

Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

**Related literature.** During the structure determination on unsolvated Vaska's compound, *trans*-IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, Cl/CO disorder was also identified and successfully resolved (Churchill, Fettinger, Buttrey, Barkan & Thompson, 1988). The solvated and unsolvated forms show similar structures for the metal complex.

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## The Structure of a Complex Containing a Chelating S<sub>3</sub><sup>2-</sup> Ligand: [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiS<sub>3</sub>]

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**Abstract.** Bis( $\eta^5$ -pentamethylcyclopentadienyl)(trisulfido)titanium(IV), [Ti(C<sub>10</sub>H<sub>15</sub>)<sub>2</sub>(S<sub>3</sub>)],  $M_r = 414.3$ , monoclinic,  $P2_1/c$ ,  $a = 8.770$  (8),  $b = 13.885$  (6),  $c = 17.20$  (1) Å,  $\beta = 103.75$  (6)°,  $V = 2034.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.353$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 7.11$  cm<sup>-1</sup>,  $F(000) = 879.9$ ,  $T = 293$  K,  $R = 0.057$  for 1829 reflections with  $I > 3\sigma(I)$ . The structure is a typical 'slipped sandwich' type with two  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> rings and a novel chelating S<sub>3</sub><sup>2-</sup> ligand which results in a non-planar TiS<sub>3</sub> ring with a dihedral angle of 49° between the plane formed by the Ti atom and the two bonded S atoms and that formed by the three S atoms [Ti—S av. 2.413 (4) Å, S—S av. 2.041 (5) Å, C<sub>5</sub>Me<sub>5</sub>TiC<sub>5</sub>Me<sub>5</sub> 136.85 (3)°, STiS 84.44 (9)°, TiSS av. 76.34 (1)°, SSS 105.3 (1)°]. The Ti—S(2) distance is 2.77 Å; it would lengthen to about 3.0 Å if the TiS<sub>3</sub> ring were planar.

**Experimental.** The complex was prepared by treating Cp<sub>2</sub>\*TiCl<sub>2</sub>, where Cp\* = C<sub>5</sub>Me<sub>5</sub>, with Li<sub>2</sub>S<sub>3</sub> in THF

(Bird, McCall, Shaver & Siriwardane, 1982; Shaver & McCall, 1984) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane to give large red-black crystals. Data were collected using a crystal 0.40 × 0.20 × 0.50 mm; Picker FACS-1 diffractometer; monochromated Mo  $K\alpha$  radiation;  $\theta$ - $2\theta$  scan mode; cell parameters from 40 reflections with  $14 \leq 2\theta \leq 40^\circ$ . The maximum value of  $(\sin\theta)/\lambda$  reached in intensity measurements was 0.54 Å<sup>-1</sup> ( $3.5 \leq 2\theta \leq 45.0^\circ$ ); the ranges of  $h$ ,  $k$  and  $l$  were  $-8 \leq h \leq 9$ ,  $0 \leq k \leq 14$  and  $0 \leq l \leq 18$ ; the standard reflections were 500, 080 and 010 and their intensity variation was 3.5%; number of reflections measured = number of unique reflections = 2678, number of unobserved reflections = 849 ( $I < 3\sigma(I)$ ). The structure was solved using *MULTAN*;  $F$  magnitudes were used in least-squares refinement, with 218 parameters refined;  $R = 0.057$ ,  $wR = 0.100$ ,  $w = 1/\sigma^2 F$ ,  $S = 0.999$ , using counting statistics.  $(\Delta/\sigma)_{\max} = 0.1$ ,  $(\Delta\rho)_{\max} = 0.3$ ,  $(\Delta\rho)_{\min} = -0.18$  e Å<sup>-3</sup>. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV); all programs used for the data collection,

