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Synthesis and coordination chemistry of itaconic estertin(IV) complexes

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Abstract

New itaconic estertin(IV) complexes $CH_3OOCCH_2CH(COOCH_3)CH_2Sn(L)Cl_2$ (**1**, L = S_2CNMe_2; **2**, L = $(Pz)_3BH$; **3**, L = OH) were synthesized and characterized by means of X-ray crystallography and spectroscopy. The crystal structures of **1** ($P2_1/n$; $a = 7.830(1)$, $b = 13.262(1)$, $c = 16.958(2)$ Å, $\beta = 91.269(9)°$; $Z = 4$; $R = 0.043$) and **3** ($P2_1/n$; $a = 11.611(2)$, $b = 12.301(2)$, $c = 12.435(2)$ Å, $\beta = 101.02(1)°$; $Z = 4$; $R = 0.043$) show that each tin atom approximates to octahedral geometry via an intramolecular carbonyl-to-tin coordination in addition to either chelation of the dithiocarbamate (for **1**) or hydroxo-bridging (for **3**). The reaction of **1** or **3** with sodium sulfide gives $CH_3OOCCH_2CH(COOCH_3)CH_2$ Sn(L)S (**4**, L = S_2CNMe_2; **5**, L = OH), whereas the same reaction of **2** does not give the analogous chemical product but instead allows dissociation of the trispyrazolylborate ligand.

Introduction

The chemistry of estertin halides has attracted considerable attention because of their industrial applicability and coordination chemistry since the discovery of a convenient synthetic route by Akzo chemists [1–5]. The halogens bonded to the tin atom in the estertin can be metathetically replaced by a potential multidentate ligand which is capable of chelating to the tin atom. Systematic investigations on the estertin complexes of multidentate ligand suggest that the bonding mode of the ester group is very sensitive to the donating atom of the ligands [6–14].

Recently the synthesis and structure of itaconic estertin chloride $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ has been reported by our group [15,16]. Depending on the chemical state, the coordination number of the tin atom in the itaconic estertin chloride is variable: in solution only one of the two carbonyl groups is coordinated to the tin atom which is thus pentacoordinated while it is hexacoordinated in the solid state forming five- and six-membered rings via two carbonyl-to-tin coordinations.

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In an effort to clarify the coordination chemistry of this novel estertin, $CH_3OOCCH_2CH(COOCH_3)CH_2Sn(L)X_2$ (L, potential multidentate ligand; X, halide or pseudo halide) was prepared and characterized by means of various spectroscopies together with X-ray crystal structure studies.

Experimental

All chemicals were of reagent grade from commercial sources and used without purification. Chemical analyses were carried out by the Chemical Analysis Laboratory at KIST. The molecular weight was determined cryoscopically in benzene using a Cryette A Automatic Cryoscope. The infrared spectra in the 4000–400 cm^{-1} region were measured on a KBr pellet with an Analect Instrument fx 6160 FT-IR spectrometer. ^1H NMR spectra in $CDCl_3$ were recorded on JEOL JNM-DMX 60 or Bruker AM-200 spectrometers, and ^{119}Sn NMR spectra in $CDCl_3$ was recorded on a Bruker AM-200 spectrometer operating at 74.63 NHz in pulse mode with Fourier transform at an ambient temperature of 23(2)°C. The chemical shifts determined are relative to internal $Me_4Si(^1H)$ and external $Me_4Sn(^{119}Sn)$ for the indicated nuclei.

$CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ [15], $Na[S_2CNMe_2]$ [17], and $K[HB(Pz)_3]$ [18] were prepared by the literature methods.

