Synthesis and Crystal Structure of a Dimethyltin Derivative of 1,4-Dithioerythritol

ChunLin MA,^{*†} Zhifo GUO,^{**} and Rufen ZHANG^{**}

^{*}Department of Materials Science and Chemical Engineering, Chemistry, Taishan University, Taian, 271021, P. R. China

^{**}Department of Chemistry Liaocheng University, Liaocheng 252059, P. R. China.

The title complex, $[(\text{CH}_3)_2(\text{HOC}_2\text{H}_5)\text{Sn}(\text{C}_4\text{H}_6\text{O}_2\text{S}_2)\text{Sn}(\text{HOC}_2\text{H}_5)(\text{CH}_3)_2]$, was synthesized starting from dimethyltin dichloride, 1,4-dithioerythritol and sodium ethoxide. The crystal structure was determined by single-crystal X-ray diffraction. It crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 7.9282(6)\text{\AA}$, $b = 11.3888(9)\text{\AA}$, $c = 11.0228(9)\text{\AA}$, $\beta = 99.594(3)^\circ$, $Z = 2$, $V = 981.36(13)\text{\AA}^3$. Its crystal structure was determined and refined to a final $R = 0.0232$ for 1730 independent reflections. The complex is the symmetric dinuclear unit made up of two distorted trigonal bipyramids.

(Received November 15, 2007; Accepted January 15, 2008; Published on wed February 26, 2008)

Since some organotin(IV) compounds have been found to exhibit antitumour activity *in vitro*, many varieties of organotin(IV) compounds have been synthesized and studied in the context of their antitumour potential.¹ However, 1,4-dithioerythritol is also a protective agent for preventing oxidation of thiol groups and a reagent for the reduction of disulfide groups in proteins.²⁻⁴ Our interest has been focused on studying the reaction under a mild condition and hoping to obtain a novel organotin complex with potential biological activities. In this paper, we report on the synthesis and crystal structure of a dimethyltin derivative of 1,4-dithioerythritol.

Dimethyltin dichloride and 1,4-dithioerythritol are commercially available, which were used without further

purification. Complex **1** was prepared under a nitrogen atmosphere using a standard Schlenk technique. The 1,4-dithioerythritol (0.154 g, 1 mmol) was added to a solution of ethanol (20 mL) with sodium ethoxide (0.136 g, 2 mmol); the mixture was stirred for 10 min, after which Me_2SnCl_2 (0.439 g, 2 mmol) was added, and the mixture was stirred for 12 h at 40°C . After cooling down to the room temperature, the solution was filtered. The solvent of the filtrate was gradually removed by evaporation under a vacuum until a solid product was obtained. The solid was then recrystallized from ether-petroleum, and yellow crystals were formed in 70% yield.

A weak yellow crystal of dimensions $0.35 \times 0.33 \times 0.30\text{ mm}$ was chosen for X-ray diffraction studies. The experimental conditions, crystal data and structure refinement results of complex **1** are summarized in Table 1; the atomic coordinates and temperature factors are listed in Table 2, and selected bond lengths and angles are listed in Table 3.

The chemical diagram and crystal structure of the title complex is shown in Figs. 1 and 2, respectively.

The complex is a symmetric dinuclear unit made up of two distorted coordination trigonal bipyramids. The five primary bonds to Sn are two methyl groups, one ethanol molecule, and

Table 1 Crystal and experimental data

Formula	$\text{C}_{11}\text{H}_{30}\text{O}_4\text{S}_2\text{Sn}_2$
Formula weight	527.85
Crystal system	monoclinic
Space group	$P2_1/n$
a	$7.9282(6)\text{\AA}$
b	$7.9282(6)\text{\AA}$
c	$11.0228(9)\text{\AA}$
β	$99.594(3)^\circ$
V	$981.36(13)\text{\AA}^3$
D_x	1.786 Mg/m^3
$F(0\ 0\ 0)$	520
θ range for data collection	2.59 to 25.01°
Reflections used	1730 [$R(\text{int}) = 0.0321$] $R1 = 0.0232$, $wR2 = 0.0630$
Measurement	BRUKER SMART 1000 CCD
Mo K_α	$\lambda = 0.71073\text{\AA}$
Structure determination	direct method
Refinement	Full-matrix
CCDC	655986

