Journal of Organometallic Chemistry, 471 (1994) 69–70

A reinvestigation of the crystal structure of the organotin complex formed in the reaction of butyltin trichloride with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-propan-2-one

Wei Chen

Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)

Abstract

In contrast to a previous report, butyltin trichloride reacts with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-propan-2-one to yield a hydroxyl-bridged aquobutyldichlorotin hydroxide dimer that is hydrogen bonded to four 2-methylbenzothiazole molecules.

Key words: Crystal structure; Tin; Hydrogen bonding

1. Introduction

Butyltin trichloride has been reported to react with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-propan-2-one to yield a complex formulated as $\{[C_6H_4SNHC(CH_3)]_2^+ \ [(C_4H_9)Cl_3SnOH]_2^-\} \cdot 2[C_6H_4SNC(CH_3)]$. Crystal structure analysis of the complex confirmed the presence of the hydroxyl bridge, and the structure was claimed to be the first example of involvement of a tin–chlorine bond in hydrogen bonding interaction [1]. The analysis did not however explain the suspiciously short (2.229(6) Å) tin–chlorine bond distance and the large temperature factor (0.152(3) Å^2) for the chlorine atom, which prompted the present reinvestigation.

2. Experimental details

Intensities of 3441 reflections were measured on an Enraf-Nonius CAD4 diffractometer (Mo Kα, 0.71073 Å) up to $2\theta_{max} = 50°$ (collection range: $0 \le h \le 10$, $-12 \le k \le 12$, $-12 \le l \le 13$). The structure was solved by the heavy atom method, and a θ-dependent absorption correction was applied [2] following isotropic refinement. Full-matrix least-squares refinements on F for 354 variables utilized anisotropic temperature factors for the non-H atoms; all H-atoms except the hydroxyl hydrogen and one hydrogen of the water were located and refined isotropically; 2813 of the 3206 independent reflections satisfying $I \ge 3\sigma(I)$ were used. The refinements converged to $R = 0.024$; $R_w = 0.029$ ($w = [\sigma(F)^2$

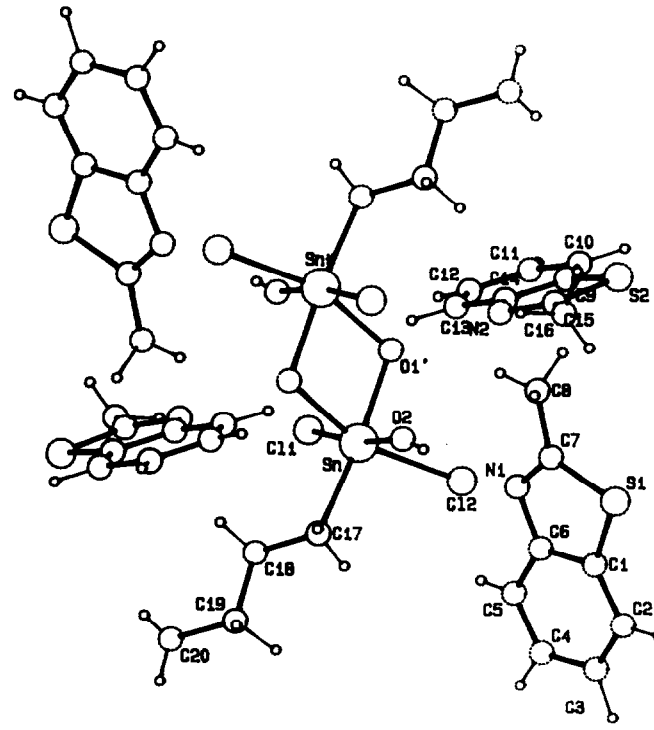

Fig. 1. Atomic labelling for $[(C_4H_9)Cl_2SnOH \cdot H_2O]_2 \cdot 4[C_6H_4SNC(CH_3)]$. Selected distances and angles: Sn–C11 2.485(1), Sn–C12, 2.427(1), Sn–O1 2.122(3), Sn–O2 2.216(4), Sn–O1′ 2.038(3), Sn–C17 2.132(5) Å; C11–Sn–C12 94.24(4), C11–Sn–O1 91.87(8), C11–Sn–O1′ 88.83(8), C11–Sn–O2 171.8(1), C11–Sn–C17 99.0(2), C12–Sn–O1 159.82(8), C12–Sn–O1′ 90.18(8), C12–Sn–O2 89.3(1), C12–Sn–C17 98.6(2), O1–Sn–O1′ 70.7(1), O1–Sn–O2 82.4(1), O1–Sn–C17 99.4(2), O1′–Sn–O2 83.8(1), O1′–Sn–C17 167.7(2), O2–Sn–C17 87.7(2)°.