Preparation of $CH_3OOCCH_2CH(COOCH_3)CH_2Sn(S_2CNMe_2)Cl_2$ (1)

A solution of $Na[S_2CNMe_2] \cdot 2\ H_2O$ (1.80 g, 10 mmol) dissolved in 100 ml of ethanol was added dropwise to an equimolar solution of $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ (3.84 g, 10 mmol) in 100 ml of ethanol. The mixture was stirred at room temperature for 2 h and then filtered. The filtrate was evaporated to obtain a white solid, which was recrystallized from a chloroform/petroleum ether (1 : 1) solution giving colourless crystals (m.p. 104–105°C) in 84% yield. Anal. Found: C, 25.50; H, 3.62; N, 3.08. $C_{10}H_{12}NO_4S_2Cl_2Sn$ calc.: C, 25.61; H, 3.65; N, 2.99%. IR (KBr, cm^{-1}): ν(C=O), 1748, 1657. ^1H NMR ($CDCl_3$): δ 4.0 (s, 3 H); 3.7 (s, 3 H); 3.4 (s, 6 H); 3.2 (br, 1 H); 2.8 (d, $J = 6$ Hz, 2 H); 1.9 (t, $J = 7$ Hz, 2 H) ppm. ^{119}Sn NMR ($CDCl_3$): δ −404.5 ppm.

Preparation of $CH_3OOCCH_2CH(COOCH_3)CH_2Sn\{(Pz)_3BH\}Cl_2$ (2)

A mixture of $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ (3.84 g, 10 mmol) and $K[(Pz)_3BH]$ (2.55 g, 10 mmol) in 100 ml of dichloromethane was stirred at room temperature for 2 h. The cloudy solution was filtered, and the solvent was removed from the filtrate by evaporation to obtain a white solid (m.p. 185–187°C) in 84% yield. Anal. Found: C, 34.10; H, 3.70; N, 15.20. $C_{16}H_{21}N_6O_4Cl_2BSn$ calc.: C, 34.20; H, 3.77; N, 14.96%. IR (KBr): ν(C=O), 1732 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.20 (d, $J = 2$ Hz, 1H); 8.07 (d, $J = 2$ Hz, 1 H); 7.90 (d, $J = 2$ Hz, 1 H); 7.73 (d, $J = 2$ Hz, 2 H); 7.64 (d, $J = 2$ Hz, 1 H); 6.30 (t, $J = 2$ Hz, 2 H); 6.22 (t, $J = 2$ Hz, 1 H); 3.71 (s, 3 H); 3.70 (s, 3 H); 2.98 (t, $J = 4$ Hz, 2 H); 2.06 (dd, $J = 6$ Hz, 3 Hz, 2 H) ppm. ^{119}Sn NMR ($CDCl_3$): δ −429.1 ppm.

Preparation of $[CH_3OOCCH_2CH(COOCH_3)CH_2Sn(OH)Cl_2]_2$ (3)

1,2-Dianilinoethane (2.12 g, 10 mmol) in 50 ml of dichloromethane was added to $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ (3.84 g, 10 mmol) in 50 ml of dichloromethane, and the solution was stirred at room temperature for 3 h. The solution was condensed to approximately 30 ml, and left overnight at −10°C to produce a white solid in 66% yield. Slow evaporation from a dioxane solution of the white solid afforded crystals (m.p. 109–112°C) for structure determination. Anal. Found: C, 29.20; H, 4.54. $C_7H_2O_5Cl_2Sn \cdot C_4H_8O_2$ calc.: C, 29.11; H, 4.44%. IR (KBr): ν(C=O) 1741, 1653 cm^{-1}.

Preparation of [$CH_3OOCCH_2CH(COOCH_3)CH_2Sn(S_2CNMe_2)S]_2$ (4)

A solution of $Na_2S \cdot 9\ H_2O$ (2.40 g, 10 mmol) in 50 ml of water was added dropwise to an equimolar solution of **1** (4.69 g, 10 mmol) in 50 ml of chloroform, and the solution was stirred at room temperature for 1 h. The chloroform layer was separated and evaporated to produce a thin yellow solid. The solid was purified from a solvent pair of chloroform/petroleum ether (1 : 1) to obtain a white solid (m.p. 142–145°C) in 90% yield. MW measured = 830.4 (calc. 860.2). Anal. Found: C, 27.40; H, 3.79; N, 2.84. $C_{10}H_{17}NO_4S_3Sn$ calc.: C, 27.92; H, 3.98; N, 2.79%. IR (KBr): ν(C=O) 1738 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.8 (s, 3 H); 3.7 (s, 3 H); 3.5 (br, 1 H), 3.4 (s, 6 H); 2.8 (d, $J = 6$ Hz, 2 H); 2.1 (m, $J = 6$ Hz, 2 H) ppm. ^{119}Sn NMR ($CDCl_3$): δ −246.4 ppm.

