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Structural chemistry of organotin carboxylates

XVII *. Diorganotin(IV) derivatives of *N*-phthaloyl-DL-valine

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Abstract

New diorganotin(IV) complexes of the general formula $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)]_2O\}_2$ (where A is the anion derived from the *N*-phthaloyl derivative of DL-valine and R = Me, ^{n}Bu and ^{n}Oct) have been prepared and characterized by spectroscopic methods and in the case of the $\{[Me_2Sn(A)]_2O\}_2$ compound, by X-ray crystallographic methods. The Sn atoms in the $[R_2Sn(A)_2]$ complexes are six-coordinate and the $\{[R_2Sn(A)]_2O\}_2$ complexes are examples of dicarboxylato tetraorganodistannoxanes. The crystal structure of $\{[Me_2Sn(A)]_2O\}_2$ shows both the endocyclic and exocyclic Sn atoms to be five-coordinate, trigonal bipyramidal. Several weak intramolecular contacts are noted with the most noteworthy being a contact of 3.15(1) Å between the imido C=*O* atom and the endocyclic Sn atom.

Introduction

The present study represents an extension of earlier work with diorganotin(IV) complexes of *N*-protected amino acids and dipeptides [2,3]. New diorganotin(IV) compounds containing the deprotonated *N*-phthaloyl-DL-valine ligand are reported including an X-ray crystal structure analysis of the $\{[Me_2Sn(O_2CCH(CHMe_2)C_8H_4NO_2)]_2O\}_2$ compound. Interest in organotin/amino acid (and peptide) systems arises from their potential applications in agriculture [4] and as anti-tumour agents [5].

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* For Part XVI, see ref. 1.

Results and discussion

Dialkyltin(IV) oxides react with *N*-phthaloyl-DL-valine (AH) in 1:2 and 1:1 (Sn: ligand) molar ratios to form $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)_2]_2O\}_2$ (R = Me, ^{n}Bu and ^{n}Oct), respectively in yields of 76–93% (Table 1). These have been characterized by IR and ^{1}H NMR spectroscopy and for the $\{[Me_2Sn(A)_2]_2O\}_2$ complex by X-ray crystallography. Satisfactory microanalytical data have been obtained for these complexes. The methyl and n-butyl compounds are white in colour and were recrystallized from benzene and absolute alcohol (3:1) solutions of the respective compound. By contrast the n-octyl compounds are viscous liquids. All the complexes are soluble in chloroform, methanol, dichloromethane and benzene and are insoluble in carbon tetrachloride.

IR spectra of *N*-phthaloyl-DL-valine (AH) and the diorganotin complexes are summarized in Table 1; the stretching frequencies of interest are those associated with the imido C=O, acid COO, Sn–C, Sn–O and Sn–O–Sn groups. The deprotonation of the carboxylic acid is evident from the disappearance of a broad band owing to the COOH group in the region 2900–2500 cm^{-1} of the ligand. In the spectrum of AH the stretching modes of imido C=O are observed at 1770 cm^{-1} which shifts little after complexation indicating the non participation of the imido C=O group in significant coordination to Sn. The values of $\Delta\nu$ (where $\Delta\nu = \nu(COO)_{asymm} - \nu(COO)_{sym}$) in the spectra of the complexes is lower than the value for the AC_2H_5 ester ($\Delta\nu$ 390 cm^{-1}) and is near to that observed in the Na salt ($\Delta\nu$ 205 cm^{-1}). These observations suggest the presence of bidentate carboxylate ligands in the complexes. The presence of two Sn–C absorption bands in the spectra of the complexes in the region 600–500 cm^{-1} indicates a non-linear *trans* configuration of the C–Sn–C moiety. A band in the region 500–400 cm^{-1} is assigned to the stretching mode of the Sn–O link and in the case of the 1:1 complexes a strong band at 650 cm^{-1} region is assigned to a Sn–O–Sn bridge.

