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o-Cyclohexadiamine Complexes of some Diorganotin, Mono-organotin and Stannic Carboxylates: Synthesis and Spectral Properties*

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_o_-Cyclohexadiamine (the base component of tetraplatin) adducts of $Ph_2Sn(OCOCH_3)_2$, $nBu_2Sn(OCOH_3)_2$, $(PhCH_2)_2Sn(OCOCH_3)_2$, $PhSn(OCOCF_3)_3$, $BuSn(OCOCH_3)_3$ and $Sn(OCOCH_3)_4$ have been synthesized and characterized by elemental analysis and spectroscopy. The compounds appear to be the first such adducts in their class.

Keywords: Organotin, synthesis, Mössbauer, NMR, _O_-cyclohexadiamine, adducts

INTRODUCTION

Organotin carboxylates are an important class of compounds.[1–4] Some derivatives have industrial applications, for example as homogeneous catalysts and agricultural fungicides. The pharmaceutical properties of organotin carboxylates have recently been investigated with reference to their antitumour activity.[5–8]

The structural chemistry of organotin carboxylates has been variously studied of late.[9] Their structures have been found to be varied, ranging from binuclear with Sn-Sn bonding in $[(CH_3)_2\ SnOCOCF_3]_2$, to oligomeric, as in $\{[(RSn(O)O_2CR^1)]_2\ [RSn(O_2CR^1)_3]\}_2$. The existence of intra- and inter-molecular bonding of oxygen to tin in these compounds would probably make their addition products with nitrogen donor molecules unstable. Indeed, adducts of organotin carboxylates are not well known.

Amine adducts of organotin and stannic halides are, however, known and widely studied.[10–14] A bipyridyl adduct of $(CH_2{=}CH)_2Sn(OCOCF_3)_2$ has been described, and some pyridine adducts of $Me_3SnOCOCF_3$ and $Me_2Sn(OCOCF_3)_2$ have also been recorded.[15] Apart from these, no other organotin carboxylate–amine adducts appear to have been reported.

This paper reports the successful synthesis and spectra of the *o*-cyclohexadiamine complexes of $Ph_2Sn(OCOCH_3)_2$, $nBu_2Sn(OCOCH_3)_2$, $(PhCH_2)_2Sn(OCOCH_3)_2$, $PhSn(OCOCF_3)_3$, $nBuSn(OCOCH_3)_3$ and $Sn(OCOCH_3)_4$.

EXPERIMENTAL

Equipment and techniques

Dry dichloromethane was obtained by drying AnalaR-grade dichloromethane over calcium chloride for 24 h, and was further dried by refluxing over P_2O_5 (16 g dm^{-3}) for 3 h under nitrogen, and then distilled. Dry acetone was prepared by refluxing AnalaR-grade acetone with *p*-toluene sulphonyl chloride (2g dm^{-3}) for 45 min and distilling the acetone. All melting points (°C) are uncorrected.

IR spectra (CsI disc) were obtained using Perkin–Elmer 2838 and Fourier Transform 1710 IR spectrophotometers. ^1H NMR spectra were obtained using a T.60 spectrometer at an operating temperature of 38 °C.

Elemental analyses (C, H and N) were performed by the University of Sussex Analytical Laboratories, UK; tin contents were determined locally using the methods reported by Farnsworth and Pekola.[16] All reagents were obtianed from Aldrich.

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Preparations

$R_2Sn(OCOCH_3)_2.o$-$C_6H_8(NH_2)_2$ (R = nBu or $PhCH_2$)

R_2SnCl_2 (0.01 mol) and $AgOCOCH_3$ (0.026 mol) were mixed in dry dichloromethane (CH_2Cl_2) and stirred for 48 h under an aluminium foil cover. The mixture was then filtered (to remove silver chloride) by suction into a flask containing *o*-cyclohexadiamine (0.01 mol) in dry CH_2Cl_2. After mixing, the clear yellowish solution obtained was concentrated by evaporation to about 20 cm^3, stoppered and left to stand overnight at room temperature. A yellowish mass of crystals separated out. This was removed, washed with a CH_2Cl_2/hexane mixture (50:50), dried *in vacuo* and recrystallized from sodium-dried toluene.

$BuSn(OCOCH_3)_3.o$-$C_6H_8(NH_2)_2$

This adduct was prepared as described above, from $BuSnCl_3$ (0.01 mol), $AgOCOCH_3$ (0.039 mol) and *o*-cyclohexadiamine (0.01 mol). The resulting white mass of crystals was recrystallized from sodium-dried toluene.