Preparation of [$CH_3OOCCH_2CH(COOCH_3)CH_2Sn(OH)S]_2$ (5)

Reaction of **3** with Na_2S according to the same procedure as for **4**, followed by purification from a solvent pair of chloroform/*n*-hexane (1 : 1), resulted in a white solid (m.p. 64–66°C) in 84% yield. Anal. Found: C, 25.10; H, 3.59. $C_7H_{12}O_5SSn$ calc.: C, 25.72): H, 3.70%. IR (KBr) ν(C=O) 1734 cm^{-1}.

Attempted reaction of 2 with Na_2S

When **2** was used instead of **1** or **3** in the reaction with Na_2S, the analogous itaconic estertin sulfide was not obtained, but an unidentifiable solid product resulted with the trispyrazolylborate ligand dissociated.

Crystallographic analysis

All the crystallographic data were obtained on an Enraf–Nonius CAD4 diffractometer with graphite monochromated molybdenum radiation ($\lambda(K_{\alpha 1}) = 0.70930$, $\lambda(K_{\alpha 2}) = 0.71359$ Å) at an ambient temperature of 23(2)°C. Single crystals suitable for X-ray analysis were glued to the interior of a walled glass capillary which was then sealed as precaution against moisture and oxygen. The qualities of the crystals were checked by photographic methods. Accurate cell dimensions were determined by the least square refinement of the diffraction geometry for 25 carefully centred reflections having $9 < \theta_{Mo\text{-}K} < 14$ (for **1**) and $10 < \theta_{Mo\text{-}K} < 14$ (for **3**). From the systematic absence, the space group $P2_1/n$ for both **1** and **3** was uniquely determined. During the data collection, three standard reflections measured after 1 h did not reveal systematic variations in intensity. The structures were solved by use of the conventional heavy atom method, followed by successive difference Fourier techniques and were refined by means of full-matrix least squares procedures using SHELX-76 [19]. Detailed crystal parameters and procedural information corresponding to data collection and structure refinement for the compounds are presented in Table 1. Final atomic coordinates and thermal parameters of **1** and **3** are listed in Tables 2 and 3, respectively.

Table 1

Crystal parameters and procedural information for 1 and 3·$C_4H_8O_2$

	1	3·$C_4H_8O_2$
Formula	$C_{10}H_{17}NCl_2O_4S_2Sn$	$SnCl_2O_5C_7H_{12}\cdot C_4H_8O_2$
F.W.	468.97	453.877
Space group	$P2_1/n$	$P2_1/n$
a (Å)	7.830(1)	11.611(2)
b (Å)	13.262(1)	12.301(2)
c (Å)	16.958(2)	12.435(2)
β (deg)	91.269(9)	101.62(5)
V (Å^3)	1760.5(5)	1739.5(5)
Z	4	4
$d_{calc.}$ (g cm^{-3})	1.769	1.732
Crystal size (mm^3)	0.30×0.44×0.50	0.38×0.42×0.74
μ (cm^{-1})	18.47	16.56
Scan method	$\omega-2\theta$	$\omega-2\theta$
Data collected	$h, k, \pm l, 3 < 2\theta < 44$	$h, k, \pm l, 3 < 2\theta < 44$
No. total observation	3497	3379
No. unique data > $3\sigma(I)$	2318	2577
No. parameters refined	181	175
Largest shift/e.s.d.	0.01	0.08
Largest peak (e Å^{-3})	1.25 (0.89 Å from Sn)	1.42
GOF	0.498	1.733
$R = (\Sigma\|F_o - F_c\|)/\Sigma\|F_o\|$	0.043	0.043
R_w $^a(\Sigma\|F_o - q_c\|w^{1/2})/\Sigma\|F_o\|w^{1/2}$	0.051	0.057

[a] $w = 0.3774(\sigma^2(F) + 0.007204\ F^2)$ for 1; $w = 1.0000/(\sigma^2(F) + 0.001797\ F^2)$ for 3·$C_4H_8O_2$.

