

N1	0.0236 (4)	0.1138 (3)	0.0871 (5)	2.4 (2)
N2	0.2115 (4)	-0.0071 (3)	0.0631 (4)	2.1 (2)
C1	0.2692 (6)	0.0668 (3)	0.1704 (6)	2.5 (3)
C2	0.4304 (6)	0.0836 (4)	0.1847 (8)	3.5 (3)
C3	0.4764 (6)	0.1600 (6)	0.2977 (8)	4.3 (3)
C4	0.3836 (6)	0.2350 (4)	0.2296 (8)	4.0 (3)
C5	0.2221 (6)	0.2166 (3)	0.2117 (7)	3.3 (3)
C6	0.1773 (5)	0.1400 (3)	0.1019 (6)	2.3 (2)
C7	-0.0805 (6)	0.1800 (3)	0.0150 (8)	3.5 (3)
C8	-0.2356 (6)	0.1546 (4)	-0.0013 (7)	3.3 (3)
C9	-0.2863 (6)	0.0858 (3)	-0.1270 (7)	2.9 (3)
C10	-0.2603 (9)	0.1068 (4)	-0.3009 (8)	4.9 (4)

Table 3. Selected bond distances (Å) and angles (°) for complexes (I) and (II)

	(I)	(II)
M—N1	2.017 (2)	1.954 (4)
M—N2	2.038 (2)	1.941 (3)
M—O	2.649 (2)	
N1—C6	1.486 (3)	1.481 (6)
N1—C7	1.480 (4)	1.477 (6)
N2—C1	1.489 (3)	1.504 (7)
N2—C9 <sup>i</sup>	1.490 (3)	1.483 (7)
C1—C6	1.513 (4)	1.493 (7)
N1—M—N1 <sup>i</sup>	180.0	180.0
N1—M—N2	84.5 (1)	86.0 (2)
N1—M—N2 <sup>i</sup>	96.5 (1)	94.1 (2)
N1—M—O	90.6 (1)	
N1—M—O <sup>i</sup>	89.5 (1)	
N2—M—N2 <sup>i</sup>	180.0	180.0
N2—M—O	83.4 (1)	
N2—M—O <sup>i</sup>	96.6 (1)	
O—M—O <sup>i</sup>	180.0	
Cu—N1—C6	107.7 (1)	109.1 (3)
Cu—N1—C7	115.7 (2)	120.9 (3)
C6—N1—C7	113.8 (2)	112.0 (4)
Cu—N2—C1	108.1 (1)	109.1 (3)
Cu—N2—C9 <sup>i</sup>	120.8 (2)	121.4 (3)
C1—N2—C9 <sup>i</sup>	115.4 (2)	112.5 (4)
N2—C1—C2	113.9 (2)	114.4 (4)
N2—C1—C6	106.6 (2)	107.2 (4)
C2—C1—C6	112.4 (2)	112.0 (4)
N1—C6—C1	107.1 (2)	106.2 (4)
N1—C6—C5	114.0 (2)	114.6 (4)
C1—C6—C5	111.1 (2)	110.5 (4)

Symmetry codes: (i)  $-x, 1-y, 1-z$ , for complex (I); (i)  $-x, -y, -z$ , for complex (II).

Table 4. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
(I)				
N1—HN1...Cl <sup>i</sup>	0.84 (2)	2.54 (2)	3.374 (2)	173 (2)
N2—HN2...Cl	0.76 (2)	2.81 (2)	3.539 (2)	162 (2)
O—HO1...Cl	0.84 (3)	2.32 (3)	3.139 (3)	164 (2)
O—HO2...Cl <sup>ii</sup>	0.74 (3)	2.44 (3)	3.147 (3)	164 (2)

Symmetry codes: (i)  $x, y, 1+z$ ; (ii)  $-x, 1-y, -z$ .