0022-328X/94/$7.00
SSDI 0022-328X(93)24244-Y

TABLE 1. Atomic coordinates and temperature factors ($\times 10^2$ Å^2)

	x	y	z	B_{eq} (Å^2)
Sn	−0.01998(3)	−0.14314(2)	0.51956(2)	2.543(6)
Cl1	−0.2920(1)	−0.07822(9)	0.5434(1)	4.11(3)
Cl2	−0.0090(1)	−0.2159(1)	0.36078(9)	4.44(3)
S1	0.6762(1)	−0.3584(1)	0.2444(1)	3.92(3)
S2	0.0533(1)	0.1597(1)	−0.06881(9)	4.35(3)
O1	0.0024(3)	−0.0297(2)	0.6057(2)	2.76(6)
O2	0.2238(3)	−0.1726(3)	0.4897(3)	3.88(8)
N1	0.4265(4)	−0.2927(3)	0.3591(3)	3.40(8)
N2	−0.0204(4)	0.1042(3)	0.1596(3)	3.41(8)
C1	0.5536(4)	−0.4606(4)	0.3035(3)	3.2(1)
C2	−0.5696(5)	−0.4236(4)	0.6997(4)	4.0(1)
C3	−0.4577(5)	−0.3586(4)	0.6413(4)	4.5(1)
C4	−0.3301(5)	−0.4081(4)	0.5807(4)	4.5(1)
C5	−0.3129(5)	−0.5228(4)	0.5784(4)	3.8(1)
C6	0.4258(4)	−0.4095(4)	0.3631(3)	2.96(9)
C7	0.5486(5)	−0.2555(4)	0.3012(4)	3.4(1)
C8	0.5843(5)	−0.1354(4)	0.2838(5)	5.1(1)
C9	−0.1327(5)	0.1846(4)	−0.0133(3)	3.5(1)
C10	−0.2526(5)	0.2317(5)	−0.0751(4)	4.8(1)
C11	−0.3898(6)	0.2406(5)	−0.0085(5)	5.6(1)
C12	−0.4089(6)	0.2034(5)	0.1148(5)	5.3(1)
C13	−0.2906(5)	0.1567(4)	0.1767(4)	4.2(1)
C14	−0.1512(5)	0.1477(3)	0.1121(3)	3.04(9)
C15	0.0937(5)	0.1046(4)	0.0768(4)	3.7(1)
C16	0.2479(6)	0.0614(5)	0.1013(5)	5.8(1)
C17	−0.0047(6)	−0.3171(4)	0.6670(5)	4.9(1)
C18	−0.1250(6)	−0.3358(4)	0.7719(4)	4.6(1)
C19	−0.1179(8)	−0.4656(5)	0.8622(5)	7.0(2)
C20	−0.2398(9)	−0.4819(6)	0.9682(6)	8.5(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = \frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

$+ (0.02F)^2 + 1]^{-1}$ [3]). The final difference map was diffuse with peaks in the −0.130 to +0.507 e Å^{-3}. All computations were performed with the MolEN package on a DEC MicroVAX minicomputer [4]. Atomic coordinates are listed in Table 1 and the atomic labelling scheme is shown in Fig. 1.

Crystal data: $C_{40}H_{52}Cl_4N_4O_4S_4Sn_2$, FW 1160.34, triclinic, $P\bar{1}$ (No. 2); a 9.5137(7), b 12.0629(8), c 12.3300(8) Å; α 65.582(5)°, β 76.153(5)°; γ 74.990(6)°; V 1230.3(2) Å^3; $F(000)$ 584; D_{calc} 1.566 g cm^{-3}; μ 14.42 cm^{-1} for $Z = 1$. Complete lists of bond angles and lengths and a table of hydrogen atom coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

The crystal structure of the complex formed from the reaction between butyltin trichloride and 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-propan-2-one reveals it to be a centrosymmetric hydroxyl-bridged aquobutyldichlorotin hydroxide dimer that is linked to four 2-methylbenzothiazole molecules by short hydrogen bonds, as indicated by the formulation $[(C_4H_9)Cl_2SnOH \cdot H_2O]_2 \cdot 4[C_6H_4SNC(CH_3)]$.

This formulation differs from that reported previously, *viz.* $\{[C_6H_4SNHC(CH_3)]_2^+[(C_4H_9)Cl_3SnOH]_2^-\} \cdot 2[C_6H_4SNC(CH_3)]$, in that the dinuclear species bears no charges as the butyltin unit is covalently bonded to two chlorine atoms and one hydroxyl group. The water molecule which forms a short coordinative bond (Sn ← O2 2.216(4) Å) to tin is hydrogen bonded to one of the two independent 3-methylbenzothiazole molecules (O ··· N 2.721(5) Å); the hydroxyl oxygen atom forms a somewhat shorter H-bond (O ··· N 2.687(4) Å) with the other independent 3-methylbenzothiazole molecule.

Acknowledgment

I thank Prof. S.-B. Teoh of Universiti Sains Malaysia for supplying the crystals.

References

1 S.-B. Teo, S.-G. Teoh, R.C. Okechukwu and H.-K. Fun, *J. Organomet. Chem., 454* (1993) 67.
2 N. Walker and D. Stuart, *Acta Crystallogr. A, 39* (1983) 158.
3 R.C.G. Killean and J.L. Lawrence, *Acta Crystallogr. B, 25* (1969) 1750.
4 Delft Instruments, MolEN structure determination system, Delft Instruments X-ray Diffraction B.V., 2624 AL Delft, The Netherlands, 1990.