Table 2

Positional and equivalent isotropic thermal parameters [a] for 1

Atom	x	y	z	U_{eq}
Sn	0.6359(1)	0.2810(0)	0.9463(0)	0.048(0)
Cl(1)	0.3385(2)	0.3174(1)	0.9736(1)	0.068(1)
Cl(2)	0.6133(3)	0.3412(2)	0.8138(1)	0.079(2)
S(1)	0.5682(2)	0.1019(1)	0.9227(1)	0.059(1)
S(2)	0.9205(2)	0.1807(1)	0.9233(1)	0.064(1)
C(8)	0.7859(9)	0.0788(5)	0.9125(3)	0.053(4)
N	0.8418(8)	−0.0117(4)	0.8969(3)	0.063(4)
C(9)	1.0210(10)	−0.0342(7)	0.8837(5)	0.078(6)
C(10)	0.7258(14)	−0.0975(6)	0.8880(6)	0.091(8)
O(1)	0.6493(7)	0.2306(3)	1.0852(3)	0.058(3)
C(1)	0.7572(10)	0.4047(5)	1.0062(4)	0.060(5)
C(2)	0.7086(9)	0.4093(5)	1.0943(4)	0.055(4)
C(3)	0.6771(8)	0.3048(5)	1.1264(4)	0.053(4)
O(2)	0.6716(7)	0.3032(4)	1.2035(3)	0.067(4)
C(4)	0.6486(12)	0.2064(6)	1.2433(5)	0.076(5)
C(5)	0.8433(9)	0.4623(6)	1.1453(5)	0.067(5)
C(6)	1.0067(9)	0.3985(5)	1.1523(4)	0.059(4)
O(3)	1.0158(7)	0.3155(4)	1.1314(4)	0.078(4)
O(4)	1.1280(6)	0.4492(4)	1.1881(3)	0.073(4)
C(7)	1.2834(10)	0.3887(8)	1.2020(5)	0.082(6)

[a] Equivalent isotropic U_{eq} was defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Preparation

The reaction of $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ with uninegative multidentate ligands such as dithiocarbamate or trispyrazolylborate smoothly afforded **1** or **2**, respectively. However, the treatment of the estertin trichloride with neutral amine, 1,2-dianilinoethane, gave a partial hydrolysis product **3** instead of the amine adduct of the estertin, a reaction already reported [20,21]. In the case of the above partial hydrolysis, the solvent of dichloromethane was used as received. However, when dried dichloromethane was used, no reaction was observed.

The metathetic reaction of **1** or **3** with sodium sulfide in a mole ratio of 1 : 1 afforded the estertin sulfide **4** or **5**, respectively. However, the reaction of **2** with sodium sulfide did not give the analogous product, but instead a solid product which seems not to be a pure compound and could not be easily characterized. The IR spectrum of the solid product indicated that the trispyrazolylborate ligand was dissociated. This reaction seems not to afford the analogous sulfide due in part to the bulky tridentate trispyrazolylborate ligand.

All the products are fairly air-stable solids with sharp melting points. It is noticeable that **5** is not soluble but **4** is soluble in benzene which allows cryoscopic measurement. Compound **3** is only slightly soluble in dioxane. The other compounds are soluble in polar organic solvents, but insoluble in water and saturated hydrocarbons.

Table 3

Positional and equivalent isotropic thermal parameters [a] for $\mathbf{3}\cdot C_4H_8O_2$

