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SYNTHESIS AND THE MOLECULAR STRUCTURE OF ACETATOTRICHLORO(TRIPHENYLPHOSPHINE OXIDE)TIN(IV)

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Acetatotrichloro(triphenylphosphine oxide)tin(IV) was synthesized by the reaction of stannic chloride, acetic acid and triphenylphosphine oxide or by the reaction of dichlorotin(IV) diacetate with tetrachlorobis(triphenylphosphine oxide)tin(IV). The structure of the complex was determined by the X-ray method. The molecule is monomeric and tin atom is six-coordinated.

The substitution reactions of stannic chloride with carboxylic acids or their salts have been described to give always dicarboxylates independent of the proportion of the reagent used,[1,2] except the reaction with silver trifluoroacetate resulting in a formation of di- or tetra-carboxylates.[1a] The presence of monocarboxylates has been suggested only as intermediates for dicarboxylates which are kinetically most stable.[1] Redistribution reactions between stannic chlorides and tin(IV) carboxylates[3] or butyl acetate[4] have been also described to give either di- or tetra-carboxylates.

This paper describes the synthesis of acetatotrichloro(triphenylphosphine oxide)tin(IV) (**1**) and its molecular structure determined by single-crystal X-ray analysis.

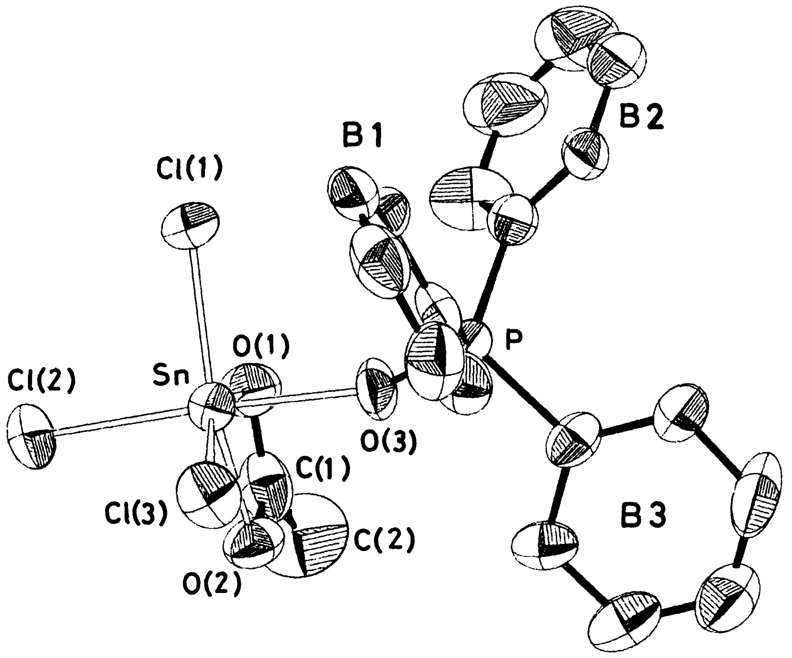
The complex (**1**) was synthesized by the reaction of stannic chloride, acetic acid and triphenylphosphine oxide. The reaction was carried out by heating a solution of the reagents in a molar ratio of 1:1:1 in benzene for 13 h, during which dry nitrogen gas was passed through a capillary in the solution, in order to remove hydrogen chloride. Ninety six percent amount of hydrogen chloride based on acetic acid was trapped from the exhaustive gas and the complex crystallized out in 83% yield from the solution when it was left at room temperature. Colorless needles (from benzene),[5)] mp 184.5-186.5°C. IR(KBr): 1592(w), 1507(m, sh), 1484(s), 1439(s), 1127(s, doublet), 1076(s, doublet), 348(m) and 329(m) cm^{-1}.

The complex (**1**) could be alternatively synthesized in a quantitative yield by a treatment of dichlorotin(IV) diacetate[6)] with tetrachlorobis(triphenylphosphine oxide)tin(IV) (**2**) in a molar ratio of 1:1 in refluxing ethylene dichloride for 0.5 h.

The medium intensity band at 1507 cm^{-1} in the IR spectrum of **1** was assigned to the stretching band of COO group by a comparison of the spectrum of **1** and that of **2**. No band assignable to C=O stretching was observed in 1500-1700 cm^{-1} spectral region except the band at 1507 cm^{-1}. The appearance of the COO stretching band of **1** in the extraordinary lower spectral region than in other tin carboxylates[1,7)] suggests an equivalency of the two C-O bonds which may be brought by the chelation of the acetate group onto tin atom.

The complex (**1**) was analyzed by the X-ray crystallographical method and the molecular structure illustrated in Fig. 1 was obtained. The crystal data are as follows: $C_{20}H_{18}Cl_3O_3PSn$, M=562.3, orthorhombic, space group Pbca, *a*=17.524(3), *b*=18.797(3), *c*=14.294(7) Å, V=4708.4 $Å^3$, Z=8, Dcal=1.564 g cm^{-3}. Reflections were measured on a Rigaku four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The structure was determined by the heavy-atom method and the refinement of the structure was performed by the block-diagonal least-square method with 1400 independent reflections. The final refinement carried out with anisotropic thermal parameter for all atoms brought the R-index to 0.045.

