Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[(μ-1,3-diphenylpropane-1,3-dionato-*O*,*O*′:*O*′)-dimethylthallium], $[(CH_3)_2Tl(bzbz)]_2$

Doyle Britton

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431, USA

Correspondence e-mail: britton@chem.umn.edu

Received 21 February 2001
Accepted 27 March 2001
Online 6 April 2001

Key indicators

Single-crystal X-ray study
T = 174 K
Mean σ(C–C) = 0.014 Å
R factor = 0.046
wR factor = 0.107
Data-to-parameter ratio = 15.3

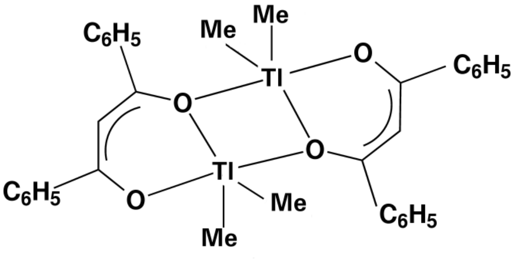
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Tl_2(CH_3)_4(C_{15}H_{11}O_2)_2]$, contains two five-coordinate Tl atoms. Two crystallographically independent molecules, symmetries 1 and $\overline{1}$, have essentially the same geometry except for the rotations of the phenyl rings. The Tl—O distances in the monomer chelate ring average 2.467 (15) Å. The Tl—O distances between the two monomer units average 2.78 (2) Å. The Tl—C distances average 2.123 (11) Å. The Tl atoms are not coplanar with the chelate rings. The independent molecules are related by an approximate pseudosymmetry.

Comment

In a discussion of the structures of some dimethylthallium compounds (Chow & Britton, 1975), we reported a partial determination of the structure of the title compound, (I). The complete structure is reported here.

There are one and one-half molecules in the asymmetric unit; using the notation suggested by Zorky and co-workers (Zorky *et al.*, 1967; Belsky *et al.*, 1995; Zorky, 1996), the structure is in *Pbca*, Z = 12 (1, $\overline{1}$). The two independent molecules are shown in Figs. 1 and 2. Selected bond lengths and angles are given in Table 1.



(I)

The six Tl—C distances average 2.123 (11) Å. The three Tl—O distances to the non-bridging O atoms in the chelates average 2.467 (15) Å, while those to the bridging O atoms average 2.445 (4) Å; this is not a significant difference. The Tl—O distances to the bridging O average 2.78 (2) Å, significantly longer than in the chelate. The increase in distance from Tl—C to Tl—O suggests that the former are predominantly covalent while the latter have more ionic character.

The overall geometries of the two molecules are quite similar. The Tl_2O_2 ring in molecule 1 is exactly planar since it lies on a center of symmetry. The other molecule is only approximately centrosymmetric. In this case, the Tl_2O_2 ring has a dihedral angle of 7.0 (3)° at the O atoms. The central Tl_2O_4 fragment is close to planarity, although the small deviations from planarity are significant. The TlO_2 fragment in

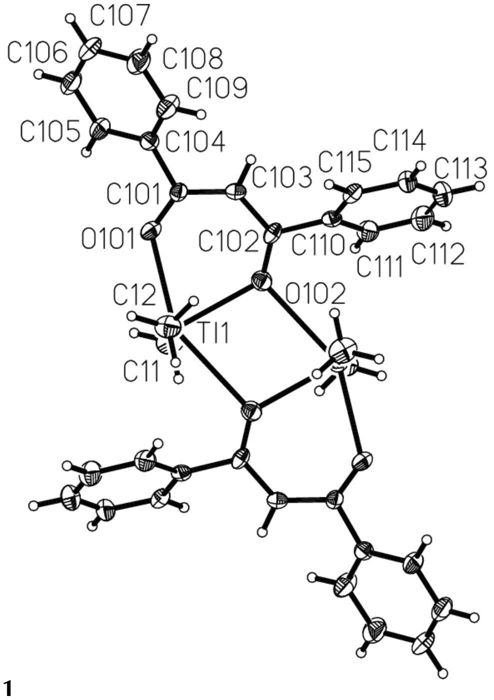


Figure 1
A view of molecule 1 with displacement ellipsoids shown at the 50% probability level. The unlabelled atoms are related to the labelled atoms by a center of symmetry.