Atom	x	y	z	U_{eq}
Sn	1.0336(< 1)	0.1357(< 1)	1.0035(< 1)	0.035(< 1)
Cl(1)	0.9176(1)	0.1778(1)	0.8266(1)	0.053(1)
Cl(2)	0.9545(2)	0.2784(1)	1.0975(1)	0.061(1)
O(1)	0.9221(3)	0.0277(3)	1.0478(3)	0.037(2)
O(2)	1.1546(3)	0.0924(3)	1.1772(3)	0.045(3)
O(3)	1.3422(3)	0.0517(3)	1.2445(3)	0.049(2)
C(1)	1.2050(5)	0.1890(5)	0.9900(5)	0.050(4)
C(2)	1.2961(6)	0.1196(6)	1.0624(6)	0.059(5)
C(3)	1.4200(7)	0.1640(8)	1.0790(7)	0.074(7)
C(4)	1.4717(5)	0.1598(6)	0.9823(5)	0.051(4)
O(4)	1.4370(7)	0.1030(8)	0.9026(6)	0.146(10)
O(5)	1.5635(6)	0.2196(5)	0.9912(4)	0.082(4)
C(5)	1.6280(9)	0.2133(9)	0.8985(7)	0.088(7)
C(6)	1.2581(5)	0.0887(5)	1.1670(4)	0.042(3)
C(7)	1.3138(6)	0.0144(6)	1.3462(5)	0.060(5)
O(1S)	0.2611(5)	−0.0433(4)	0.5804(4)	0.073(1)
O(2S)	0.1686(4)	−0.0356(4)	0.7722(4)	0.066(1)
C(1S)	0.1724(8)	0.0337(7)	0.5921(7)	0.083(2)
C(2S)	0.0960(7)	−0.0088(6)	0.6680(7)	0.076(2)
C(3S)	0.2582(7)	−0.1096(6)	0.7611(7)	0.074(2)
C(4S)	0.3319(6)	−0.0642(6)	0.6848(6)	0.066(2)

[a] Equivalent isotropic U_{eq} was defined as one-third of the thermal of the orthogonalized U_{ij} tensor.

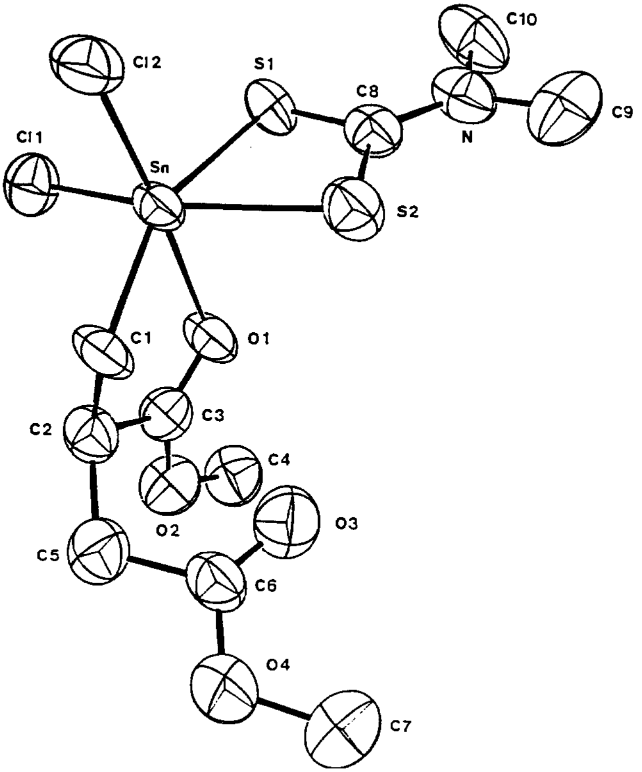

Fig. 1. ORTEP drawing of 1 showing 50% probability thermal ellipsoids and the numbering scheme.

Crystal structures of 1 and 3

The molecular geometry of 1 is depicted in Fig. 1, where the atomic numbering scheme is defined. The bond distances and angles appear in Table 4. The tin atom is hexacoordinated with Cl(1), Cl(2), S(1), S(2), O(1), and C(1) in a distorted octahedral arrangement where Cl(1) and Cl(2) occupy mutually *cis* positions (Cl(1)-Sn-Cl(2), 93.5(1)°). The dithiocarbamate ligand is bonded to the tin atom in an anisobidentate fashion (Sn-S(1), 2.463(2); Sn-S(2), 2.631(2) Å) with a typical small bite angle (S(1)-Sn-S(2), 70.6(1)° [9,10], which is in part responsible for the distortion of the octahedral geometry. A feature of particular interest is that the carbonyl group involved in the six-membered ring in the structure of the starting compound $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$ [15] is released from the tin atom to accommodate a bidentate dithiocarbamate ligand in 1, while the other carbonyl-to-tin coordination in the five-membered ring is retained. Such a result is direct evidence that the five-membered ring is more stable than the six-membered ring in the metallacyclic structure. The bond lengths of Sn-O(1) (2.448(5) Å), Sn-C(1) (2.140(6) Å), Sn-Cl(1) (2.433(2) Å), and Sn-Cl(2), 2.388(2) Å) are slightly longer than the corresponding lengths (Sn-O(1), 2.400(11); Sn-C(1), 2.127(18); Sn-Cl(1), 2.315(4); Sn-Cl(2), 2.379(4) Å) in the starting compound, presumably due to a decrease in Lewis acidity of the tin atom by the partial change of donor atoms.

