

Aquatrimethyl(tricyanomethanido)tin(IV), $[\text{Sn}(\text{CH}_3)_3(\text{C}_4\text{N}_3)(\text{H}_2\text{O})]$

BY DOYLE BRITTON AND YEH MEI CHOW

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

(Received 20 April 1983; accepted 27 July 1983)

Abstract. $M_r = 271.88$, orthorhombic, $P2_12_12_1$, $a = 10.748$ (5), $b = 15.480$ (8), $c = 6.814$ (4) Å, $V = 1134$ (2) Å³, $Z = 4$, $D_m = 1.580$, $D_x = 1.593$ (3) g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 22.3$ cm⁻¹, $T = 295$ (2) K, $F(000) = 528$, $R = 0.045$, 908 observed reflections. The Sn atoms have approximate trigonal-bipyramidal coordination with three methyl groups on the equator and an N atom from the $\text{C}(\text{CN})_3$ and the O atom from the water molecule at the poles. The two N atoms not bonded to Sn are hydrogen bonded to the water molecule.

Introduction. This work is part of a series of studies on the Sn coordination in di- and trimethyltin compounds (Hall & Britton, 1972; Konnert, Britton & Chow, 1972). See also Britton & Dunitz (1981) for a systematic discussion of the question.

Experimental. The title compound was prepared by the reaction of equimolar amounts of trimethyltin chloride and potassium tricyanomethanide in water followed by extraction with ether, and evaporation of the ether solution to provide suitable crystals. Density measured by flotation in a $\text{CH}_3\text{I}-\text{CCl}_4$ mixture. Crystal $0.04 \times 0.11 \times 0.40$ mm, sealed in a glass capillary for data collection. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. 24 reflections with $11^\circ < \theta < 16^\circ$ used to determine the cell parameters. Systematic extinctions ($h00$, h odd; $0k0$, k odd; $00l$, l odd) uniquely defined the space group. No absorption corrections; ψ scans about the needle axis showed a maximum variation of 11% in transmission coefficients. Data collected in the range $0^\circ < \theta < 25^\circ$ for one octant only; 1259 unique reflections, of which 908 with $I > \sigma(I)$ were used in the subsequent calculations. Three check reflections measured every 5000 s of exposure time showed no significant change with time. Structure solved from Patterson and Fourier syntheses and refined using full-matrix least-squares refinement on F^2 s. H atoms could not be located; six half-hydrogen atoms were included for each methyl group at idealized positions with fixed isotropic thermal parameters. All the remaining atoms were refined with anisotropic thermal parameters. Refinement converged with $wR = 0.043$ and $S = 1.033$; $w = 1/\sigma^2(F)$ was calculated

from $\sigma^2(I) = \sigma^2(I_c) + (0.05I)^2$, where $\sigma(I_c)$ is the standard deviation in I based on counting statistics alone. There was no significant difference between the structure reported and its enantiomer. $(\Delta/\sigma)_{\text{max}}$ in final cycle of refinement was 0.04. The extreme variation from zero on the final difference Fourier synthesis was 0.26 e \AA^{-3} . Atomic scattering factors and anomalous dispersion corrections for all atoms from *International Tables for X-ray Crystallography* (1974). All computer programs taken from the Enraf–Nonius *Structure Determination Package* and have been described by Frenz (1978).

Table 1. Atomic coordinates ($\times 10^4$), e.s.d.'s and equivalent isotropic thermal parameters

	$B = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.			
	x	y	z	$B(\text{\AA}^2)$
Sn	966 (1)	1604 (1)	1453 (1)	4.24
O	2878 (7)	2101 (5)	2326 (18)	8.5
C(1)	-3096 (9)	282 (6)	1153 (18)	4.1
C(2)	-1989 (10)	714 (7)	947 (18)	4.5
N(2)	-1045 (9)	1069 (6)	751 (15)	5.4
C(3)	-4172 (10)	721 (7)	1743 (18)	4.8
N(3)	-5066 (10)	1064 (7)	2195 (23)	7.8
C(4)	-3132 (9)	-633 (7)	962 (16)	3.9
N(4)	-3108 (9)	-1366 (6)	772 (17)	5.7
C(5)	1413 (12)	1674 (10)	-1543 (22)	7.2
C(6)	154 (11)	2681 (8)	2831 (22)	5.9
C(7)	1338 (12)	427 (9)	2885 (25)	7.2

Table 2. Bond distances (Å) and angles ($^\circ$)

Sn–C(5)	2.100 (16)	C(1)–C(2)	1.371 (17)
Sn–C(6)	2.103 (14)	C(1)–C(3)	1.401 (17)
Sn–C(7)	2.104 (15)	C(1)–C(4)	1.423 (16)
Sn–N(2)	2.363 (11)	C(2)–N(2)	1.162 (16)
Sn–O	2.274 (9)	C(3)–N(3)	1.140 (16)
O...N(3)	2.733 (15)	C(4)–N(4)	1.142 (14)
O...N(4)	2.715 (13)		
C(6)–Sn–C(7)	123.9 (7)	C(3)–C(1)–C(4)	119.1 (10)
C(7)–Sn–C(5)	116.9 (6)	C(4)–C(1)–C(2)	119.9 (11)
C(5)–Sn–C(6)	119.2 (6)	C(2)–C(1)–C(3)	120.6 (11)
N(2)–Sn–O	176.5 (6)	C(1)–C(2)–N(2)	178.9 (15)
N(2)–Sn–C(5)	91.8 (6)	C(1)–C(3)–N(3)	178.2 (14)
N(2)–Sn–C(6)	89.3 (5)	C(1)–C(4)–N(4)	176.9 (13)
N(2)–Sn–C(7)	88.0 (6)	Sn–O...N(3)	121.5 (4)
O–Sn–C(5)	91.7 (5)	Sn–O...N(4)	120.2 (4)
O–Sn–C(6)	89.4 (5)	N(3)...O...N(4)	117.1 (5)
O–Sn–C(7)	90.0 (5)	C(3)–N(3)...O	164.5 (8)
Sn–N(2)–C(2)	160.2 (8)	C(4)–N(4)...O	144.7 (7)