Table 2 Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for title the complex

Atom	x	y	z	U_{eq}
Sn(1)	2598(1)	1583(1)	1942(1)	40(1)
S(1)	3067(2)	1470(1)	-146(1)	48(1)
O(1)	1245(3)	10(2)	1566(2)	41(1)
O(2)	4107(5)	3367(3)	1900(4)	55(1)
C(1)	2318(5)	-43(4)	-365(4)	48(1)
C(2)	817(5)	-303(3)	304(4)	40(1)
C(3)	540(7)	2612(5)	2351(6)	73(2)
C(4)	4504(8)	959(5)	3376(5)	83(2)
C(5)	5772(8)	3427(5)	1594(6)	73(2)
C(6)	6098(18)	4201(10)	882(12)	123(4)

[†] To whom correspondence should be addressed.
E-mail: macl@lcu.edu.cn

Table 3 Selected bond lengths (Å) and angles (°)

Sn(1)-O(1)	2.093(3)	Sn(1)-O(2)	2.363(3)
Sn(1)-C(3)	2.118(5)	Sn(1)-S(1)	2.3950(12)
Sn(1)-C(4)	2.119(5)		
O(1)-Sn(1)-C(3)	97.38(17)	C(4)-Sn(1)-O(2)	90.12(18)
O(1)-Sn(1)-C(4)	97.99(17)	O(1)-Sn(1)-S(1)	85.45(8)
C(3)-Sn(1)-C(4)	120.4(3)	C(3)-Sn(1)-S(1)	118.88(18)
O(1)-Sn(1)-O(2)	167.59(12)	C(4)-Sn(1)-S(1)	119.5(2)
C(3)-Sn(1)-O(2)	86.47(17)	O(2)-Sn(1)-S(1)	82.37(10)

Fig. 1 Structural chemical diagram.

Fig. 2 Molecular structure.

one oxygen atom and one sulfur atom. The coordination mode, bond lengths and bond angles of the two Sn atoms are completely same. Taking (Sn(1)) for example, the trigonal equatorial plane is occupied by the sulfur S(1) atom and two carbon atoms, C(3) and C(4), whereas the axial positions were located by two oxygen atoms with an axial-Sn-axial angle of O(1)-Sn(1)-O(2) 167.59°. The sum of the equatorial angles around the Sn(1) atom (C(3)-Sn(1)-S(1), C(4)-Sn(1)-S(1) and C(3)-Sn(1)-C(4)) is 358.78°. In this way the ligand behaves as a

Fig. 3 Two-dimensional network connected by O-H...O hydrogen bonds, hydrogen atoms, carbon atoms of the ethanol group; the Sn-methyl groups have been omitted for clarity.

bidentate species and chelates the tin atom by means of the oxygen and the sulfur. The consequence is the formation of a five-member ring with an S-Sn-O bite angle of 82.37(10)°.

The bond lengths around Sn(1) are close to those found in [Me₂Sn(*o*-SC₆H₄CO₂)]₆(H₂O).⁵ What is more, the discrete molecules are connected through an O-H...O hydrogen bond into a two-dimensional network (see Fig. 3).

Acknowledgements

The authors thank the National Natural Science Foundation of China (20271025) for financial support.

References

1. M. Gielen, *Appl. Organomet. Chem.*, **2002**, *16*, 481.
2. W. L. Zahler and W. W. Cleland, *J. Biol. Chem.*, **1968**, *243*, 716.
3. Y. Burstein and A. Patchornik, *Biochemistry*, **1972**, *11*, 2939.
4. W. W. Cleland, *Biochemistry*, **1963**, *3*, 480.
5. C. L. Ma, Q. F. Zhang, R. F. Zhang, and D. Q. Wang, *Chem. Eur. J.*, **2006**, *12*, 420.