Table 4

Bond distances (Å) and angles (°) for 1

Sn-Cl(1)	2.433(2)	C(1)-C(2)	1.552(9)
Sn-Cl(2)	2.388(2)	O(1)-C(3)	1.224(8)
Sn-S(1)	2.463(2)	C(2)-C(3)	1.511(9)
Sn-S(2)	2.631(2)	O(2)-C(3)	1.308(8)
Sn-O(1)	2.448(5)	O(2)-C(4)	1.464(9)
Sn-C(1)	2.140(6)	C(2)-C(5)	1.520(9)
S(1)-C(8)	1.744(7)	C(5)-C(6)	1.536(10)
S(2)-C(8)	1.720(7)	O(3)-C(6)	1.160(8)
N-C(8)	1.306(8)	O(4)-C(6)	1.303(8)
N-C(9)	1.456(10)	O(4)-C(7)	1.471(10)
N-C(10)	1.462(11)		
Cl(2)-Sn-Cl(1)	93.5(1)	N-C(8)-S(2)	122.4(6)
S(1)-Sn-Cl(1)	91.1(1)	C(9)-N-C(8)	123.2(7)
S(1)-Sn-Cl(2)	99.1(1)	C(10)-N-C(8)	121.7(7)
S(2)-Sn-Cl(1)	161.0(1)	C(10)-N-C(9)	115.1(7)
S(2)-Sn-Cl(2)	94.3(1)	C(3)-O(1)-Sn	109.5(4)
S(2)-Sn-S(1)	70.6(1)	C(2)-C(1)-Sn	111.8(4)
O(1)-Sn-Cl(1)	83.8(1)	C(3)-C(2)-C(1)	110.9(5)
O(1)-Sn-Cl(2)	175.8(1)	C(5)-C(2)-C(1)	112.5(6)
O(1)-Sn-S(1)	84.1(1)	C(5)-C(2)-C(3)	109.7(6)
O(1)-Sn-S(2)	89.2(1)	C(2)-C(3)-O(1)	124.0(6)
C(1)-Sn-Cl(1)	100.0(2)	O(2)-C(3)-O(1)	123.3(7)
C(1)-Sn-Cl(2)	102.3(2)	O(2)-C(3)-C(2)	112.6(6)
C(1)-Sn-S(1)	155.1(2)	C(4)-O(2)-C(3)	118.8(6)
C(1)-Sn-S(2)	95.1(2)	C(6)-C(5)-C(2)	110.8(6)
C(1)-Sn-O(1)	75.1(2)	O(3)-C(6)-C(5)	123.8(7)
C(8)-S(1)-Sn	88.8(2)	O(4)-C(6)-C(5)	110.5(6)
C(8)-S(2)-Sn	83.9(2)	O(4)-C(6)-O(3)	125.7(7)
S(2)-C(8)-S(1)	116.6(4)	C(7)-O(4)-C(6)	112.6(6)
N-C(8)-S(1)	121.0(6)		