The ^{1}H NMR spectra of the acid (AH) and of the complexes, recorded in $CDCl_3$ solution, are summarized in Table 2. In the spectrum of the free ligand a single resonance is observed at δ 9.39 ppm which is absent in the spectra of the complexes indicating the replacement of the carboxylic acid proton by a diorganotin moiety on complex formation. The positions of resonances associated with the phenyl H atom change little upon coordination. A doublet due to the N-CH protons shifts upfield (4.61–4.28 ppm) indicating the coordination of the carboxylate group. Two doublets are resolved due to the methyl protons ($-CH(CH_3)_2$) of A in the Me_2Sn complexes whereas these overlap with the multiplets due to the Sn-bound alkyl groups in the $^n Bu_2Sn$ and $^n Oct_2Sn$ complexes. A multiplet due to the methine protons shift to lower field in the complexes confirming carboxylate coordination to Sn. In the Me_2Sn complexes the presence of a single resonance due to the $Sn-(CH_3)_2$ shows a *trans* configuration of the methyl groups. In each of the $^n Bu_2Sn$ and $^n Oct_2Sn$ complexes a very broad multiplet due to the alkyl H atoms is observed. The integration of the individual resonances is consistent with the formulation of the compounds as $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)]_2O\}_2$.

The spectroscopic evidence suggests that the 1:2 compounds have six-coordinate Sn centres. On the basis of crystallographic studies on related compounds the geometries of the Sn atoms may be inferred to be based on a skew-trapezoidal planar arrangement [6]. In this description the organo groups lie over the longer

Table 1

Physical and infrared spectral data (cm^{-1}) for the $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)]_2O\}_2$ complexes [a]

Complex	Yield (%)	M.p. (°C)	ν(C=O) imido I	ν(C=O) imido II	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(Sn–C)	ν(Sn–O)	ν(Sn–O–Sn)
AH			1770m	1740vs	1690s	1390vs	300	–	–	–
ANa			1775m	1710vs	1600s	1395vs	205	–	–	–
AC_2H_5			1770m	1740vs	1680sh	1290vs	390	–	–	–
$[Me_2Sn(A)_2]$	80	171–172	1775m	1720vs	1615s	1380vs	235	580w 530m	470m	–
$[^nBu_2Sn(A)_2]$	93	155–156	1770m	1715vs	1620s	1390vs	230	610w 525m	460m	–
$[^nOct_2Sn(A)_2]$	87	liq	1775m	1720vs	1610s	1380vs	230	605w 530m	470m	–
$\{[Me_2Sn(A)]_2O\}_2$	89	220	1770m	1710vs	1600s	1375vs	225	570w 525m	480m	650m
$\{[^nBu_2Sn(A)]_2O\}_2$	76	139–141	1780m	1730vs	1600s	1385vs	215	615sh 535m	495m	650m
$\{[^nOct_2Sn(A)]_2O\}_2$	78	liq	1770m	1710vs	1620s	1385vs	235	605w 530m	470m	650m

[a] Spectra were recorded as Nujol mulls, the symbols s, m, b, w and sh have their usual meanings.

Table 2

^1H NMR data (δ; ppm) for the $[R_2Sn(A)_2]$ and $\{[R_2Sn(A)]_2O\}_2$ complexes [a]