$Sn(OCOCH_3)_4.o$-$C_6H_8(NH_2)_2$

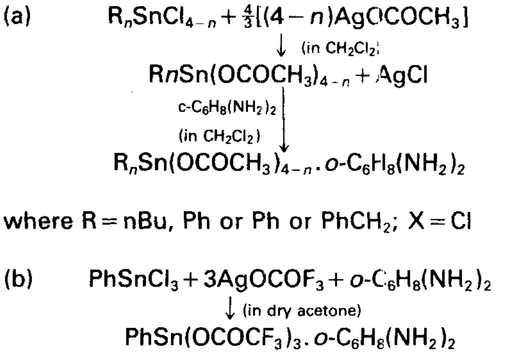
$SnCl_4$ (0.01 mol and $AgOCOCH_3$ (0.052 mol) were mixed in dry CH_2Cl_2 and stirred for 48 h under nitrogen, under an aluminium foil cover. The mixture was then filtered by suction into a flask containing *o*-cyclohexadiamine (0.01 ml) in sodium-dried toluene (70 cm^3). After mixing, the solution was concentrated to about 30 cm^3 and cooled. Light brownish crystals separated out. The toluene supernatant was decanted off and the mass of crystals redissolved in near-boiling toluene (40 cm^3), filtered and cooled again. Yellowish crystals separated out. The mass was separated by decanting off the supernatant, washed with cold dry toluene (2 × 10 cm^3) and dried *in vacuo*.

$PhSn(OCOCF_3)_3.o$-$C_6H_8(NH_2)_2$

Solutions of $AgOCOCF_3$ (0.03 mol) and *o*-cyclohexadiamine (0.01 mol) in dry acetone (50 cm^3 each) were mixed. To the mixture was added $PhSnCl_3$ (0.01 mol) in dry acetone (50 cm^3) slowly, with stirring. The resulting white precipitate was boiled under reflux for 10 min under an aluminium foil cover and under nitrogen. The precipitate coagulated and was removed by filtration. The clear yellowish filtrate was evaporated until a reddish brown oil was obtained. This solidified on drying *in vacuo*. The dry yellow solid was crystallized from chloroform.

RESULTS AND DISCUSSION

The preparation of all the compounds except **IV** below (Table 1) involved a first-step synthesis of the parent organotin carboxylate by a substitution reaction, followed by addition of the Lewis base to the organotin carboxylate solution immediately after filtering off the silver chloride (Scheme 1).



(a)

$$\begin{array}{c} R_nSnCl_{4-n} + \tfrac{4}{3}[(4-n)AgOCOCH_3] \\ \downarrow \text{(in } CH_2Cl_2\text{)} \\ RnSn(OCOCH_3)_{4-n} + AgCl \\ \text{c-}C_6H_8(NH_2)_2 \; \text{(in } CH_2Cl_2\text{)} \downarrow \\ R_nSn(OCOCH_3)_{4-n}.o\text{-}C_6H_8(NH_2)_2 \end{array}$$

where R = nBu, Ph or Ph or $PhCH_2$; X = Cl

(b)

$$\begin{array}{c} PhSnCl_3 + 3AgOCOF_3 + o\text{-}C_6H_8(NH_2)_2 \\ \downarrow \text{(in dry acetone)} \\ PhSn(OCOCF_3)_3.o\text{-}C_6H_8(NH_2)_2 \end{array}$$

Scheme 1 (a) Preparation of compounds **I–III**, **V** and **VI**. (b) Preparation of **IV**.

Most reported methods of synthesis of organotin carboxylates involve the reaction of the organotin oxide or hydroxide with the carboxylic acid. This makes it difficult to synthesize some organotin carboxylates, as the carboxylic acid tends to attack and break the Sn–Ph bond. With the use of silver carboxylate in this work, this problem now appears to be overcome. A slight excess of the silver carboxylate was necessary, however, where it was only sparingly soluble in the reaction medium. Any delay in the addition of the Lewis base led to the crystallization of the high-melting, poorly soluble organotin carboxylate, possibly as a polymer or oligomer produced by intermolecular binding[17] of the oxygen atom of the acetoxy moiety and tin. The presence of the Lewis base in the reaction medium prevents this type of coordinate bonding, as the nitrogen atom of the Lewis base coordinates to the tin atom, sterically preventing the formation of any stable intermolecular O–Sn bonds. Indeed, so long as the Lewis base was present in the reaction mixture, the organotin or stanic carboxylate did not crystallize or precipitate out; if crystallization occurred, slowly as the low-melting diamine adduct.