The structure with the labeling scheme for **3** is shown in Fig. 2. The bond distances and angles are given in Table 5. Compound **3** is a centrosymmetric dimer consisting of a planar four-membered ring, Sn_2O_2, which is a parallelogram with different bond lengths of Sn-O(1), 2.008(3) and Sn-O(1)′, 2.201(1) Å and different bond angles of O(1)-Sn-O(1)′ (71.1(1)°) and Sn-O(1)-Sn′ (108.9(2)°). The dioxane molecule solvated is hydrogen bonded to the oxygen of the parallelogram (O(2s) ··· O(1), 2.661(6) Å; H(10) ··· O(2s), 1.84(5) Å). Like the structure of **1**, the carbonyl-to-tin coordination involved in the six-membered ring is also released to afford a hydroxo bridging and thus each tin atom is hexacoordinated with Cl(1), Cl(2), O(1), O(1)′, O(2) and C(1) in a distorted octahedral arrangement with Cl(1) and Cl(2) occupying mutually *cis* positions (Cl(1)-Sn-Cl(2), 95.2(1)°). Thus, the local geometry and bond lengths around the tin atom in **3** are very similar to those in $^{i}PrSn(OH)Cl_2 \cdot H_2O$ [21]. The remarkable difference between the molecular structure of **1** and **3** is that the carbonyl-to-tin coordination of **3** (Sn-O(2), 2.387(4) Å) is shorter than that of **1** (Sn-O(1), 2.448(5) Å). This explains that the electronic effect of the donating atom plays an important role in the coordination chemistry of organotin compounds.

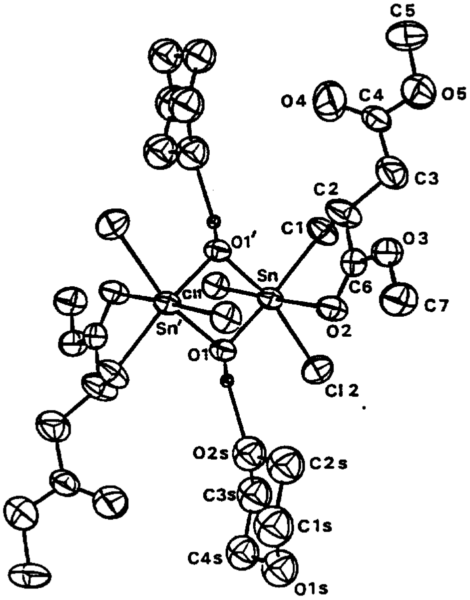

Fig. 2. ORTEP drawing of $3 \cdot C_4H_8O_2$ showing 50% probability thermal ellipsoids and the numbering scheme.

Table 5

Bond distances (Å) and angles (°) for $3 \cdot C_4H_8O_2$

Sn–Cl(1)	2.394(1)	O(3)–C(7)	1.444(7)
Sn–Cl(2)	2.392(2)	C(1)–C(2)	1.507(8)
Sn–O(1)	2.008(3)	C(2)–C(3)	1.514(10)
Sn–O(2)	2.387(4)	C(2)–C(6)	1.504(8)
Sn–C(1)	2.133(5)	C(3)–C(4)	1.449(10)
O(1)–H(10)	0.857(57)	C(4)–O(4)	1.213(9)
O(2)–C(6)	1.235(7)	C(4)–O(5)	1.281(9)
O(3)–C(6)	1.308(7)	O(5)–C(5)	1.499(8)
Cl(2)–Sn–Cl(1)	95.2(1)	C(6)–C(2)–C(3)	114.1(6)
O(1)–Sn–Cl(1)	96.9(1)	C(4)–C(3)–C(2)	114.5(6)
O(1)–Sn–Cl(2)	91.1(1)	O(4)–C(4)–C(3)	125.0(7)
O(2)–Sn–Cl(1)	178.1(1)	O(5)–C(4)–C(3)	112.6(6)
O(2)–Sn–Cl(2)	86.3(1)	O(5)–C(4)–O(4)	122.3(7)
O(2)–Sn–C(1)	84.2(1)	C(5)–O(5)–C(4)	116.1(7)
C(1)–Sn–Cl(1)	102.8(2)	O(3)–C(6)–O(2)	122.4(5)
C(1)–Sn–Cl(2)	105.6(2)	C(2)–C(6)–O(2)	122.7(5)
C(1)–Sn–O(1)	152.6(2)	C(2)–C(6)–O(3)	114.9(5)
C(1)–Sn–O(2)	75.6(2)	H(10)–O(1)–Sn	136.0(33)
Cl(1)–Sn–O(1)′	93.0(1)	C(6)–O(2)–Sn	108.9(3)
Cl(2)–Sn–O(1)′	161.2(1)	C(7)–O(3)–C(6)	119.2(5)
O(1)–Sn–O(1)′	71.1(1)	C(2)–C(1)–Sn	109.4(4)
O(2)–Sn–O(1)′	85.9(1)	C(3)–C(2)–C(1)	114.3(6)
C(1)–Sn–O(1)′	89.0(2)	C(6)–C(2)–C(1)	111.5(5)
Sn–O(1)–Sn′	108.9(2)		