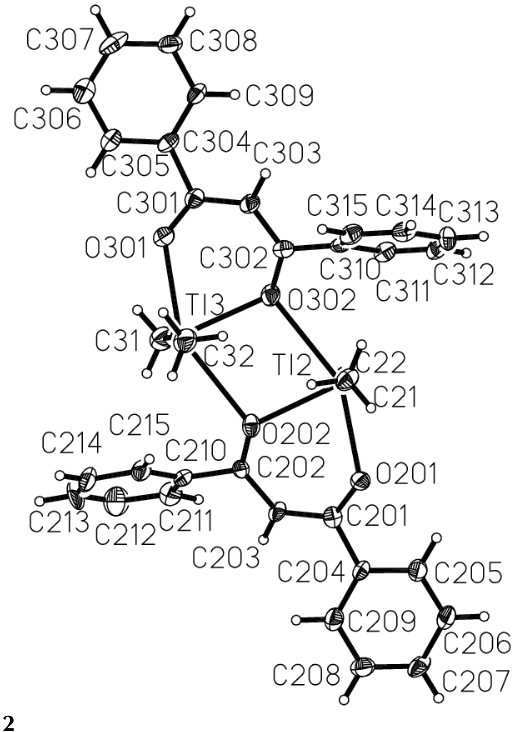


Figure 2
A view of molecule 2 with displacement ellipsoids shown at the 50% probability level. The central four-membered ring is bent across the O202—O302 direction by 7.0 (3)°.

the chelate ring has a dihedral angle of 6.0 (4)° to the TlO_2 fragment in the bridging ring at Tl1; the corresponding angles at Tl2 and Tl3 are 3.9 (4) and 4.6 (4)°, respectively.

The C_3O_2 fragment in the chelate ring is approximately planar but has a dihedral angle of 23.8 (3)° to the TlO_2 fragment in the ring for Tl1; the corresponding angles for Tl2 and Tl3 are 26.9 (3) and 26.7 (4)°, respectively. Similar angles, 11.7 and 25.0°, are found in $Sn(bzbz)_2$ (Uchida *et al.*, 1977). However, this bending is not universal. The same ligand forms a compound with terbium in which there are two similar chelate rings (Ward *et al.*, 1999), but where the dihedral angles are 0.5 and 2.1°. When the phenyl groups are replaced with methyl, the chelate ring is exactly planar (Chow & Britton, 1975). Presumably the bending, when it occurs, is a consequence of the packing.

We would expect the phenyl rings to tend to be coplanar with the chelate ring in order to maximize the delocalization in the π system. In the free ligand, these dihedral angles are 4 and 17° in one polymorph (Hollander *et al.*, 1973), and 8 and 24° in the other (Etter *et al.*, 1987). In our compound, the phenyl rings furthest from the bridging ring make dihedral angles to the C_3O_2 fragment of 29.2 (4), 24.3 (4) and 21.4 (4)° at Tl1, Tl2, and Tl3, respectively. The phenyl rings nearest the bridging ring make dihedral angles to the C_3O_2 fragment of 47.2 (4), 50.5 (3) and 61.1 (3)° at Tl1, Tl2, and Tl3, respectively. These larger angles are a consequence of the crowding in this molecule. This crowding also has the consequence that the Tl is only five-coordinate rather than six-coordinate, as it is when the chelating and bridging ligand is acetate, tropolonate or acetylacetonate.

The packing is shown in Fig. 3. There is a pseudosymmetric relationship bewteen the two independent molecules. It is far from exact but can be approximated as a pseudo-glide plane where the coordinates of molecule 2 are given by $0.55 - x_1$, $y_1 - \frac{1}{6}$, z_1, where x_1, y_1, z_1 are the coordinates of molecule 1. This is reflected in the intensities in the $0kl$ layer, where the $l = 6n$ reflection are much more intense than the $l = 6n\pm2$ reflections.

Experimental

A crystal from a previous preparation was used.

Crystal data

$[Tl_2(CH_3)_4(C_{15}H_{11}O_2)_2]$
$M_r = 915.35$
Orthorhombic, *Pbca*
$a = 14.0160\ (7)$ Å
$b = 38.4862\ (12)$ Å
$c = 17.2175\ (5)$ Å
$V = 9287.5\ (6)$ Å^3
$Z = 12$
$D_x = 1.964$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7473 reflections
$\theta = 1.1\text{–}25.2°$
$\mu = 10.43$ mm^{-1}
$T = 174\ (2)$ K
Prism, colorless
0.40 × 0.35 × 0.20 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.025$, $T_{max} = 0.124$
45 301 measured reflections

8309 independent reflections
7122 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$
$\theta_{max} = 25.2°$
$h = -15 \rightarrow 16$
$k = -45 \rightarrow 28$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.107$
$S = 1.14$
8309 reflections
542 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 96.0P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 2.00$ e Å^{-3}
$\Delta\rho_{\min} = -2.31$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.000173 (15)

Table 1
Selected geometric parameters (Å, °).

