

## The trigonal–bipyramidal triiodo–thallium(III) complex $[\text{TlI}_3\{(\text{CH}_3)_2\text{SO}\}_2]$

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Received 20 June 2001

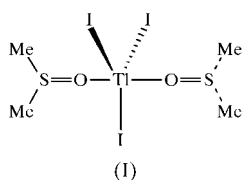
Accepted 3 December 2001

Online 20 February 2002

The title compound, bis(dimethyl sulfoxide)triiodo–thallium(III),  $[\text{TlI}_3(\text{C}_2\text{H}_6\text{OS})_2]$ , was crystallized from equimolar amounts of  $\text{Tl}^{\text{I}}$  and  $\text{I}_2$  in a dimethyl sulfoxide (DMSO) solution. After the initial redox reaction, the thallium(III)–iodo complex forms and precipitates as a DMSO solvate. In the crystal structure, Tl is surrounded by three iodide ligands in the equatorial plane and two *O*-coordinated DMSO molecules in the axial positions, forming a slightly distorted trigonal bipyramid. The complex lies on a twofold rotation axis, making the DMSO molecules and two of the I atoms crystallographically equivalent.

### Comment

The formation of  $\text{Tl}^{\text{III}}$ –halide complexes has been studied extensively both in solution and in the solid state (Lee, 1971). Most of these studies dealt with tetrahalo complexes, which can easily be obtained from solutions of thallium and an excess of halide. The thallium(III) tetraiodide anion is usually prepared using large monovalent cations, such as quaternary ammonium and arsonium ions, *e.g.* in  $[(\text{C}_6\text{H}_5)_4\text{As}]\text{TlI}_4$  and  $[(\text{C}_4\text{H}_9)_4\text{N}]\text{TlI}_4$ , providing the first evidence that the  $[\text{TlI}_4]^-$  complex is formed in the presence of  $\text{Tl}^{\text{III}}$  and  $\text{I}^-$  (Cotton *et al.*, 1965). Considering crystal structure studies of thallium(III) iodide complexes, only the structures of the tetraiodo anion ( $\text{TlI}_4^-$ ) with the organic cations  $[(\text{C}_4\text{H}_9)_4\text{N}]^+$  and  $[\text{C}_5\text{H}_5\text{NH}]^+$  have been determined (Glaser *et al.*, 1982; Drew & Lewis, 1970). In both cases, the  $\text{TlI}_4^-$  entity is a distorted tetrahedron, with Tl–I distances in the range 2.760–2.797 Å and angles between 106.0 and 112.7°.

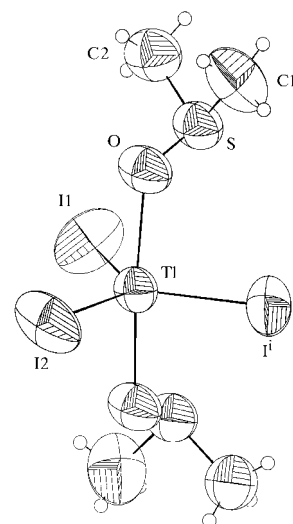


The first preparation of thallium triiodide dates from 1864 (Lee, 1971) and its properties have stimulated much interest. In the subsequent development of thallium iodide chemistry,

several complexes with the formula  $\text{TlX}_3\text{L}_2$ , such as  $\text{TlI}_3(\text{OPPh}_3)_2$ , have been prepared. Elemental analysis, as well as vibrational spectroscopy, indicated compositions and structures consistent with a trigonal–bipyramidal species (Bermejo & Gayoso, 1985). The crystal structure determination of the mixed-halide  $\text{TlBrI}_2(\text{OPPh}_3)_2$  confirmed the trigonal–bipyramidal structure of the complex.

Hitherto, there has been no structural characterization of a  $\text{TlI}_3$  species and the X-ray structure determination of yellow–red crystals obtained from a DMSO solution containing  $\text{TlI}/\text{I}_2$  in a 1:1 molar ratio was undertaken to fill this gap. Selected geometric parameters of the title complex, (I), are given in Table 1, and an *ORTEP*II (Johnson, 1976) plot of the structure is shown in Fig. 1. The molecule forms a trigonal bipyramid with the three I atoms residing in the trigonal plane. The molecule sits astride a crystallographic twofold axis, which passes through the Tl and I2 positions. The trigonal bipyramid is slightly distorted and superficially resembles the molecular structures of  $\text{TlX}_3 \cdot 3\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}$ ) (Glaser, 1979) and  $\text{TlBrI}_2$  (Castineiras *et al.*, 1986). In  $\text{TlI}_3(\text{DMSO})_2$ , the Tl atom resides in the equatorial plane, whereas for the trichloro and tribromo derivatives, the Tl atom is out of the plane by 0.071 (1) and 0.101 (1) Å, respectively.  $\text{TlI}_3(\text{DMSO})_2$  is similar to  $\text{TlI}_2\text{Br}(\text{OPPh}_3)_2$  in that  $\text{Tl}^{\text{III}}$  is located in the plane of the halides. For the title complex, the Tl–O distance is 2.469 (6) Å. The mean Tl–I distance is 2.709 (1) Å, which is slightly longer than in  $\text{TlI}_2\text{Br}(\text{OPPh}_3)_2$  [Tl–I = 2.676 (1) Å]. The three I–Tl–I angles are closer to 120° than those in  $\text{TlX}_3 \cdot 4\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}$ ) and  $\text{TlI}_2\text{Br}(\text{OPPh}_3)_2$ . A larger deviation of this angle from 120° in  $\text{TlI}_2\text{Br}(\text{OPPh}_3)_2$  is to be expected due to the different ionic radii of the I and Br ions in the  $\text{Tl}^{\text{III}}$  coordination sphere. The O–Tl–O angle in all four crystal structures deviates slightly from 180°.

