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Synthesis and characterization of new di-*n*-butyl [bis{dimethyl-2-(3-oxo-5-phenyl(4-subtituted)penten-5-ato)malonates}]tin(IV): The crystal structure of di-*n*-butyl[bis{dimethyl-2-[5-(4-nitrophenyl)-3-oxo-penten-5-ato]malonate}]tin(IV)

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Abstract

The synthesis of four new di-*n*-butyl[bis{dimethyl-2-(3-oxo-5-phenyl(4-subtituted)penten-5-ato)malonates}]tin(IV) 2a-2d is reported. These complexes have been characterized by ¹H, ¹³C, ¹¹⁹Sn NMR, HMQC, HMBC, infrared spectroscopy and mass spectrometry (FAB). Their structures in CDCl₃ solution show a distorted octahedral geometry with a *trans* disposition of the *n*-butyl substituents. The ¹¹⁹Sn NMR study at low variable-temperature indicates the presence of *trans anti-* and *syn-* isomers, and solid-state ¹³C and ¹¹⁹Sn NMR spectra of compound 2d give also evidence of the mixture of *trans* isomers. The X-ray diffraction study of compound 2d at 168 K shows only the *trans syn-* isomer, where the metal is six-coordinated in a skewed trapezoidal bipyramidal (STB) geometry.

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1. Introduction

Organotin(IV) enolates have been the subject of studies with electrophiles such as carbonyl compounds [1-3]and organic halides [4-8]. They usually exist as a mixture of *C*-stannyl ketone and *O*-stannylenolate, the ratio depending on structural factors [9-11]. NMR studies have indicated that tin(IV)enolates exhibit high-coordinated *O*-stannyl enolates in the presence of HMPA, which may promote completely selectivity coupling at the halides moiety of α -haloketones [12]. Tin(IV)enolates have been prepared by transmetallation of lithium enolates, transesterefication of enolates and hydrostannation of conjugate carbonyl compounds [13]. In spite of the fact that tin(IV)enolates are relativity more stable than their lithium and silicon analogues, there are few reports concerning their structures [14]. On the other hand, it is known that β -diketones exist as a mixture of diketonic and keto-enolic tautomers and have been subject to investigation on their coordination behaviour with several metals [15–17]. In particular organotin(IV) derivatives of β -diketones have been synthesized [17– 22] for structural studies [16,18–26] as well as for their antitumor activity [17,20,22]. Recently, we reported the

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Fig. 1. Synthesis of di-n-butyltin(IV) enolates 2a-2d.

synthesis of new di-n-butylhydroxytin(IV)enolates, which exhibit higher states of aggregation in solution at low temperature and their FAB mass spectra showed a dimer structure [27]. Our current interest in the synthesis of organotin(IV) compounds [28-31] prompted us to extend our investigations to the synthesis of new organotin(IV) enolates, which could have biological properties [32]. This paper describes the synthesis of four new di-n-butyl[bis{dimethyl-2-(3-oxo-5-phenyl(4-subtituted)penten-5-ato)malonates}tin(IV) 2a–2d by the reaction of di-n-butyl(IV) oxide and 1,3-diketone malonates 1a-1d in a 1:2 molar ratio, in which 1a-1d exist as enolates [33,34] (Fig. 1). All compounds were characterized by ¹H, ¹³C, ¹¹⁹Sn NMR, HMQC, HMBC, infrared spectroscopy and mass spectrometry (FAB). The compound 2d was also characterized by solid state ¹³C and ¹¹⁹Sn NMR and its structure was further established by a single crystal X-ray diffraction study at 168 K.

2. Results and discussion

The reaction of 1,3-diketone malonates 1a-1d with di-n-butyltin(IV) oxide in a 2:1 ratio, led to di-n-butyltin(IV)enolates 2a-2d (Fig. 1). The compounds 2a-2c were obtained as oils, while 2d was a solid. The ¹H NMR spectra in CDCl₃ of all the compounds 2a-2dshow only one set of signals for each magnetically equivalent H nucleus, thus both $(n-Bu)_2$ Sn protons and those of the ligands are in a 1:2 ratio, respectively. This can indicate the formation of a unique species or a fastexchanging equilibrium on the NMR timescale. The H6 and H8 protons appeared as broad signals (0.1 and 0.19 ppm) at higher field with respect to the free ligands (1a-1d), which suggests a shielding of these protons upon coordination [16], giving evidence for the formation of a Sn-O bonded enolate moiety and a $C=O \rightarrow Sn$ coordination bond, while the broadening of these signals can suggest a fluxionality between the possible isomers [16,19]. ¹H NMR data are summarized in Table 1. The ¹³C NMR data for compounds **2a–2d** are summarized in Table 2. For all compounds the assignment of the *n*-butyl moieties are based on ¹H–¹³C HMQC and ¹H–¹³C HMBC experiments. Thus α and β carbons correlate with the broad signal around 1.5 ppm of H α and H β . The γ -carbon correlates with the signal around 1.27 ppm and δ -carbon correlates with the triplet signal of the methyl group.