(II)				
N1—HN1...O	0.75 (3)	2.13 (3)	2.883 (6)	173 (4)
N2—HN2...Cl	0.84 (3)	2.46 (3)	3.270 (4)	165 (3)
O—HO1...Cl <sup>i</sup>	0.88 (4)	2.31 (4)	3.171 (5)	164 (4)
O—HO2...Cl <sup>ii</sup>	0.82 (4)	2.34 (5)	3.156 (6)	178 (5)

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $x, y, 1+z$ .

All non-H atoms were placed by a combination of difference Fourier and least-squares calculations. Methyl H atoms were located from difference Fourier maps, while other H atoms were placed in calculated positions. Anisotropic displacement

parameters were used for all non-H atoms and H atoms were refined isotropically.

For both compounds, data collection: *SDP* (Enraf–Nonius, 1985); cell refinement: *SDP*; data reduction: *SDP*; program(s) used to solve structures: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to refine structures: *NRCVAX*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *NRCVAX*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1220). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Diiodobis( $\eta^5$ -trimethylsilylcyclopentadienyl)titanium(IV)

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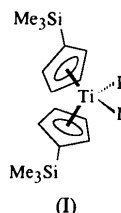
(Received 30 January 1996; accepted 14 May 1996)

## Abstract

The title compound, [TiI<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>], has crystallographic C<sub>2</sub> symmetry with the metal atom in a distorted tetrahedral environment bonded to two I atoms [Ti—I 2.771 (3) Å] and to two cyclopentadienyl rings [Ti—C 2.308 (14)–2.387 (17) Å].

**Comment**

Klouras (1982) reported the synthesis of  $[\text{TiI}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ , (I), by the reaction of  $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  and KI, and later Bruce, Sclafani & Tyler (1986) described an alternative synthesis of (I) using  $\text{BI}_3$  instead of KI. We obtained suitable crystals of the title compound by reaction of  $[\text{Ti}(\text{SPh})_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  and  $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ , and further crystallization in diethyl ether at 293 K.



This is the first crystal structure determination of a diiodide derivative of bis-substituted cyclopentadienylnitium(IV). There are, however, 122 examples in the Cambridge Structural Database (Allen & Kennard, 1993) of bis-substituted cyclopentadienyldichlorotitanium complexes. This set includes the exact dichloro analogue  $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  (Klouras & Nastopoulos, 1991).

In the present structure, the molecule of (I) has crystallographically imposed  $C_2$  symmetry. The unique Ti—I distance is 2.771 (3) Å and the Ti—C distances range from 2.308 (14) to 2.387 (17) Å. By contrast, in the dichloro analogue, the molecule has no imposed symmetry and the dimensions are Ti—Cl 2.367 (1) and 2.362 (1) Å, with Ti—C 2.353 (3)–2.413 (2) Å.

The distances from the metal atom to the ring centroids are 2.03 (1) Å and the angle subtended at the metal by the two ring centroids is 130.5 (3)° compared with values of 2.06 Å and 131.0° in the dichloro analogue.

While there are no previously reported diiodo-cyclopentadienyl-titanium complexes comparable to the structure reported here, the Ti—I distances of 2.771 (3) Å can be compared to those of similar

bonds. There are, however, only seven structures in the Cambridge Structural Database (Allen & Kennard, 1993) containing a Ti—I bond. Distances are generally comparable to this value, for example, 2.759 Å in iodobis( $\eta^5$ -tetramethylcyclopentadienyl)titanium (Trojanov, Rybakov, Thewalt, Varga & Mach, 1993), 2.785 Å in [ $(\eta^6\text{-benzene})\text{-hexakis-}\mu^2\text{-iodo-}\mu^4\text{-1,3,5-tris-(diiodoaluminium)benzene}]\text{tetratitanium benzene solvate}$  (Trojanov & Rybakov, 1988; Trojanov & Tafenko, 1990). The remaining dimensions in the complex are as expected. The two bulky  $\text{SiMe}_3$  substituents are positioned as far apart as possible.