Complex	C_6H_4	N-CH	-CH-	$-(CH_3)_2$		Sn-R	
						$-CH_2-$	$-CH_3$
AH	7.95–7.75 (m, 4H)	4.70–4.41 (d, 1H)	2.55–2.37 (m, 1H)	1.31–1.11 (d, 3H)	1.01–0.81 (d, 3H)	–	–
$[Me_2Sn(A)_2]$	7.85–7.69 (m, 8H)	4.61–4.57 (d, 2H)	2.68–2.61 (m, 2H)	1.13–1.10 (d, 6H)	0.96–0.87 (d, 6H)	–	1.07 (s, 6H)
$[^nBu_2Sn(A)_2]$	7.85–7.68 (m, 8H)	4.59–4.55 (d, 2H)	2.75–2.64 (m, 2H)	1.13–1.10 (d, 6H)		0.96–0.83 [b] (m, 24H)	
$[^nOct_2Sn(A)_2]$	7.85–7.69 (m, 8H)	4.60–4.56 (d, 2H)	2.72–2.68 (m, 2H)	1.14–1.11 (d, 6H)		1.79–1.24 (m, 28H)	0.96–0.83 [c] (t, 12H)
$\{[Me_2Sn(A)]_2O\}_2$	7.84–7.69 (m, 8H)	4.32–4.28 (d, 2H)	2.60–2.53 (m, 2H)	1.07–1.04 (d, 6H)	0.83–0.80 (d, 6H)	–	0.69 (s, 12H)
$\{[^nBu_2Sn(A)]_2O\}_2$	7.82–7.69 (m, 8H)	4.42–4.31 (d, 2H)	2.78–2.63 (m, 2H)			1.31–0.85 [d] (bm, 48H)	
$\{[^nOct_2Sn(A)]_2O\}_2$	7.86–7.70 (m, 8H)	4.42–4.36 (d, 2H)	2.68–2.71 (m, 2H)			1.42–0.89 [d] (bm, 80H)	

[a] Spectra recorded in $CDCl_3$ solution; the symbols b, m, s and t have their usual meanings. [b] Overlap of one $-(CH_3)_2$ doublet with Sn–R region. [c] Overlap of one $-(CH_3)_2$ doublet with $-CH_3$ resonances. [d] Overlap of $-(CH_3)_2$ doublets with Sn–R.

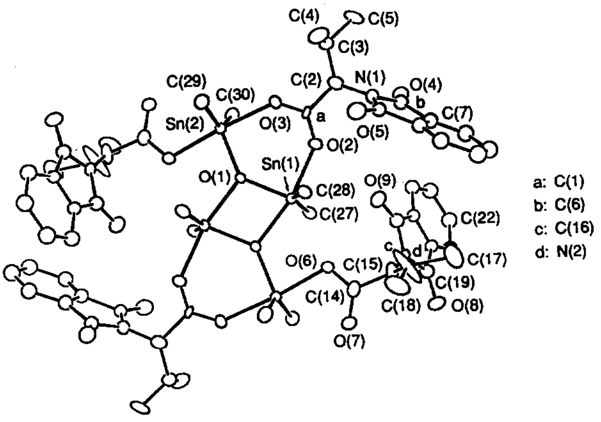

Fig. 1. Molecular structure and crystallographic numbering scheme employed fir $\{[Me_2Sn(O_2CCH(CHMe_2)C_8H_4NO_2)]_2O\}_2$.

Sn–O bond distances formed by the asymmetrically coordinating carboxylate groups. The 1 : 1 compounds are assumed to have the familiar dicarboxylato tetraorganodistannoxane structure. A crystal structure analysis of $\{[Me_2Sn(A)]_2O\}_2$ confirms this assignment.

The molecular structure of $\{[Me_2Sn(A)]_2O\}_2$, obtained as its dihydrate, is shown in Fig. 1 and selected interatomic parameters are listed in Table 3. The structure features a centrosymmetric Sn_2O_2 moiety which is connected to two exocyclic Me_2Sn groups. A bridge between the Sn(1) and Sn(2) atoms is provided by a

Table 3

Selected interatomic parameters (Å, deg) for $\{[Me_2Sn(O_2CCH(CHMe_2)C_8H_4NO_2)]_2O\}_2$