The unambiguous assignment of H β and H γ are based on ${}^{1}\text{H}{-}^{13}\text{C}$ HMBC, where the signal of the γ -carbon correlates with the signal around 1.27 ppm. All these compounds exhibit ${}^{1}J({}^{119}Sn-{}^{13}C), {}^{2}J({}^{119}Sn-{}^{13}C)$ and ${}^{3}J({}^{119}Sn{}^{-13}C)$ coupling constants within the range of trans six-coordinated tin compounds [16,17,19-21,26,38]. In particular, ${}^{1}J({}^{119}Sn-{}^{13}C)$ values for compounds 2a-2d are 872, 879, 866 and 860 Hz, respectively and on the basis of the empirical equation of Holecek and Lycka [39], it was possible to determine θ (C–Sn– C) of these compounds in CDCl₃ solution: the calculated values are 160.2° for 2a, 160.9° for 2b, 159.7° for 2c and 159.1° for 2d, which indicate that the tin atom is in a skewed trapezoidal bipyramidal environment, where the trapezoidal plane is defined by four oxygen atoms derived from two asymmetrically coordinating enolate ligands and the tin-bound organo substituents are orientated over the weakly bound oxygen atoms [17,21]. The value calculated for 2d agrees well with the angle of $157.1(3)^{\circ}$ found in the crystal structure.

The ¹¹⁹Sn NMR spectra of 2a-2c at 19 °C and for 2d at 25 °C in chloroform show only one peak, which can indicate a unique species or a fast exchanging equilibrium on the NMR time scale (Table 3). Their chemical shifts are within the range of di-*n*-butyltin(IV) hexacoordinated compounds [19,23,35–38]. In order to obtain more information about the structure of these compounds, a variable-temperature NMR study of 2a-2d

Table 1 ¹H NMR data for compounds **2a–2d**



Compound	<i>n</i> -BuSn	H8	H9	H10	H12	H6	Harom
2a	H _δ : 0.78 (t) J = 7.2 H _γ : 1.27 (se) J = 7.2 H _{α,β} : 1.48 (m)	2.42 (b)	2.26 (q) J = 7.4	3.50 (t) J = 7.4	3.72 (s)	5.97 (s)	7.41 (m) 7.87 (d) <i>J</i> = 7.5
2b	H _δ : 0.78 (t) J = 7.2 H _γ : 1.25 (se) J = 7.2 H _{α,β} : 1.44 (m)	2.42 (b)	2.26 (q) J = 7.4	3.52 (t) J = 7.4	3.71 (s)	5.97 (s)	7.42 (d) 7.82 (d) J = 8.2
2c	H _δ : 0.79 (t) J = 7.3 H _γ : 1.28 (se) J = 7.3 H _{α,β} : 1.50 (m)	2.47 (b)	2.27 (q) J = 7.3	3.50 (t) J = 7.3	3.73 (s)	5.99 (s)	7.69 (d) 7.98 (d) <i>J</i> = 8.4
2d	H_{δ} : 0.78 (t) J = 7.3 H_{γ} : 1.29 (se) J = 7.3 H_{α} : 1.50 (b)	2.49 (bt) J = 7.3	2.27 (q) J = 7.3	3.50 (t) J = 7.3	3.73 (s)	6.00 (s)	8.02 (d) 8.26 (d) J = 8.8

 δ (¹H) relative to Si(CH_3)_4; δ (¹¹⁹Sn) relative to Sn(CH_3)_4; solvent CDCl_3.

The protons of the *t*-Bu group exhibit a singlet at 1.34 ppm.

b: broad; bt: broad triplet; d: doublet; m: unresolved pattern; q: quartet; s: singlet; t: triplet; se: sextet and |J| Hz.

was undertaken from 45 to $-25 \,^{\circ}$ C for **2a–2c** and in the case of 2d until -45 °C. Thus the spectra at 45 °C exhibit one signal within the range typical of hexacoordinated tin(IV) compounds, the same result was observed upon lowering the temperature to $-5 \,^{\circ}\text{C}$ for 2a and 2b, but not for 2c and 2d, which showed two absorptions with slightly different chemical shifts but equal intensity, indicating the presence of both trans syn- and anti-isomers, in which the alkyl groups must be *trans*, and the isomerism is attributed to a different arrangement of the two ligands as shown in Fig. 2 [19,21]. The same result is found for compound 2d at 5 °C in which the signals are in ca. 1:4 ratio. All compounds show these two signals at -25 °C, with equal intensity for 2a and 2b, while for 2c and 2d in ca. 1:1.5 ratio. The spectrum of 2d at -35 °C showed three signals in a ca. 1:2:4 ratio, the first one at δ –183.54 associated to a five-coordinate species and the other two to the six-coordinate species, this result suggests the existence of an equilibrium between trans isomers through

a five-coordinate species. Its spectrum at -45 °C exhibited only the signals that belong to the *trans* isomers in ca. 1:2 ratio.