**Experimental**

$[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$  (0.13 g, 0.22 mmol) was added to a toluene solution (30 ml) of  $[\text{Ti}(\text{SPh})_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$  (0.16 g, 0.22 mmol). After stirring under nitrogen for 3 h, the red-brown solution was filtered and the solvent removed *in vacuo*. Crystallization of the solid residue from a diethyl ether solution (10 ml) at 256 K afforded brown crystals of  $[\text{TiI}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ .

*Crystal data*

$[\text{TiI}_2(\text{C}_8\text{H}_{13}\text{Si})_2]$

$M_r = 576.27$

Monoclinic

$C2/c$

$a = 13.440$  (9) Å

$b = 7.205$  (9) Å

$c = 22.388$  (9) Å

$\beta = 92.36$  (1)°

$V = 2166$  (3) Å<sup>3</sup>

$Z = 4$

$D_x = 1.767$  Mg m<sup>-3</sup>

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.7107$  Å

Cell parameters from 775 reflections

$\theta = 5\text{--}25^\circ$

$\mu = 3.35$  mm<sup>-1</sup>

$T = 293$  (2) K

Parallelepiped

$0.25 \times 0.20 \times 0.17$  mm

Red

*Data collection*

Marresearch image plate

95 frames at 2° intervals,

counting time 2 min

Absorption correction:

refined from  $\Delta F$

(*DIFABS*; Walker &

Stuart, 1983)

$T_{\min} = 0.44$ ,  $T_{\max} = 0.58$

2284 measured reflections

1516 independent reflections

858 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0614$

$\theta_{\max} = 24.91^\circ$

$h = 0 \rightarrow 15$

$k = -8 \rightarrow 8$

$l = -26 \rightarrow 26$

No standard reflections

*Refinement*

Refinement on  $F^2$

$R(F) = 0.0653$

$wR(F^2) = 0.2789$

$S = 0.609$

1516 reflections

100 parameters

H atoms riding with  $U(\text{H}) =$

$1.2U_{\text{eq}}(\text{C})$

$w = 1/[\sigma^2(F_o^2) + (0.2921P)^2 + 99.5474P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.031$

$\Delta\rho_{\max} = 0.737$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.856$  e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

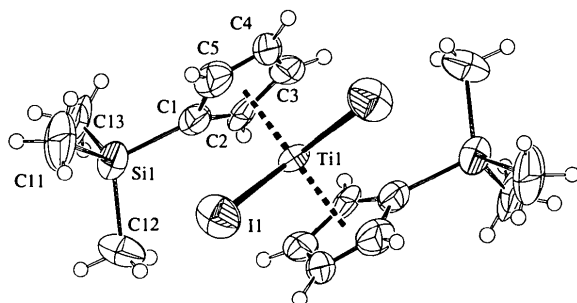


Fig. 1. The structure of the title compound with ellipsoids scaled to 40% probability. H atoms are included as small circles of arbitrary radii.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub>
II	0.04159 (11)	1.1690 (2)	0.33591 (6)	0.0813 (7)
Ti1	0	0.9000 (5)	1/4	0.0420 (10)
Si1	-0.0968 (4)	0.7370 (8)	0.4057 (2)	0.0685 (14)
C11	-0.154 (2)	0.931 (4)	0.4444 (11)	0.129 (10)
C12	0.0368 (15)	0.696 (3)	0.4304 (10)	0.087 (6)
C13	-0.1719 (15)	0.527 (3)	0.4207 (9)	0.093 (7)
C1	-0.1102 (11)	0.776 (2)	0.3210 (7)	0.053 (4)
C2	-0.0922 (11)	0.639 (2)	0.2779 (7)	0.050 (4)
C3	-0.1300 (13)	0.703 (3)	0.2238 (8)	0.058 (4)
C4	-0.1711 (13)	0.872 (3)	0.2331 (7)	0.073 (6)
C5	-0.1573 (14)	0.919 (3)	0.2903 (9)	0.076 (5)