The complex (**1**) is monomeric.[8)] The acetate group acts as bidentate forming a four-membered chelate ring, and the tin atom is six-coordinated by acetate group, triphenylphosphine oxide and three chlorine atoms.[9)] The bond lengths and angles are shown in Fig. 1. The angles of Sn-O(1)-C(1) and Sn-O(2)-C(1) are nearly equal and the bond lengths of C(1)-O(1) and C(1)-O(2) are essentially identical, showing that the acetate group in **1** is highly symmetric. The tin atom deviates toward the atom Cl(2) out of the mean plane of atoms Cl(1), Cl(3), O(2) and O(1). The bond length of Sn-Cl(2) is somewhat longer than Sn-Cl(1) and Sn-Cl(3). These facts may indicate that the atom Cl(2) is more susceptible to further substitution than the



Bond lengths [l/Å]	
Sn-Cl(1)	2.326(5)
Sn-Cl(2)	2.365(5)
Sn-Cl(3)	2.327(5)
Sn-O(1)	2.143(10)
Sn-O(2)	2.152(10)
Sn-O(3)	2.087(10)
C(1)-O(1)	1.252(19)
C(1)-O(2)	1.258(19)
C(1)-C(2)	1.466(28)
O(3)-P	1.494(11)
P-C(B1)	1.781(14)
P-C(B2)	1.809(17)
P-C(B3)	1.798(15)

Bond angles [φ/°]

Cl(1)-Sn-Cl(2)	94.7(2)	Cl(3)-Sn-O(3)	89.0(3)	Sn-O(1)-C(1)	93.1(9)
Cl(2)-Sn-Cl(3)	95.9(2)	O(1)-Sn-O(2)	59.2(4)	Sn-O(2)-C(1)	92.5(9)
O(1)-Sn-Cl(2)	90.9(3)	O(1)-Sn-O(3)	82.1(4)	O(2)-C(1)-O(1)	115.3(14)
O(2)-Sn-Cl(2)	89.3(3)	O(1)-Sn-Cl(1)	96.0(3)	O(2)-C(1)-C(2)	122.8(15)
Cl(1)-Sn-Cl(3)	108.0(2)	Cl(1)-Sn-O(3)	89.8(3)	O(1)-C(1)-C(2)	123.6(15)
Cl(3)-Sn-O(2)	96.0(3)	O(2)-Sn-O(3)	83.9(3)	Sn-O(3)-P	148.8(6)

Fig. 1. The molecular structure of acetatotrichloro(triphenylphosphine oxide)tin(IV).

atom Cl(1) or Cl(3).

The reaction of stannic chloride, chloroacetic acid and triphenylphosphine oxide proceeded analogously to give trichloro(chloroacetato)(triphenylphosphine oxide)tin(IV) (3), colorless prisms (from benzene),12) mp 172.0-173.5°C. IR(KBr): 1590(w), 1523(m), 1488(w), 1460(m), 1439(s), 1392(w), 1260(m), 1126(s, doublet), 1075(m, doublet), 922(w), 806(m), 350(m) and 337(m) cm^{-1}. The band at 1523 cm^{-1} of 3 corresponds to the band at 1507 cm^{-1} of 1, because the COO stretching bands of acetic acid, sodium acetate and ethyl acetate shift to a spectral region higher by 20 cm^{-1} on mono-chlorination of the methyl groups.13) The molecular structure of 3 seems probably to be similar to that of 1.

References and Notes

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5) Elemental analyses, Found: C, 42.83; H, 3.25; Cl, 18.88%. Calcd for $C_{20}H_{18}Cl_3O_3PSn$: C, 42.71; H, 3.23; Cl, 18.91%.

6) This compound was prepared from stannic chloride and acetic acid (molar ratio 1:2) in benzene in a manner similar to technique used for **1**, mp 202-204°C (from benzene), Found: C, 15.45; H, 1.96; Cl, 22.76%.

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8) Cryoscopic molecular weight determination was attempted for this compound, but the value always varied. The initial value was 1.3-1.4 times greater than the formula weight and increased gradually during the determination. Analogous phenomena have been recognized for other halogenotin(IV) carboxylates and explained by an association or a decomposition.1a,2a,7c)

9) For the structure of dichlorotin(IV) diacetate, two conflicting proposals have been made independently; Polymeric structure with double carboxylate bridges1a) and monomeric structure.10,11)

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12) Elemental analyses, Found: C, 40.53; H, 2.70; Cl, 23.50%. Calcd for $C_{20}H_{17}Cl_4O_3PSn$: C, 40.25; H, 2.87; Cl, 23.76%.

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