Sn(1)–O(1)	2.034(8)	Sn(2)–O(1)	2.005(7)
Sn(1)–O(1)′ [a]	2.204(8)	Sn(2)–O(3)	2.275(9)
Sn(1)–O(2)	2.261(8)	Sn(2)–O(6)′	2.197(9)
Sn(1)–C(27)	2.12(1)	Sn(2)–C(29)	2.12(1)
Sn(1)–C(28)	2.12(1)	Sn(2)–C(30)	2.09(1)
O(2)–C(1)	1.21(1)	O(6)–C(14)	1.25(2)
O(3)–C(1)	1.23(1)	O(7)–C(14)	1.23(2)
C(1)–C(2)	1.55(2)	C(14)–C(15)	1.48(1)
O(1)–Sn(1)–O(1)′	76.7(3)	O(1)–Sn(2)–O(3)	91.5(3)
O(1)–Sn(1)–O(2)	89.7(3)	O(1)–Sn(2)–O(6)′	82.8(3)
O(1)–Sn(1)–C(27)	106.9(4)	O(1)–Sn(2)–C(29)	112.9(4)
O(1)–Sn(1)–C(28)	104.7(4)	O(1)–Sn(2)–C(30)	106.8(5)
O(1)′–Sn(1)–O(2)	165.5(4)	O(3)–Sn(2)–O(6)′	172.6(3)
O(1)′–Sn(1)–C(27)	93.6(4)	O(3)–Sn(2)–C(29)	83.8(5)
O(1)′–Sn(2)–C(28)	97.6(4)	O(3)–Sn(2)–C(30)	87.1(5)
O(2)–Sn(1)–C(27)	85.6(4)	O(6)′–Sn(2)–C(29)	94.1(4)
O(2)–Sn(1)–C(28)	90.5(4)	O(6)′–Sn(2)–C(30)	99.0(5)
C(27)–Sn(1)–C(29)	148.2(6)	C(29)–Sn(2)–C(30)	139.4(6)
Sn(1)–O(1)–Sn(1)′	103.3(2)	Sn(1)–O(1)–Sn(2)	134.4(2)
Sn(1)–O(1)–Sn(2)′	122.2(2)	Sn(2)–O(3)–C(1)	130.2(9)
Sn(1)–O(2)–C(1)	135.5(9)	Sn(2)–O(6)–C(14)	110.6(8)

[a] Primed atoms are related by a centre of inversion.

bidentate carboxylate group; Sn(1)–O(2) 2.261(8) and Sn(2)–O(3) 2.275(9) Å. The second carboxylate ligand functions essentially in the monodentate mode (Sn(2)–O(6)′ 2.197(9) Å). This ligand coordinates the exocyclic Sn atom exclusively such that the pendant O(7) atom is orientated away from the rest of the molecule and is 2.901(9) Å from the Sn(2) atom. The O(6) atom simultaneously forms a close intramolecular contact with the Sn(1) atom such that Sn(1) ··· O(6) is 2.939 Å. The Sn(1) atom also forms a close intramolecular contact with the imido C=*O*(9) atom at 3.15(1) Å. On the basis of the Sn atom geometries it is suggested that the weaker Sn ··· O interactions are not indicative of significant bonding interactions.

The Sn(1) atom exists in a distorted trigonal bipyramidal geometry with the basal plane defined by the O(1), C(27) and C(28) atoms. The axial sites are occupied by the O(2) and O(1)′ atoms and the Sn(1) atom lies 0.058(2) Å out of the basal plane in the direction of the O(1)′ atom. Distortions from the ideal geometry are manifested in the C(27)–Sn(1)–C(28) angle of 148.2(6)° and the axial angle of 165.5(4)° and may be related to the close approach of the O(6) and O(9) atoms. If the O(6) and O(9) atoms were considered to be within bonding distance of the Sn(1) atom, the coordination geometry would be best described as being based on a pentagonal bipyramid with the methyl groups occupying the axial positions. The Sn(2) atom also exists in a distorted trigonal bipyramidal geometry. The Sn(2) atom lies 0.111(3) Å out of the basal plane defined by the O(1), C(29) and C(30) atoms in the direction of the O(6)′ atom. Significantly, the distortions from the ideal geometry about the Sn(2) atom are less than for the Sn(1) atom; C(29)–Sn(2)–C(30) and O(3)–Sn(2)–O(6)′ are 139.4(6) and 172.6(3)°, respectively. These distortions, too, may be related to the close approach of the O(7) atom. The O(7) atom is 3.02(1) Å from the molecule of water of crystallization indicating the existence of an hydrogen bond between these atoms.