Discussion. The final positional parameters and the equivalent isotropic thermal parameters are given in Table 1.* The atom labelling and the anisotropic thermal ellipsoids are shown in Fig. 1. Bond distances and angles are given in Table 2; they are generally normal. The geometry in SnR_3XY environments has been discussed at length by Britton & Dunitz (1981). The Sn—C distances of 2.10 (2) Å found here are at the low end of the range, 2.14 (4) Å, found in their survey of 36 such compounds. The Sn—N(2) and Sn—O distances are 0.38 and 0.37 Å longer, respectively, than the usual single-bond distances. This agrees well with the 0.36 Å longer distance expected in each bond if the $\text{Sn}(\text{CH}_3)_3$ group is planar, which this one is. The geometry of the $\text{C}(\text{CN})_3$ group is normal. No H atoms could be found in the difference electron density maps, but the $\text{O}\cdots\text{N}(3)$ and $\text{O}\cdots\text{N}(4)$ distances of 2.73 (1) and 2.72 (1) Å, respectively, are consistent with the interpretation that these correspond to O—H \cdots N hydrogen bonds.

* Tables of anisotropic thermal parameters, H-atom positions, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38771 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

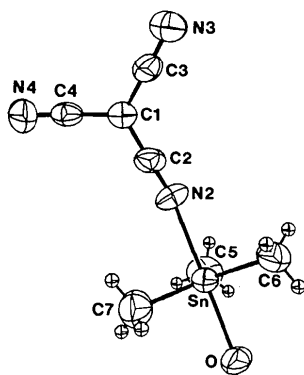


Fig. 1. The atoms are shown in approximately the same orientation as those in the middle of Fig. 2. Two sets of three half-hydrogen atoms are arbitrarily placed at tetrahedral positions on each methyl C atom; one such set is shown in each case. Thermal ellipsoids are shown at the 50% probability level except for the H atoms, which are shown with arbitrary radii. The H atoms in the H_2O are not shown.

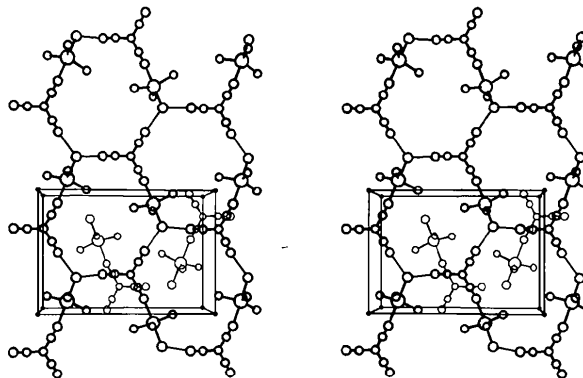


Fig. 2. The packing of the title compound. The unit-cell origin is the lower, left, forward corner with **a** pointing up, **b** to the right, and **c** to the rear. The O—H \cdots N hydrogen bonds are shown as lighter lines.

The packing is shown in Fig. 2. It has a pleasing efficiency. The hexagonal networks that occur parallel to (001) allow all of the N atoms in the $\text{C}(\text{CN})_3^-$ ion to be involved in bonding. The large holes in the hexagonal network are filled by the methyl groups, with two methyl groups from Sn atoms in the same network and one from an Sn atom in the network above or below. The hexagonal network is similar to those found in $\text{AgC}(\text{CN})_3$ (Konnert & Britton, 1966), where the hexagonal holes are filled by the interweaving of the networks, and in $\text{KCu}(\text{CN})_3 \cdot \text{H}_2\text{O}$ (Cromer & Larson, 1962), where the holes are filled by K and H_2O .

This work was begun with the support of the National Science Foundation and the Petroleum Research Fund of the American Chemical Society. We thank them both for their help.

References

- BRITTON, D. & DUNITZ, J. D. (1981). *J. Am. Chem. Soc.* **103**, 2971–2979.
 CROMER, D. T. & LARSON, A. C. (1962). *Acta Cryst.* **15**, 397–403.
 FRENZ, B. A. (1978). In *Computing in Crystallography*, edited by H. SCHENK *et al.*, pp. 64–71. Delft Univ. Press.
 HALL, J. B. & BRITTON, D. (1972). *Acta Cryst.* **B28**, 2133–2136.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KONNERT, J. & BRITTON, D. (1966). *Inorg. Chem.* **5**, 1193–1196.
 KONNERT, J., BRITTON, D. & CHOW, Y. M. (1972). *Acta Cryst.* **B28**, 180–187.