

# 1:1 Adducts of Dimethyltin(IV) Dichloride forming Six-co-ordinated Solids

Seik-Weng Ng and J. J. Zuckerman\*

Department of Chemistry, University of Oklahoma, Norman, OK 73019, U.S.A.

The crystal structures of the 1:1 adducts of dimethyltin(IV) dichloride with diphenylcyclopropanone and with 2,6-dimethylpyridine (2,6-lutidine) *N*-oxide reveal dimer formation through bridging chlorine atoms to create six-co-ordination at tin, and the structure of the 1:1 salicylaldehyde adduct is reinterpreted in similar terms as an associated solid with bridging phenolic oxygen atoms; Mössbauer quadrupole splitting data, where available, corroborate the suggestion of six-co-ordination for the known 1:1 complexes.

It is a curious fact that with certain pointed ligands in which the donor atom carries only a single attachment, *i.e.*, is unbranched, dimethyltin(IV) dichloride forms 1:1 adducts. These less sterically-demanding ligands should proceed to the ubiquitous 1:2 complexes<sup>1</sup> without difficulty, but syntheses involving some thirty  $>C=O$ ,<sup>2-7</sup>  $>C=S$ ,<sup>8</sup>  $>S=O$ ,<sup>8,9</sup>  $\geq N \rightarrow O$ ,<sup>9,10</sup> or  $\geq P=O$ <sup>11</sup> systems† stop at the intermediate, 1:1 stage.‡ Occasionally, both 1:1 and 1:2 complexes which utilize the same ligand can be isolated.<sup>3,4,8,9,12,15</sup> The products have been universally formulated with five-co-ordinate, trigonal bipyramidal geometries at the tin atom.

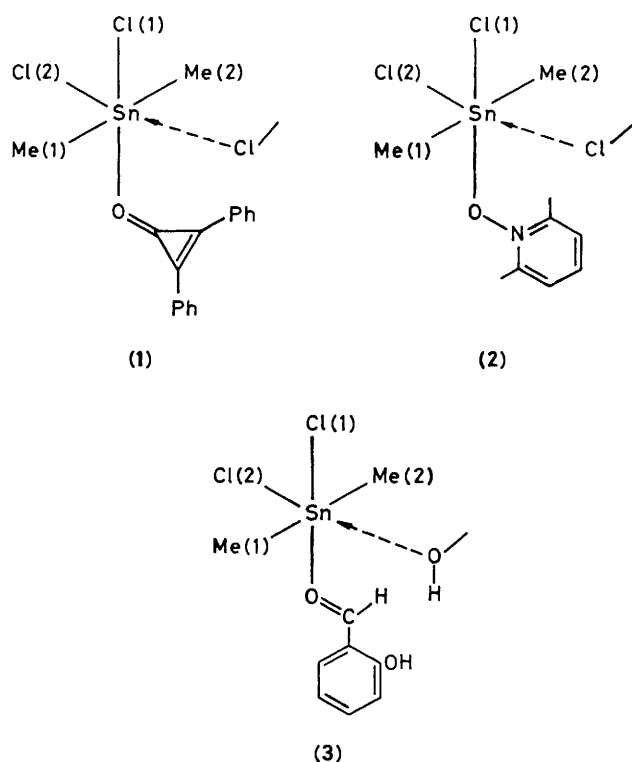


Figure 1. The geometry at the tin atom in the 1:1 dimethyltin(IV) dichloride adducts of diphenylcyclopropanone (1), 2,6-dimethylpyridine (2,6-lutidine) *N*-oxide (2), and salicylaldehyde (3).<sup>16,17</sup>

† In the 1:1 *N,N*-dimethylthionicotinamide complexes with dimethyltin(IV) dichloride the co-ordination, from i.r. evidence, is through the nitrogen atom on the pyridine ring,<sup>9</sup> and a 1:1 complex of 3,5-dimethylpyrazole is also known.<sup>12</sup> A 1:1 complex with dimethyl selenoxide could not be isolated,<sup>13</sup> and another with *N,N*-dimethylaminonitrosobenzene has been claimed, but its characterization was not described.<sup>3</sup>

‡ Arsine oxides<sup>14</sup> also yield 1:1 complexes with other dialkyl- and diphenyl-tin(IV) dichlorides.

We have solved the crystal structures of two such 1:1 adducts; the dimethyltin(IV) dichloride complexes of diphenylcyclopropanone (1)<sup>9,7</sup> and 2,6-dimethylpyridine (2,6-lutidine) *N*-oxide (2), and we have reinterpreted the reported structural data for the unchelated 1:1 complex with salicylaldehyde (3).<sup>16,17</sup> Our results reveal bridging by chlorine atoms of adjacent molecules in the first two adducts to form dimers and by the otherwise unco-ordinated phenolic oxygen atom in the last-named complex to form an associated solid containing six-co-ordinate tin atoms in severely distorted octahedral geometries, as shown in Figure 1.