The structure adopted by $\{[Me_2Sn(A)]_2O\}_2$ is as found for the common structural motif for dicarboxylato tetraorganodistannoxanes, $\{[R_2Sn(O_2CR')]_2O\}_2$ [6]. An interesting feature of the present structure, however, is the relative close approach of a non-carboxylato hetero atom of the carboxylate R′ group to the Sn atom, the weak nature of this interaction not withstanding. This has not been observed previously for O or S potential donor atoms in the R′ moiety although the participation in bonding to Sn by an N hetero atom has been observed in the structure of $\{[{}^nBu_2Sn(O_2CC_5H_4N\text{-}o)]_2O\}_2$ leading to a new structural type for dicarboxylato tetraorganodistannoxanes [7].

Experimental

Materials

Dimethyl, di-n-butyl and di-n-octyltin oxides were obtained commercially (Alfa). DL-Valine was obtained from Sisco and *N*-phthaloyl-DL-valine was prepared by the literature method [8].

Preparation of complexes

To a solution of *N*-phthaloyl-DL-valine (2 mmol) in a mixture of dry benzene (30 cm^3) and absolute ethanol (10 cm^3) was added the dialkyltin oxide (1 or 2 mmol). The mixture was refluxed on a water bath with azeotropic removal of water. The dialkyltin oxide went into solution within 10–15 mins to give a clear solution.

Table 4

Crystal data and refinement details for $\{[Me_2Sn(O_2CCH(CHMe_2)C_8H_4NO_2)]_2O\}_2 \cdot 2H_2O$

Formula	$C_{60}H_{72}N_4O_{18}Sn_4 \cdot 2H_2O$
Mol. wt.	1648.0
Crystal system	orthorhombic
Space group	*Pccn*
a, Å	13.524(2)
b, Å	34.658(5)
c, Å	15.305(2)
V, Å^3	7173.7
Z	4 (tetramers)
D_c, g cm^{-3}	1.526
$F(000)$	3296
μ, cm^{-1}	13.20
T, K	293
No. of data collected	5366
No. of unique data	4700
No. of unique reflections used with $I \geqslant 2.5\sigma(I)$	2502
R	0.048
k	4.644
g	0.0004
R_w	0.052
Residual ρ_{max}, e Å^{-3}	1.09

Refluxing was continued for 3–4 h, cooled, and the solvent removed by distillation under reduced pressure. A white solid obtained was collected and recrystallized from a mixture of dry benzene and absolute ethanol (3 : 1 ratio) in the case of the methyl- and butyltin complexes. For each of the octyltin complexes the viscous liquid obtained was washed with CCl_4.

Physical measurements

Melting points were determined in open capillaries and are uncorrected. Elemental analysis for C, H and N were carried out by the Microanalytical Service, R.S.I.C. Panjab University, Chandigarh. Tin was estimated as SnO_2. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1430 spectrophotometer. The ^1H spectra were recorded on a Bruker AC 200 spectrometer using TMS as an internal standard.

Crystallography

Intensity data for $\{[Me_2Sn(O_2CCH(CHMe_2)C_8H_4NO_2)]_2O\}_2 \cdot 2H_2O$ were measured at 293 K on an Enraf–Nonius CAD4F diffractometer fitted with graphite monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å. The ω–2θ scan technique was employed to measure 5366 data up to a maximum Bragg angle of 22.5°. The data were corrected for Lorentz and polarization effects but not for absorption. Relevant crystal data are given in Table 4.