For compounds **II** and **III**, the organotin carboxylate solution was filtered directly by suction into solutions of the Lewis base. In preparing compound **IV**, all the reagents had to be mixed together at the same time. All the compounds

Table 1 Melting points, yield and elemental analysis results for the organotin carboxylate adducts

	Compound[a]	Yield (%)	m.p. (°C)	Found (%) C	H	N	Sn	(Calcd , %) C	H	N	Sn
I	$nBu_2Sn(OCOCH_3)_2.L$	81	94.96	46.78	8.49	6.36	25.86	46.47	8.23	6.02	25.54
II	$nBuSn(OCOCH_3)_3.L$	70	138.140	41.11	7.21	6.13	25.60	41.14	6.90	6.60	25.43
III	$Sn(OCOCH_3)_4.L$	51	74.76	36.05	6.14	5.92	25.85	35.85	5.55	5.97	25.32
IV	$PhSn(OCOCF_3)_3.L$	48	84.86	32.95	3.20	4.42	18.40	33.30	2.93	4.32	18.29
V	$Ph_2Sn(OCOCH_3)_2.L$	58	108.110	51.86	6.01	5.65	23.85	52.31	5.59	5.55	23.51
VI	$(PhCH_2)_2Sn(OCOCH_3)_2.L$	69	148.150	53.82	6.41	5.24	22.40	54.07	6.38	5.25	22.28

[a] $L = C_6H_8(NH_2)_2$.

were produced in adequate or good yields, and all melted at low to medium temperatures. Elemental analysis results agreed well with the calculated values (Table 1).

Some of the IR absorption bands of the compounds are presented in Table 2. Most noteworthy is the shift of the N—H stretch from about 3350 cm^{-1} in the uncomplexed *o*-cyclohexadiamine (diaminocyclohexane) to about 3200 cm^{-1} in the complexes, as shown in the table. This shift appears the easiest means of identifying the complexation of the diaminocyclohexane to the organotin and stannic carboxylate Lewis acids. The ν (OCO) bands at about 1600 cm^{-1} are strong, indicating the conversion of the parent organotin and stannic chloride to the carboxylates. It must be mentioned that the bands are broad and strong with multiple peaks, including one at 1560 cm^{-1}, which, from Maeda *et al.*[18] on dimethyltin diacetate, suggests either intermolecular or intramolecular bridging by the acetoxy groups. Since all the compounds are low-melting, it is unlikely that they are polymeric in nature, leaving intramolecular —OCO— bridging as the most plausible explanation for the 1560 cm^{-1} peaks.

The proton NMR spectra of the compounds are complex, with the signals of the cyclohexyl moiety protons superimposing on those of the butyls of the butyltin carboxylates between 1 and 2 ppm. However, the —$OCOCH_3$ protons occur as a singlet at approx. 2 ppm. The —NH_2 protons occur at 2.1 ppm as quintets. The phenyl protons in the phenyltin carboxylates occur as two multiplets at 7.3 (*meta-* and *para*-H) and 7.7 ppm (*ortho*-H). The ring protons of the benzyl group in the dibenzyltin diacetate complex occur essentially as a singlet at 7.2 ppm, and the —CH_2— protons at 2.7 ppm.

The Mössbauer bonds (Table 3) of the adducts, and of two of the parent carboxylates [$Sn(OCOCH_3)_4$ and $Bu_2Sn(OCOCH_3)_2$] of 3.56 mm s^{-1} suggest that in these compounds there is an octahedral geometry about the tin atom with the butyl groups in the *trans* position. The E_q values for the three diorganotin adducts (**I**, **V**, **VI**) also suggest that the tin atom has a coordination number of six; however, in these cases the organic groups occupy *cis* positions. The line widths for $Sn(OCOCH_3)_4.L$ are unexpectedly large, suggesting that this compound is precipitated as a mixture of isomers.

The structures of these compounds can only be unequivocally assigned from X-ray crystallographic data. The structures of organotin chloride adducts are usually straightforward. However, replacement of the chlorides with carboxylate groups (as in this work) introduces new complexi-

Table 2 IR spectra of the organotin carboxylate adducts (frequency ν in cm^{-1})

	Compound	ν(N—H)	ν(C=O) and ν(OCO)*	ν(Sn—Ph) or ν(Sn—CH_2—)
I	$nBu_2Sn(OCOCH_3)_2.C_6H_8(NH_2)_2$	3200 m	1520–1630 vs	660 s
II	$nBuSn(OCOCH_3)_3.C_6H_8(NH_2)_2$	3195 m	1550–1670 vs	670 m
III	$Sn(OCOCH_3)_4.C_6H_8(NH_2)_2$	3190 m	1570–1700 vs	
IV	$PhSn(OCOCF_3)_3.C_6H_8(NH_2)_2$	3200 m	1560–1680	1080 w
V	$Ph_2Sn(OCOCH_3)_2.C_6H_8(NH_2)_2$	3240 m	1540–1620 vs	1070 w
VI	$(PhCH_2)_2Sn(OCOCH_3)_2.C_6H_8(NH_2)_2$	3210 m	1570–1650 vs	655 s