Dimethyltin(IV) dichloride-diphenylcyclopropanone, (1),  $C_{34}H_{32}Cl_4O_2Sn_2$ , forms colourless crystals, m.p. 111 °C, in the monoclinic space group *C2/c* with  $a = 17.049(16)$ ,  $b = 10.027(10)$ ,  $c = 19.834(16)$  Å, and  $\beta = 96.00(6)^\circ$ ,  $V = 3372$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.678$  g cm<sup>-3</sup>. The structure was determined by the heavy atom method from 4890 reflections measured at  $138 \pm 2$  K on an Enraf-Nonius CAD/4 automatic diffractometer using zirconium-filtered, monochromatic Mo- $K_\alpha$  radiation to a final *R* value of 0.0296 for the 4251 reflections included in the least-squares sums.<sup>18</sup>

Dimethyltin(IV) dichloride-2,6-dimethylpyridine *N*-oxide, (2),  $C_{18}H_{30}Cl_4N_2O_2Sn_2$ , forms colourless crystals, m.p. 147 °C, in the monoclinic space group *C2/c* with  $a = 15.581(4)$ ,  $b = 12.781(4)$ ,  $c = 13.098(4)$  Å, and  $\beta = 102.26(3)^\circ$ ,  $V = 2549$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.787$  g cm<sup>-3</sup>. The structure was determined by direct methods from 1880 reflections measured at  $138 \pm 2$  K using zirconium-filtered, monochromatic Mo- $K_\alpha$  radiation to a final *R* value of 0.0364 for the 1880 reflections included in the least-squares sums.‡

Relevant structural data for the three 1:1 complexes are listed in Tables 1 and 2. The bridging contacts are almost 1 Å longer than the terminal Sn-Cl bonds within the same structure, and hence the association is weak, giving rise to highly asymmetric Sn-Cl  $\rightarrow$  Sn bridges and large departures from  $\langle C-Sn-C \rangle$  linearity.

Table 1. Bond lengths (Å) with standard deviations in parenthesis for the dimethyltin(IV) dichloride adducts (1), (2), and (3).

	(1)	(2)	(3) <sup>a</sup>
Sn-C(1)	2.116(3)	2.110(4)	2.098(17)
Sn-C(2)	2.111(3)	2.112(4)	2.107(17)
Sn-Cl(1)	2.4745(7) <sup>b</sup>	2.528(1) <sup>b</sup>	2.403(6)
Sn-Cl(2)	2.3713(6)	2.400(1)	2.347(5)
Sn-O	2.380(2)	2.289(3)	2.680(12)
Sn-X <sup>c</sup>	3.5607(7)	3.399(1)	3.366(11)

<sup>a</sup> Refs. 16 and 17. <sup>b</sup> This chlorine atom bridges. <sup>c</sup> X=Bridging atom.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

**Table 2.** Bond angles ( $^{\circ}$ ) with standard deviations in parentheses for the dimethyltin(IV) dichloride adducts (1), (2), and (3).

	(1)	(2)	(3) <sup>a</sup>
C(1)-Sn-C(2)	142.2(1)	145.3(2)	131.4(7)
C(1)-Sn-Cl(1)	99.81(8)	93.7(1)	101.8(5)
C(1)-Sn-Cl(2)	104.43(8)	110.7(1)	110.8(5)
C(1)-Sn-O	84.82(9)	87.4(1)	81.2(6)
C(1)-Sn-X <sup>b</sup>	69.45(7)	72.3(1)	76.7(6)
C(2)-Sn-Cl(1)	93.16(6)	95.1(1)	101.2(5)
C(2)-Sn-Cl(2)	110.46(8)	102.9(1)	109.1(5)
C(2)-Sn-O	86.75(9)	85.3(2)	79.6(5)
C(2)-Sn-X	79.25(8)	76.4(1)	73.1(5)
Cl(1)-Sn-Cl(2)	91.94(2)	89.50(3)	94.9(2)
Cl(1)-Sn-O	172.32(5)	177.44(7)	174.6(3)
Cl(1)-Sn-X	77.26(2)	79.46(3)	68.4(2)
Cl(2)-Sn-O	80.92(5)	87.95(7)	79.9(3)
Cl(2)-Sn-X	166.10(2)	168.79(3)	163.1(2)
O-Sn-X	110.23(5)	103.09(7)	116.7(3)

<sup>a</sup> Refs. 16 and 17. <sup>b</sup> X=Bridging atom.

The <sup>119</sup>Sn Mössbauer quadrupole splittings (Q.S.) for (1), (2), and (3) are 3.52,<sup>7</sup> 3.80, and 3.33<sup>16</sup> mm s<sup>-1</sup>, respectively. In general Q.S. values for diorganotin(IV) derivatives increase with carbon-tin-carbon angle opening, and for octahedral geometries<sup>19</sup> were used to predict the angles formed by the dimethyltin groups in the above three complexes as 143.1, 153.5, and 137.2 $^{\circ}$ , respectively, vs. the angles 142.2, 145.3, and 131.4 $^{\circ}$ <sup>17</sup> actually found. Thus the higher Q.S. values and larger bond angles corroborate the higher co-ordination numbers in these solids. In the 1:2 complex with pyridine *N*-oxide which exhibits a Q.S. of 4.02 mm s<sup>-1</sup>,<sup>9</sup> the tin atom is located on a crystallographic centre of symmetry to give a perfect *trans*, *trans*, *trans*-octahedral geometry with the carbon-tin-carbon system linear.<sup>20</sup>

High Q.S. values have been measured for the other 1:1 adducts of dimethyltin(IV) dichloride,<sup>9,11</sup> suggesting that all are six-co-ordinate, presumably through chlorine bridging. The dimerization or oligomerization would be most likely where the non-sterically demanding, pointed ligands are involved.

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