For DMSO as a solvating ligand bonded to  $\text{Tl}^{\text{III}}$ , only one complex has been reported in the literature, *viz.*  $[\text{TlCl}_5(\text{DMSO})](\text{Hpyr})_2$  (James *et al.*, 1983). Here, the Tl–O distance of 2.42 Å is shorter than in the title complex



**Figure 1**  
*ORTEP*II view (Johnson, 1976) of  $[\text{TlI}_3(\text{DMSO})_2]$ . The displacement ellipsoids represent 70% probability and the H atoms are shown with arbitrary radii. See Table 1 for symmetry code.

[2.469 (6) Å]. Very recently, the structure of the  $\text{Tl}^{\text{III}}$ -DMSO complex  $[\text{Tl}(\text{DMSO})_6](\text{ClO}_4)_3$  was determined in our laboratory and the  $\text{Tl}-\text{O}$  bond distance was found to be 2.224 (3) Å (Ma *et al.*, 2001). Thus, the  $\text{Tl}-\text{O}$  distance in the  $\text{Tl}^{\text{III}}$ -halide-DMSO complexes is much longer than that in  $\text{Tl}$ -DMSO perchlorate, which is certainly caused by the strong  $\text{Tl}-\text{halide}$  bonds. The mean  $\text{Tl}-\text{I}$  distance of 2.709 (1) Å in  $[\text{TlI}_3(\text{DMSO})_2]$  is shorter than that in  $\text{TlI}_4^-$  [2.764 (4) Å]. This is in part due to the large ionic radius of the iodide ion, but also to the fact that the number of strongly coordinated ligands increases from  $\text{TlI}_3$  to  $\text{TlI}_4^-$  (the  $\text{Tl}-\text{O}$  bond is weak, see above). The common oxidation states of thallium are  $\text{Tl}^{\text{I}}$  and  $\text{Tl}^{\text{III}}$ . The oxidation potential for  $\text{Tl}^{3+}/\text{Tl}^+$  is 1.25 V, and that for  $\text{I}_3^-/\text{I}^-$  is 0.53 V (Lee, 1971), which means that  $\text{Tl}^{\text{III}}$  should not be stable in the presence of iodide. However, the studied compound clearly shows that the  $\text{TlI}_3$  complex exists and contains both  $\text{Tl}^{\text{III}}$  and  $\text{I}^-$ . This is certainly due to the stabilizing effect of the strong bond between the soft  $\text{Tl}^{3+}$  and  $\text{I}^-$  ions. This effect is also present in pyridine solution, where the formation of extremely strong complexes with the composition  $\text{TlI}_n^{3-n}$  has been observed by means of  $^{205}\text{Tl}$  NMR spectroscopy (unpublished results from our laboratory).

## Experimental

The title compound was synthesized by mixing equimolar amounts of thallium(I) iodide and iodine in DMSO solution. The yellow-red crystals were crystallized from a red-brown 0.1 M  $\text{TlI}_3$  solution (1:1  $\text{TlI}_3/\text{I}_2$ ) in a closed flask over a period of a month. The Raman spectrum of the crystals was recorded using a Renishaw system 1000 spectrometer, equipped with a Leica DMLM microscope. The band positions and assignments are: 2905m ( $\text{CH}_3$  stretch); 1402w, 987w and 936w ( $\text{CH}_3$  bend); 707m and 672s (CS stretch); 405m ( $\text{Tl}-\text{O}$  stretch); 322w and 301m (OSC bend); 161vs and 123.4vs ( $\text{Tl}-\text{I}$  stretch), where vs is very strong, s strong, m medium and w weak.