Table 3 Mössbauer spectra of the tin carboxylate adducts

	Compound	*d*	E_q	1	2
I	$Bu_2Sn(OCOCH_3)_2.L$	0.99	2.58	1.04	1.30
II	$BuSn(OCOCH_3)_3.L$	0.77	2.08	1.00	0.95
III	$Sn(OCOCH_3)_4.L$	−0.33	0.74	1.66	1.91
IV	$PhSn(OCOCF_3)_3.L$	0.70	2.43	1.06	1.05
V	$Ph_2Sn(OCOCH_3)_2.L$	0.76	2.27	1.14	1.17
VI	$(PhCH_2)_2Sn(OCOCH_3)_2.L$	0.96	2.16	1.24	1.09
	$Bu_2Sn(OCOCH_3)_2$[a]	1.35	3.56	—	—
	$Sn(OCOCH_3)_4$[b]	0.08	0.20	—	—

[a] Ref. 19. [b] Ref. 20.

ties: the oxygen atoms of the carboxylates are capable of coordinating intramolecularly to the tin in addition to the amine Lewis-base atoms). This idea is strengthened by the appearance of the —OCO—IR bands at rather low wavenumbers with peaks at about 1560 cm^{-1} as discussed above. This would suggest the central tin atom has a coordination number greater than six, thereby distorting the basic octahedral arrangement exhibited by analogous organotin halide adducts. Coordination numbers greater than six are known for related tin compounds.[21] The compounds are currently being screened for biological, especially antitumour, properties.

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REFERENCES

1. A. G. Davies and P. J. Smith, in *Comprehensive Organometallic Chemistry*, edited by G. Wilkinson, F. G. A. Stone and E. W. Abel, Vol. 2, Pergamon Press, Oxford (1982).
2. C. J. Evans and S. Karpel, *Organotin Compounds in Modern Technology*, J. Organomet. Chem. Library Vol. 16. Elsevier, Amsterdam (1985).
3. S. J. Blunden, P. A. Cusack and R. Hill, *The Industrial Uses of Tin Chemicals*. Royal Society of Chemistry, London (1985).
4. I. Omae, *Organotin Chemistry*, J. Organomet. Chem. Library Vol. 21. Elsevier, Amsterdam (1989).
5. M. Gielen, Tin as a vital nutrient: implication in cancer prophylaxis and other physiological processes, in *Antitumour Active Organotin Compounds*, edited by N. F. Carderelli, Chapt. 13. CRC Press, Boca Raton, FL (1986).
6. I. Haiduc and C. Silvest, *Coord. Chem. Rev.* **99**, 253 (1990).
7. A. Meriem, R. Willen, M. Biesemans, B. Mathieu, D. Devos, P. Lelleveled and M. Gielen, *Appl. Organomet. Chem.* **5**, 195–201 (1991).
8. S. W. Ng, V. G. K. Das, M. Gielen and E. T. Tiekink, *Appl. Organomet. Chem.* **6**, 19–25 (1992).
9. E. R. T. Tiekink, *Appl. Organomet. Chem.* **5**, 1–23 (1991).
10. A. S. Mufti and R. C. Pollar, *J. Chem. Soc.* 5055 (1965).
11. M. Frankel, D. Gertner, D. Wagner and A. Zilkha, *J. Organomet. Chem.* **9**, 83 (1967).
12. R. J. P. Corriu, J. M. Fernandes and C. Guerin, *J. Organomet. Chem.* **152**, 21 (1978).
13. L. H. Sommer, J. McLick and C. M. Golino, *J. Am. Chem. Soc.* **94**, 669 (1972).
14. C. Eaborn and S. P. Hopper, *J. Organomet. Chem.* **11**, 479 (1968).
15. J. J. Bonire, *Polyhedron* **4**, (10) 707–710 (1985).
16. M. Farnsworth and J. Pekola, *Anal. Chem.* **31**, 410 (1959).
17. B. F. E. Ford and J. R. Sams, *J. Organomet. Chem.* **31**, 47 (1971).
18. Y. Maeda and R. Okaware, *J. Organomet. Chem.* **10**, 247 (1967).
19. A. G. Maddock and R. H. Platt, *J. Chem. Soc.* (*A*) 1191 (1971).
20. J. N. R. Ruddick, *Rev. Si, GeSn, Pb compds* **2**, 115 (1976).
21. T. P. Lockhart, J. C. Calabrese and F. Davidson, *Organometallics* **6**, 2479 (1987).