) | 0.09 (2) | 0.006 (12) | 0.006 (13) | 0.040 (14) |
| C3 | 0.09 (2) | 0.007 (8) | 0.08 (2) | 0.007 (11) | -0.018 (18) | 0.008 (12) |
| C4 | 0.063 (16) | 0.041 (13) | 0.019 (10) | 0.018 (11) | 0.007 (10) | 0.003 (8) |
| Tl1A | 0.0223 (2) | 0.0223 (2) | 0.0223 (2) | -0.0035 (3) | -0.0035 (3) | -0.0035 (3) |
| O1A | 0.020 (4) | 0.020 (4) | 0.020 (4) | 0.005 (5) | 0.005 (5) | -0.005 (5) |
| C1A | 0.020 (7) | 0.020 (7) | 0.020 (7) | 0.003 (8) | 0.003 (8) | -0.003 (8) |
| C2A | 0.025 (8) | 0.041 (8) | 0.041 (9) | 0.011 (6) | 0.007 (7) | -0.010 (7) |

Geometric parameters (Å, °)

| | | | |
|--|------------|-----------------------------|-----------|
| Tl1—O1 ⁱ | 2.463 (12) | C4—H4A | 0.9800 |
| Tl1—O1 ⁱⁱ | 2.493 (11) | C4—H4B | 0.9800 |
| Tl1—O1 | 2.506 (12) | C4—H4C | 0.9800 |
| O1—C1 | 1.42 (2) | Tl1A—O1A | 2.490 (8) |
| O1—Tl1 ⁱⁱ | 2.463 (12) | Tl1A—O1A ⁱⁱⁱ | 2.490 (8) |
| O1—Tl1 ⁱ | 2.492 (11) | Tl1A—O1A ^{iv} | 2.490 (8) |
| C1—C2 | 1.47 (3) | O1A—C1A | 1.38 (4) |
| C1—C3 | 1.51 (3) | O1A—Tl1A ⁱⁱⁱ | 2.490 (8) |
| C1—C4 | 1.54 (3) | O1A—Tl1A ^{iv} | 2.490 (8) |
| C2—H2A | 0.9800 | C1A—C2A ^v | 1.50 (2) |
| C2—H2B | 0.9800 | C1A—C2A ^{vi} | 1.50 (2) |
| C2—H2C | 0.9800 | C1A—C2A | 1.50 (2) |
| C3—H3A | 0.9800 | C2A—H2A1 | 0.9800 |
| C3—H3B | 0.9800 | C2A—H2A2 | 0.9800 |
| C3—H3C | 0.9800 | C2A—H2A3 | 0.9800 |
| O1 ⁱ —Tl1—O1 ⁱⁱ | 81.0 (4) | H3B—C3—H3C | 109.5 |
| O1 ⁱ —Tl1—O1 | 78.3 (4) | C1—C4—H4A | 109.5 |
| O1 ⁱⁱ —Tl1—O1 | 77.8 (4) | C1—C4—H4B | 109.5 |
| O1 ⁱ —Tl1—Tl1 ^{vii} | 41.8 (3) | H4A—C4—H4B | 109.5 |
| O1 ⁱⁱ —Tl1—Tl1 ^{vii} | 41.2 (3) | C1—C4—H4C | 109.5 |
| O1—Tl1—Tl1 ^{vii} | 84.3 (2) | H4A—C4—H4C | 109.5 |
| C1—O1—Tl1 ⁱⁱ | 119.7 (10) | H4B—C4—H4C | 109.5 |
| C1—O1—Tl1 ⁱ | 119.3 (11) | O1A—Tl1A—O1A ⁱⁱⁱ | 78.9 (6) |