### Crystal data

$[\text{TlI}_3(\text{C}_2\text{H}_6\text{OS})_2]$	$D_x = 3.008 \text{ Mg m}^{-3}$
$M_r = 741.34$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 10 534 reflections
$a = 8.8785$ (3) Å	$\theta = 2.9-27.5^\circ$
$b = 14.9833$ (6) Å	$\mu = 15.76 \text{ mm}^{-1}$
$c = 12.5835$ (5) Å	$T = 298 \text{ K}$
$\beta = 102.065$ (2)°	Cube, yellow-red
$V = 1637.00$ (10) Å <sup>3</sup>	$0.30 \times 0.27 \times 0.20 \text{ mm}$
$Z = 4$	

### Data collection

Nonius KappaCCD diffractometer	1842 independent reflections
$\varphi$ scans	1715 reflections with $I > 2\sigma(I)$
Absorption correction: by integration ( <i>HABITUS</i> ; Herrendorf & Bärnighausen, 1993)	$R_{\text{int}} = 0.065$
$T_{\text{min}} = 0.039$ , $T_{\text{max}} = 0.265$	$\theta_{\text{max}} = 27.4^\circ$
7155 measured reflections	$h = -9 \rightarrow 11$
	$k = -18 \rightarrow 19$
	$l = -15 \rightarrow 16$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 14.8122P]$
$R(F) = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 1.62 \text{ e } \text{Å}^{-3}$
1842 reflections	$\Delta\rho_{\text{min}} = -1.87 \text{ e } \text{Å}^{-3}$
59 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0017 (2)

**Table 1**

Selected geometric parameters (Å, °).

$\text{TlI}-\text{O1}$	2.469 (6)	$\text{S1}-\text{O1}$	1.521 (7)
$\text{TlI}-\text{I2}$	2.6916 (10)	$\text{S1}-\text{C1}$	1.772 (13)
$\text{TlI}-\text{I1}$	2.7173 (7)	$\text{S1}-\text{C2}$	1.775 (12)
$\text{O1}^{\text{i}}-\text{TlI}-\text{O1}$	173.8 (3)	$\text{I1}^{\text{i}}-\text{TlI}-\text{I1}$	121.31 (5)
$\text{O1}-\text{TlI}-\text{I2}$	93.09 (15)	$\text{O1}-\text{S1}-\text{C1}$	104.5 (6)
$\text{O1}-\text{TlI}-\text{I1}^{\text{i}}$	89.26 (18)	$\text{O1}-\text{S1}-\text{C2}$	104.8 (5)
$\text{O1}-\text{TlI}-\text{I1}$	87.71 (18)	$\text{C1}-\text{S1}-\text{C2}$	96.7 (6)
$\text{I2}-\text{TlI}-\text{I1}$	119.34 (3)		

Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .

The data set indicated the monoclinic symmetry, and the reflection condition  $hkl: h + k = 2n$  indicated a  $C$ -centred lattice. Additionally, a zonal extinction  $h0l: l = 2n$  was observed. Of the two possible space groups,  $Cc$  and  $C2/c$ , the latter centrosymmetric space group was confirmed in the course of the structure determination and refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

The authors wish to express their thanks to the Swedish Research Council (VR) for continuous economic support and to the Swedish Institute for the scholarship covering GM's stay in Stockholm.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1035). Services for accessing these data are described at the back of the journal.

## References

- Bergerhoff, G. (1996). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bermejo, M. R. & Gayoso, M. (1985). *Synth. React. Inorg. Met. Org. Chem.* **15**, 951–963.
- Castineiras, A., Hiller, W., Strähle, J., Bermejo, M. R. & Gayoso, M. (1986). *An. Quim.* **82**, 282–286.
- Cotton, F. A., Johnson, B. F. G. & Wing, R. M. (1965). *Inorg. Chem.* **4**, 502–507.
- Drew, M. G. B. & Lewis, D. F. (1970). *Inorg. Nucl. Chem. Lett.* **6**, 163–166.
- Glaser, J. (1979). *Acta Chem. Scand.* **A33**, 789–794.
- Glaser, J., Goggin, P. L., Sandström, M. & Lutsko, V. (1982). *Acta Chem. Scand. Ser. A*, **36**, 55–62.
- Herrendorf, W. & Bärnighausen, H. (1993). *HABITUS*. Universities of Giessen and Karlsruhe, Germany.
- James, B. D., Millikan, M. B. & Mackay, M. F. (1983). *Inorg. Chem. Acta*, **77**, L251–253.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lee, A. G. (1971). *The Chemistry of Thallium*, pp. 44–84. Amsterdam: Elsevier.
- Ma, G., Molla-Abbassi, A., Kritikos, M., Ilyukhin, A., Kessler, V., Skripkin, M., Sandström, M., Glaser, J., Näslund, J. & Persson, I. (2001). *Inorg. Chem.* **40**, 6432–6438.
- Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *maXus*. Nonius, The Netherlands, MacScience, Japan, and The University of Glasgow, Scotland.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.