Spectroscopic properties

Among the IR stretching modes, the ν(C=O) bands in the region of 1650–1750 cm^{-1} have been known to depend on the nature of carbonyl-to-metal bonding [22–24]. The appearance of two strong bands in the IR spectra of **1** (1748, 1657 cm^{-1}) and **3** (1741, 1652 cm^{-1}) with a separation value of about 90 cm^{-1} indicates coexistence of the coordinated and uncoordinated carbonyl groups, which is consistent with the above-mentioned X-ray structure. The C=O stretching frequencies of the coordinated carbonyl groups in **1** (1657 cm^{-1}) and in **3** (1652 cm^{-1}) are not significantly different, in spite of the remarkable difference between the bond lengths of Sn–O(1) (2.448(5) Å) in **1** and Sn–O(2) (2.387(4) Å) in **3**, since the dative Sn–O interactions are relatively weak and do not affect the relevant C=O bonding as seen from their proximate bond lengths of **1** (C(3)–O(1), 1.224(8) Å) and **3** (C(6)–O(2), 1.235(7) Å).

In contrast, the single ν(C=O) band of **2** (1732 cm^{-1}), **4** (1738 cm^{-1}), and **5** (1734 cm^{-1}) are in the same region as that of the uncoordinated ester groups illustrated in $(CH_3OOCCH_2CH_2)_2Sn(S_2CNMe_2)Cl$ (1725 cm^{-1}) [14], which indicates that all the carbonyl groups in **2**, **4** and **5**, are not coordinated to the tin atom. The ^1H NMR also discloses the bonding nature of the carbonyl group in solution. From our previous criterion [9,10], the $\delta(CH_3O–)$ values of soluble compounds **1** (4.0, 3.7 ppm), **2** (3.7 ppm), and **4** (3.7 ppm), strongly indicate that the bonding mode of the carbonyl groups of the itaconate ligand of these complexes in the solid state is retained in solution.

The ^{119}Sn NMR spectroscopy [25–31] provides information on the coordination number of the tin atom in solution. The $\delta(^{119}Sn)$ values of **1** (−404.5 ppm in $CDCl_3$) and **2** (−429.1 ppm in $CDCl_3$) are near to that (−386.4 ppm in $CDCl_3$) of $CH_3OOCCH_2CH_2Sn(S_2CNMe)Cl_2$ [9] and that (−482.4 ppm) of $CH_3OOCCH_2CH_2Sn\{(Pz)_3BH\}Cl_2$ [12], respectively, which have been known to involve a hexacoordinated tin atom. The ^{119}Sn chemical shift of **1** implies that the structure of hexacoordinated tin is retained in solution. For **2**, assuming from the above-mentioned spectroscopic data that all the carbonyls are released from the tin atom, then the hexacoordinated region of the $\delta(^{119}Sn)$ value suggests that the trispyrazolylborate ligand is tridentate as expected. On the other hand, the drastic deshielding of the chemical shift for **4** ($\delta(^{119}Sn)$ −246.4 ppm) compared with that of **1** strongly suggests that the tin atom is pentacoordinated in **4**. The spectroscopic data together with cryoscopic measurement of **4** suggest that its structure is similar to that of the dimeric form $[CH_3OOCCH_2CH_2Sn(S_2CNMe_2)S]_2$ with an Sn_2S_2 four-membered ring as reported in our previous paper [10]. The structure of **5** also seems to be similar to the Sn_2S_2 ring moiety although its cryoscopic data could not be measured because of its low solubility in benzene.

In conclusion, the NMR data in solution are consistent with the structures in the solid state. The study of the title compounds indicates that the bonding mode of the carbonyl group is very sensitive to the donating atom around the tin atom and that the coordination involved in the six-membered ring is weaker than in the five-membered ring.

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