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiS<sub>3</sub>

$B_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$B_{eq}(\text{\AA}^2)$
Ti	0.24929 (12)	0.68903 (8)	0.16446 (6)	2.31 (4)
S(1)	0.16828 (24)	0.80566 (15)	0.25029 (12)	4.37 (9)
S(2)	-0.03310 (23)	0.77812 (16)	0.16433 (14)	4.69 (9)
S(3)	-0.02105 (20)	0.63653 (15)	0.13719 (12)	4.07 (8)
C(11)	0.4158 (8)	-0.4522 (5)	0.1942 (4)	3.1 (3)
C(12)	0.4891 (7)	-0.3811 (5)	0.2472 (4)	2.9 (3)
C(13)	0.3896 (7)	-0.3616 (5)	0.2999 (3)	2.8 (3)
C(14)	0.2570 (8)	-0.0797 (5)	-0.2211 (4)	3.2 (3)
C(15)	0.7269 (8)	-0.5263 (5)	-0.2116 (4)	3.2 (3)
C(111)	0.4969 (12)	-0.5162 (6)	0.1453 (5)	5.5 (4)
C(122)	0.6562 (8)	-0.3496 (7)	0.2620 (5)	5.7 (4)
C(133)	0.4357 (12)	-0.3005 (6)	0.3731 (5)	5.6 (4)
C(144)	0.1360 (9)	-0.0706 (7)	-0.1759 (5)	5.3 (4)
C(155)	0.1644 (10)	-0.5580 (6)	0.1754 (6)	5.9 (4)
C(21)	0.3862 (7)	-0.1953 (5)	0.1011 (4)	2.9 (3)
C(22)	0.4052 (7)	-0.2839 (5)	0.0682 (4)	2.7 (3)
C(23)	0.7417 (7)	-0.6831 (5)	-0.0264 (4)	2.8 (3)
C(24)	0.8505 (7)	0.2420 (5)	-0.0278 (4)	2.9 (3)
C(25)	0.7670 (8)	0.1669 (5)	-0.0750 (4)	3.3 (3)
C(211)	0.4838 (10)	0.1290 (6)	-0.1448 (5)	5.0 (4)
C(222)	0.4408 (8)	-0.6776 (6)	-0.0583 (4)	4.1 (3)
C(233)	0.2212 (9)	-0.4071 (5)	-0.0222 (4)	4.1 (3)
C(244)	-0.0195 (9)	-0.2377 (7)	-0.0233 (5)	5.0 (4)
C(255)	0.1659 (10)	-0.0674 (6)	0.0838 (6)	5.2 (4)

Table 2. Selected bond lengths (Å) and angles (°) for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiS<sub>3</sub>

Ti—S(1)	2.409 (2)	Ti—C(13)	2.464 (6)
Ti—S(2)	2.768 (3)	Ti—C(14)	2.473 (6)
Ti—S(3)	2.417 (3)	Ti—C(15)	2.393 (7)
S(1)—S(2)	2.052 (4)	Ti—C(21)	2.414 (7)
S(2)—S(3)	2.029 (3)	Ti—C(22)	2.414 (6)
Ti—C(11)	2.425 (7)	Ti—C(23)	2.397 (6)
Ti—C(12)	2.444 (7)	Ti—C(24)	2.496 (6)
S(1)TiS(3)	84.4 (1)	Ti—C(25)	2.507 (7)
TiS(1)S(2)	76.2 (1)	TiS(3)S(2)	76.4 (1)
		S(1)S(2)S(3)	105.3 (1)

structure solution and refinement are part of the X-ray crystallographic system for the PDP-8 mini-computer (Larson & Gabe, 1978).

Atomic parameters are given in Table 1,† and selected intramolecular bond distances and angles in Table 2. Fig. 1 shows the molecular structure and the numbering scheme.

**Related literature.** The complexes Cp<sub>2</sub>\*MS<sub>3</sub>, where M = Ti, Zr, Hf, are members of a family of complexes containing catenated polysulfano ligands of the type S<sub>x</sub><sup>2-</sup>, where x > 1; reviews on this area have appeared (Draganjac & Rauchfuss, 1985; Wachter, 1989). The structure of Cp<sub>2</sub>\*TiS<sub>3</sub> is the only characterization of a chelating S<sub>3</sub><sup>2-</sup> ligand and is related to the structures

† Lists of structure factors, anisotropic thermal parameters and complete intramolecular distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53502 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