Table 2. Selected geometric parameters (Å, °)

II—Ti1	2.771 (3)	Si1—C12	1.883 (15)
Ti1—C1	2.387 (17)	Si1—C1	1.923 (17)
Ti1—C2	2.350 (14)	C1—C5	1.38 (2)
Ti1—C3	2.308 (14)	C1—C2	1.41 (2)
Ti1—C4	2.315 (19)	C2—C3	1.37 (2)
Ti1—C5	2.34 (2)	C3—C4	1.36 (3)
Si1—C11	1.83 (2)	C4—C5	1.33 (3)
Si1—C13	1.86 (2)		
II—Ti1—II <sup>†</sup>	91.24 (13)	Cg1—Ti1—II <sup>†</sup>	106.73 (18)
Cg1—Ti1—II <sup>†</sup>	107.42 (18)	Cg1—Ti1—Cg1 <sup>†</sup>	130.5 (3)

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

† Cg1 is the centroid of the C1—C5 ring.

The 180 mm diameter image plate was 75 mm from the crystal. Rotation was about  $\varphi$ . The data are 84% complete to the stated  $\theta_{\max}$  (1805 independent reflections theoretically available). Crystal decay was assessed from the scaling factors derived automatically for each frame.

Data collection: XDS (Kabsch, 1988). Cell refinement: XDS. Data reduction: XDS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: PLATON (Spek, 1994).

We thank EPSRC and the University of Reading for funds for the Image Plate System and the ERASMUS scheme of the European Commission for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Tetrakis(2,3,5,6-tetramethylpyrazinium) Tetra- $\mu_3$ -iodo-hexa- $\mu$ -iodo-dodecaiodo-hexaantimonate(4-) Tetrahydrate

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## Abstract

The title compound, (C<sub>8</sub>H<sub>13</sub>N<sub>2</sub>)<sub>4</sub>[Sb<sub>6</sub>I<sub>22</sub>].4H<sub>2</sub>O, crystallizes with an Sb<sub>6</sub>I<sub>22</sub><sup>4-</sup> anion consisting of edge-shared distorted octahedra [Sb—I range 2.789 (2)–3.421 (2) Å] and monoprotonated tetramethylpyrazinium cations which are bridged by solvent water molecules to form infinite chains [N···O range 2.69 (1)–2.95 (1) Å]. The anion has a structure corresponding to a section from a layer of the CdI<sub>2</sub> structure, similar to that previously observed when crystallized with a bis(cyclopentadienyl)iron(III) cation [Pohl, Lotz, Saak & Haase (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 344–345].

## Comment

The structural diversity of iodoantimonates is well known. Discrete anions such as Sb<sub>2</sub>I<sub>8</sub><sup>2-</sup> (Pohl, Saak & Haase, 1987b), Sb<sub>2</sub>I<sub>9</sub><sup>3-</sup> (Pohl, Saak & Haase, 1987a), Sb<sub>3</sub>I<sub>11</sub><sup>4-</sup> (Pohl, Lotz, Saak & Haase, 1989), Sb<sub>5</sub>I<sub>18</sub><sup>6-</sup> (Pohl, Lotz, Saak & Haase, 1989; Carmalt, Norman & Farrugia, 1993), Sb<sub>6</sub>I<sub>22</sub><sup>4-</sup> (Pohl, Haase, Lotz & Saak, 1988; Pohl, Lotz, Saak & Haase, 1989) and Sb<sub>8</sub>I<sub>28</sub><sup>6-</sup> (Pohl, Saak & Haase, 1987a,c; Pohl, Lotz, Haase & Saak, 1988; Carmalt, Norman & Farrugia, 1993) have been structurally characterized, as have polymeric species with formula units of SbI<sub>4</sub><sup>-</sup> (Hendrixson, ter Horst & Jacobson, 1990), Sb<sub>2</sub>I<sub>7</sub><sup>-</sup> (Pohl, Lotz, Haase