| | | | |
|--|-------------|--|-------------|
| Tl1 ⁱⁱ —O1—Tl1 ⁱ | 97.0 (4) | O1A—Tl1A—O1A ^{iv} | 78.9 (6) |
| C1—O1—Tl1 | 114.7 (11) | O1A ⁱⁱⁱ —Tl1A—O1A ^{iv} | 78.9 (6) |
| Tl1 ⁱⁱ —O1—Tl1 | 101.8 (4) | C1A—O1A—Tl1A ⁱⁱⁱ | 117.7 (11) |
| Tl1 ⁱ —O1—Tl1 | 101.0 (4) | C1A—O1A—Tl1A ^{iv} | 117.7 (11) |
| O1—C1—C2 | 109.8 (17) | Tl1A ⁱⁱⁱ —O1A—Tl1A ^{iv} | 100.1 (5) |
| O1—C1—C3 | 109.2 (17) | C1A—O1A—Tl1A | 117.7 (11) |
| C2—C1—C3 | 110 (2) | Tl1A ⁱⁱⁱ —O1A—Tl1A | 100.1 (5) |
| O1—C1—C4 | 109.1 (16) | Tl1A ^{iv} —O1A—Tl1A | 100.1 (5) |
| C2—C1—C4 | 110 (2) | O1A—C1A—C2A ^v | 111.4 (15) |
| C3—C1—C4 | 109 (2) | O1A—C1A—C2A ^{vi} | 111.4 (15) |
| C1—C2—H2A | 109.5 | C2A ^v —C1A—C2A ^{vi} | 107.4 (16) |
| C1—C2—H2B | 109.5 | O1A—C1A—C2A | 111.4 (15) |
| H2A—C2—H2B | 109.5 | C2A ^v —C1A—C2A | 107.4 (16) |
| C1—C2—H2C | 109.5 | C2A ^{vi} —C1A—C2A | 107.4 (16) |
| H2A—C2—H2C | 109.5 | C1A—C2A—H2A1 | 109.5 |
| H2B—C2—H2C | 109.5 | C1A—C2A—H2A2 | 109.5 |
| C1—C3—H3A | 109.5 | H2A1—C2A—H2A2 | 109.5 |
| C1—C3—H3B | 109.5 | C1A—C2A—H2A3 | 109.5 |
| H3A—C3—H3B | 109.5 | H2A1—C2A—H2A3 | 109.5 |
| C1—C3—H3C | 109.5 | H2A2—C2A—H2A3 | 109.5 |
| H3A—C3—H3C | 109.5 | | |
| O1 ⁱ —Tl1—O1—C1 | -137.9 (13) | Tl1—O1—C1—C4 | -53.8 (18) |
| O1 ⁱⁱ —Tl1—O1—C1 | 139.0 (13) | O1A ⁱⁱⁱ —Tl1A—O1A—C1A | 139.7 (13) |
| Tl1 ^{vii} —Tl1—O1—C1 | -179.8 (12) | O1A ^{iv} —Tl1A—O1A—C1A | -139.7 (13) |
| O1 ⁱ —Tl1—O1—Tl1 ⁱⁱ | 91.4 (5) | O1A ⁱⁱⁱ —Tl1A—O1A—Tl1A ⁱⁱⁱ | 10.8 (5) |
| O1 ⁱⁱ —Tl1—O1—Tl1 ⁱⁱ | 8.2 (4) | O1A ^{iv} —Tl1A—O1A—Tl1A ⁱⁱⁱ | 91.49 (15) |
| Tl1 ^{vii} —Tl1—O1—Tl1 ⁱⁱ | 49.5 (3) | O1A ⁱⁱⁱ —Tl1A—O1A—Tl1A ^{iv} | -91.49 (15) |
| O1 ⁱ —Tl1—O1—Tl1 ⁱ | -8.2 (4) | O1A ^{iv} —Tl1A—O1A—Tl1A ^{iv} | -10.8 (5) |
| O1 ⁱⁱ —Tl1—O1—Tl1 ⁱ | -91.4 (5) | Tl1A ⁱⁱⁱ —O1A—C1A—C2A ^v | 68.4 (10) |
| Tl1 ^{vii} —Tl1—O1—Tl1 ⁱ | -50.1 (3) | Tl1A ^{iv} —O1A—C1A—C2A ^v | -171.6 (10) |
| Tl1 ⁱⁱ —O1—C1—C2 | -53 (2) | Tl1A—O1A—C1A—C2A ^v | -51.6 (10) |
| Tl1 ⁱ —O1—C1—C2 | 66 (2) | Tl1A ⁱⁱⁱ —O1A—C1A—C2A ^{vi} | -171.6 (10) |
| Tl1—O1—C1—C2 | -174.2 (19) | Tl1A ^{iv} —O1A—C1A—C2A ^{vi} | -51.6 (10) |
| Tl1 ⁱⁱ —O1—C1—C3 | -173.5 (18) | Tl1A—O1A—C1A—C2A ^{vi} | 68.4 (10) |
| Tl1 ⁱ —O1—C1—C3 | -55 (2) | Tl1A ⁱⁱⁱ —O1A—C1A—C2A | -51.6 (10) |
| Tl1—O1—C1—C3 | 65 (2) | Tl1A ^{iv} —O1A—C1A—C2A | 68.4 (10) |
| Tl1 ⁱⁱ —O1—C1—C4 | 67.6 (19) | Tl1A—O1A—C1A—C2A | -171.6 (10) |
| Tl1 ⁱ —O1—C1—C4 | -173.7 (14) | | |

Symmetry codes: (i) $-x+3/2, -z+3/2, y-1/2$; (ii) $-x+3/2, z+1/2, -y+3/2$; (iii) $-x+1, y, -z+1$; (iv) $-x+1, -y+1, z$; (v) $-z+1, -x+1, y$; (vi) $-y+1, z, -x+1$; (vii) $x, -y+2, -z+1$.