The structure was solved by direct-methods [9] and refined by a full-matrix least-squares procedure based on F [10]. The crystallographic asymmetric unit is comprised of one half molecule, located about a crystallographic centre of inversion, and one water molecule of crystallization. The Sn, O, N and non-aromatic C atoms were refined with anisotropic thermal parameters and H atoms were included in the model in their calculated positions (except for the C(15) and C(16) atoms). There was disorder in the structure in the region of the second carboxylate ligand so that the C(14)–C(15) and C(15)–C(16) bond distances were constrained to 1.52(2) Å. After the inclusion of a weighting scheme of the form $w = k/[\sigma^2(F)$

Table 5

Fractional atomic coordinates for $\{[Me_2Sn(O_2CCH(CHMe_2)C_8H_4NO_2)]_2O\}_2 \cdot 2H_2O$

Atom	x	y	z
Sn(1)	−156(1)	−419(1)	4488(1)
Sn(2)	−39(1)	466(1)	3112(1)
O(1)	−47(6)	154(2)	4216(5)
O(2)	−482(7)	−538(3)	3065(6)
O(3)	130(7)	−75(3)	2282(5)
O(4)	−1835(7)	−1251(3)	1454(7)
O(5)	1333(8)	−1012(3)	2252(7)
O(6)	−68(7)	952(3)	4032(5)
O(7)	−249(8)	1290(3)	2834(7)
O(8)	1597(8)	2064(3)	3660(7)
O(9)	426(8)	1304(3)	5868(7)
N(1)	−241(8)	−1046(3)	1728(7)
N(2)	774(9)	1671(3)	4650(7)
C(1)	−232(10)	−398(4)	2375(8)
C(2)	−453(11)	−631(5)	1532(9)
C(3)	−42(11)	−481(5)	683(9)
C(4)	1069(13)	−461(6)	644(11)
C(5)	−471(14)	−685(5)	−81(9)
C(6)	−1012(11)	−1314(4)	1701(10)
C(7)	−549(11)	−1673(5)	2058(9)
C(8)	−1007(12)	−2038(5)	2178(10)
C(9)	−363(12)	−2331(5)	2515(11)
C(10)	598(13)	−2263(5)	2723(11)
C(11)	987(12)	−1887(5)	2584(10)
C(12)	400(11)	−1618(5)	2264(9)
C(13)	589(11)	−1190(4)	2079(9)
C(14)	−157(10)	1265(4)	3631(10)
C(15)	−130(11)	1624(4)	4148(11)
C(16)	−986(13)	1811(9)	4431(18)
C(17)	−809(16)	2219(6)	4824(14)
C(18)	−1863(11)	1789(7)	3895(12)
C(19)	1582(10)	1898(4)	4376(10)
C(20)	2352(10)	1861(4)	5026(8)
C(21)	3234(11)	2030(5)	5057(10)
C(22)	3856(12)	1935(5)	5776(10)
C(23)	3509(12)	1686(5)	6418(11)
C(24)	2578(10)	1528(4)	6389(10)
C(25)	1993(9)	1626(4)	5675(8)
C(26)	988(11)	1512(4)	5465(10)
C(27)	−1675(9)	−538(4)	4701(8)
C(28)	1301(9)	−634(4)	4333(8)
C(29)	1412(9)	589(4)	2659(9)
C(30)	−1497(10)	491(4)	2672(10)
O(w)	3723(13)	6775(6)	8531(15)

$+ |g| F^2]$, the refinement was continued until convergence; final refinement details are listed in Table 4. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Fractional atomic coordinates are listed in Table 5 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP [11] at 15% probability ellipsoids. Scattering factors were as incorporated in the SHELX-76 program [10] and the refinement was performed on a SUN4/280 computer. Other crystallographic details (available from ERTT) comprise thermal parameters, H-atom parameters, all bond distances and angles, and tables of observed and calculated structure factors.

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