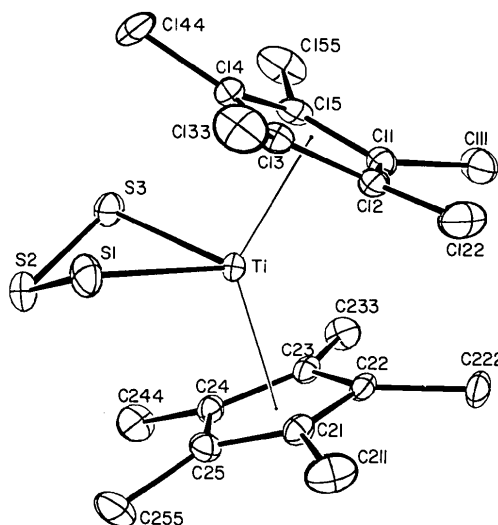


Fig. 1. ORTEP drawing of Cp<sub>2</sub>\*TiS<sub>3</sub> showing the numbering scheme; thermal ellipsoids are scaled to enclose 30% probability.

of Cp<sub>2</sub>\*VS<sub>2</sub> (Koch & Chebolu, 1983; Gambarotta, Floriani, Chiesi-Villa & Guastini, 1983), Cp<sub>2</sub>MS<sub>4</sub> where M = Mo (Block & Allmann, 1975) and W (Davis & Bernal, 1972) and Cp<sub>2</sub>MS<sub>5</sub> where M = Ti (Epstein & Bernal, 1971; Muller, Petersen & Dahl, 1976), Zr and Hf (Shaver, McCall, Day & Vollmer, 1987). Structures of complexes containing bridging S<sub>3</sub><sup>2-</sup> ligands (Wachter, 1989) and a terminal SSSPh<sup>-</sup> group (Shaver, McCall, Bird & Ansari, 1983) have been reported.

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## A Dimeric Stannoxane Structure: $[\text{Sn}_2(\text{Cl})(\text{O})(\text{OH})(\text{C}_6\text{H}_5)_4]_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$

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**Abstract.** Bis[chloro-1 $\kappa$ Cl- $\mu$ -hydroxo- $\mu$ -oxo-(tetra-phenyl-1 $\kappa^2$ C,2 $\kappa^2$ C)ditin]-*N,N*-dimethylformamide (1/2),  $[\text{Sn}_2(\text{Cl})(\text{O})(\text{OH})(\text{C}_6\text{H}_5)_4]_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$ ,  $M_r = 1374.6$ , orthorhombic, *Pbca*,  $a = 17.231(4)$ ,  $b = 17.552(2)$ ,  $c = 18.345(3)$  Å,  $V = 5548(3)$  Å<sup>3</sup>,  $Z = 4$  (dimers),  $D_x = 1.646$  Mg m<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 1.770$  mm<sup>-1</sup>,  $F(000) = 2704$ ,  $T = 293(1)$  K,  $R = 0.022$  for 2245 observed reflections. The title compound adopts the familiar tetraorganostannoxane structural motif with a centrosymmetric  $R_4\text{Sn}_2\text{O}_2$  moiety connected to two exocyclic  $R_2\text{SnCl}$  units. The two pairs of Sn atoms are also linked by hydroxy bridges such that each Sn atom exists in a distorted trigonal bipyramidal geometry. For the endocyclic Sn atom, the hydroxy O atom and stannoxane O atom occupy approximate *trans* positions and for the other Sn atom, the axial sites are occupied by the hydroxy O atom and the Cl atom. Connected to the hydroxy H atoms at each end of the 'ladder' structure, *via* hydrogen bonds, are two dimethylformamide molecules of solvation.

**Experimental.** The title compound is a hydrolysis product (Vollano, Day & Holmes, 1984) of  $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$  which was obtained as colourless crystals from a reaction between  $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$  (Aldrich) and the sodium salt of pipercolic acid (Sigma) performed in dimethylformamide solution. Enraf-Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo  $K\alpha$  radiation;  $\omega:2\theta$  scan technique. Cell parameters by least squares on 25 reflections ( $3 \leq \theta \leq 9^\circ$ ) (de Boer & Duisenberg, 1984) on a spherical crystal of 0.30 mm diameter, no absorption correction applied. There was significant decomposition of the crystal during the data collection as judged by the fall in the net intensities of two reference reflections ( $\bar{2}34$  and  $0\bar{4}0$ ) measured every 7200 s. The data collection was stopped when the average intensity