Tl1—C11	2.125 (10)	Tl2—O201	2.447 (6)
Tl1—C12	2.136 (10)	Tl2—O302	2.764 (6)
Tl1—O102	2.448 (6)	Tl3—C31	2.102 (11)
Tl1—O101	2.482 (6)	Tl3—C32	2.122 (11)
Tl1—O102^{i}	2.762 (6)	Tl3—O302	2.439 (6)
Tl2—C22	2.120 (11)	Tl3—O301	2.472 (6)
Tl2—C21	2.133 (10)	Tl3—O202	2.808 (6)
Tl2—O202	2.441 (6)		
C11—Tl1—C12	170.0 (4)	O202—Tl2—O302	76.6 (2)
O102—Tl1—O101	74.7 (2)	O201—Tl2—O302	152.0 (2)
O102—Tl1—O102^{i}	76.2 (2)	C31—Tl3—C32	170.5 (4)
O101—Tl1—O102^{i}	150.3 (2)	O302—Tl3—O301	74.7 (2)
C22—Tl2—C21	171.2 (4)	O302—Tl3—O202	75.8 (2)
O202—Tl2—O201	75.6 (2)	O301—Tl3—O202	150.2 (2)

Symmetry code: (i) $-x, 2-y, 1-z$.

The faces of the crystal were not regular enough to allow for a numerical absorption correction. The Tl-atom positions from the previous work were used as the starting point for the solution. The Tl atoms were eventually moved to equivalent positions to make the asymmetric unit more compact.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

I thank Dr Victor G. Young Jr, Director of the University of Minnesota X-ray Diffraction Laboratory, for his help. The sample was prepared by Dr Y. M. Chow.

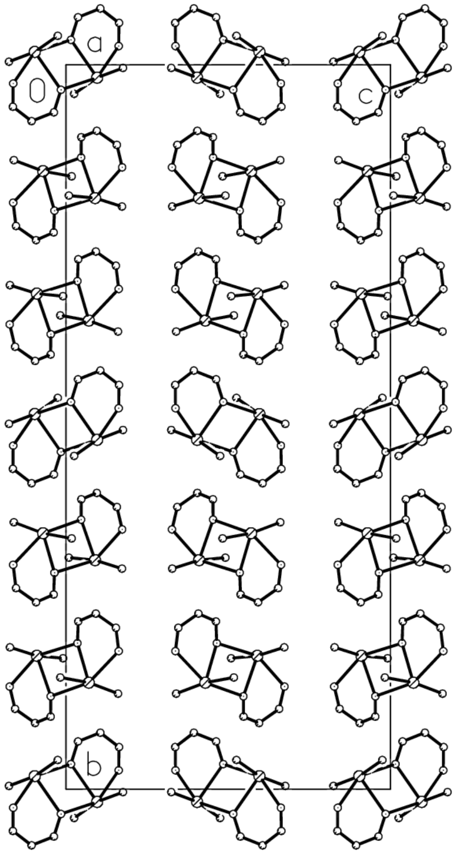


Figure 3
The packing viewed along the a direction. The phenyl C atoms and all of the H atoms have been omitted for clarity.

References

Belsky, V. K., Zorkaya, O. N. & Zorky, P. M. (1995). *Acta Cryst.* A**51**, 473–481.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Chow, Y. M. & Britton, D. (1975). *Acta Cryst.* B**31**, 1929–1934.
Etter, M. C., Jahn, D. A. & Urbańczyk-Lipkowska, Z. (1987). *Acta Cryst.* C**43**, 260–263.
Hollander, F. J., Templeton, D. H. & Zalkin, A. (1973). *Acta Cryst.* B**29**, 1552–1553.
Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin USA.
Uchida, T., Kozawa, K. & Obara, H. (1977). *Acta Cryst.* B**33**, 3227–3229.
Ward, M. D., McCleverty, J. A., Mann, K. L. V., Jeffery, J. C., Motson, G. R. & Hurst, J. (1999). *Acta Cryst.* C**55**, 2055–2058.
Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28.
Zorky, P. M., Belsky, V. K., Lazareva, S. G. & Porai-Koshits, M. A. (1967). *J. Struct. Chem.* **8**, 267–270.