values were 80% of the initial values. This gave a total of 4084 reflections ( $1.5 \leq \theta \leq 22.5^\circ$ ) measured in the range  $-18 \leq h \leq 0$ ,  $-18 \leq k \leq 0$ ,  $-19 \leq l < 1$ . 3630 unique reflections ( $R_{\text{amal}} 0.052$ ) and 2245 satisfied  $I \geq 2.5\sigma(I)$ . Structure solved by Patterson method, full-matrix least-squares refinement on 309 parameters based on  $F$  (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms included at their calculated positions except for the hydroxy H atom, H(2), which was located from a difference map but not refined. At convergence,  $R =$

Table 1. Fractional atomic coordinates and  $B_{\text{eq}}$  values (Å<sup>2</sup>)

	$x$	$y$	$z$	$B_{\text{eq}}$
Sn(1)	0.04713 (2)	-0.06808 (2)	0.34159 (2)	3.97
Sn(2)	-0.06489 (2)	-0.07016 (2)	0.49161 (2)	3.48
O(1)	0.0253 (2)	-0.0180 (2)	0.4387 (2)	3.69
O(2)	0.0487 (2)	-0.1279 (2)	0.3901 (2)	4.48
Cl	0.1528 (1)	0.0272 (1)	0.3277 (1)	5.22
C(111)	-0.0200 (3)	-0.0267 (3)	0.2523 (3)	4.29
C(112)	-0.0948 (3)	-0.0498 (4)	0.2411 (4)	5.80
C(113)	-0.1373 (4)	-0.0218 (5)	0.1826 (4)	7.11
C(114)	-0.1082 (4)	0.0299 (5)	0.1369 (4)	6.82
C(115)	-0.0337 (5)	0.0540 (5)	0.1478 (4)	9.28
C(116)	0.0093 (4)	0.0273 (5)	0.2056 (3)	7.73
C(121)	0.1246 (3)	-0.1621 (4)	0.3502 (3)	5.15
C(122)	0.1094 (4)	-0.2198 (4)	0.3983 (4)	6.64
C(123)	0.1656 (6)	-0.2764 (5)	0.4123 (5)	9.41
C(124)	0.2349 (6)	-0.2737 (6)	0.3753 (7)	10.02
C(125)	0.2499 (5)	-0.2175 (6)	0.3285 (6)	10.68
C(126)	0.1960 (4)	-0.1610 (4)	0.3148 (4)	7.18
C(211)	-0.1781 (3)	-0.0290 (3)	0.4675 (3)	4.14
C(212)	-0.2262 (3)	-0.0701 (4)	0.4230 (4)	6.24
C(213)	-0.3016 (4)	-0.0450 (5)	0.4093 (4)	7.94
C(214)	-0.3286 (4)	0.0186 (5)	0.4415 (4)	7.64
C(215)	-0.2814 (4)	0.0618 (4)	0.4850 (4)	7.29
C(216)	-0.2057 (3)	0.0375 (4)	0.4989 (3)	5.52
C(221)	-0.0387 (3)	-0.1654 (3)	0.5573 (3)	4.41
C(222)	-0.0067 (4)	-0.1577 (4)	0.6259 (4)	6.01
C(223)	0.0080 (5)	-0.2209 (5)	0.6690 (4)	8.08
C(224)	-0.0076 (5)	-0.2926 (5)	0.6449 (6)	9.37
C(225)	-0.0391 (5)	-0.3014 (5)	0.5760 (6)	9.88
C(226)	-0.0564 (4)	-0.2385 (4)	0.5333 (4)	6.58
O(F1)	-0.1347 (3)	-0.2534 (3)	0.3559 (3)	9.98
N(F1)	-0.2464 (3)	-0.3173 (3)	0.3398 (3)	6.14
C(F1)	-0.1735 (4)	-0.3021 (4)	0.3260 (4)	6.59
C(F2)	-0.2892 (4)	-0.3764 (4)	0.3005 (4)	6.94
C(F3)	-0.2901 (5)	-0.2718 (4)	0.3921 (5)	9.85