These results show the existence of the mixture of trans isomers in solution at low temperature, where chemical shifts of the major isomers for 2c and 2d are at lower frequency. The solid state ¹¹⁹Sn NMR spectrum of 2d (Fig. 3) at room temperature exhibits two signals at -386.07 and -402.10 in a ca. 1:1.5 ratio, as was observed at -25 °C in solution. Its solid state 13 C NMR spectrum at room temperature exhibits a set of signals for each magnetically equivalent C nucleus, except for C₅ and C₇, which exhibit two signals each, at δ 200.76, 199.00 and 177.30, 174.40, respectively. The chemical shifts of the major isomer are at a lower frequency than those on the minor isomer, in approximately 0.8:1 ratio (Fig. 4). This result can be attributed again to a different arrangement of the two ligands, giving evidence of the existence of the two transisomers.

Table 2 ¹³C NMR data for compounds **2a–2d**



Chemical shifts in ppm with respect to TMS, ${}^{n}J({}^{13}C-{}^{119/117}Sn)$ coupling constant between square brackets.

The IR data are summarized in Table 4. The spectra exhibit two $v_{(C=O)}$ carbonyl oxygen bands, one of them assigned to the CO₂CH₃ groups in the range between 1740 and 1734 cm⁻¹ and the other one to the enolate group between 1615 and 1540 cm⁻¹. Also a broad band due to Sn–O is observed between 434 and 302 cm⁻¹.

Table 3 ¹¹⁹Sn NMR variable-temperature data for compounds **2a–2d**

	Compound					
	2a	2b	2c	2d		
45 °C	-382.93	-385.37	-379.12	-377.15		
35 °C				-377.44		
19 °C	-383.74	-385.97	-379.66	-377.59^{a}		
15 °C				-378.09		
5 °C				-377.25[1]		
				-379.61[4]		
−5 °C	-384.39	-386.45	-379.90[1]	-376.46[1]		
			-381.07[1]	-379.61[1]		
−15 °C				-376.56[1]		
				-380.01[1]		
−25 °C	-383.81[1]	-386.54[1]	-379.07[1]	-376.60[1]		
	-385.08[1]	-386.84[1]	-381.74[1.5]	-380.16[1.5]		
−35 °C				-183.54[1]		
				-376.60[2]		
				-380.16[4]		
−45 °C				-376.60[1]		
				-380.21[2]		

 δ : (ppm); solvent CDCl₃.

^a Spectrum obtained at 25 °C [ratio].

The FAB mass spectra for 2a-2d exhibit the molecular ion, which by the loss of one *n*-Bu group give the base peaks. Therefore, the fragment ion corresponding to the loss of one ligand from the molecular ion is observed. The spectra show others fragment ions and a possible fragmentation pattern is given in Fig. 5.

Compound **2d** was recrystallized from methanol to provide suitable colourless crystals for X-ray diffraction. Intensity data were collected at 168 K and the crystal structure corresponds to one of the two isomers seen in solution and solid state. An ORTEP view of the compound with the numbering scheme is given in Fig. 6.

Bond distances are listed in Table 5. The tin atom is sixcoordinate, showing the metal in skewed trapezoidal bipyramidal arrangement (STB), where four O atoms from two ligands, and two C atoms from the *n*-butyl groups form the coordination polyhedron. This is a distorted octahedron characterized by two different sets of



Fig. 2. trans-isomers for compound 2a-2d.



Fig. 3. Solid state ¹¹⁹Sn NMR spectrum for compound 2d.



Fig. 4. Solid state ¹³C NMR spectrum for compound 2d.

Table 4 IR data for compounds **2a–2d**

Compound	C–H _{arom}	C–H _{aliph}	C=O	C=C-C-O	Sn–O
2a ^a	3062	2954	1734	1594	440-304
		2868		1559	
				1540	
2b ^a	3032	2956	1740	1615	434-302
		2868		1543	
2c ^a	3036	2956	1736	1598	436-318
		2870		1560	
2d ^b	3080	2954	1738	1610	450-312
		2928		1570	
		2870			

v (cm⁻¹), ^aNet liquid, ^bFilm.

Sn–O bond. In this context, one ligand has a short bond length Sn₁–O₁ = 2.112(4) Å (primary bond) and a longer one, Sn₁–O₂ = 2.292(5) Å (secondary bond). For the other ligand, the corresponding values are Sn₁– O₃ = 2.115(3) Å and Sn₁–O₄ = 2.349(4) Å. The *n*-Bu groups are *trans* to each other although a strong distortion from 180° is found and the angle is 157.1(3)°. This asymmetry in bond length is a result of the asymmetric nature of the ligand, as well as the presence of the following intermolecular contacts: NO(6)···H(191)_{arom} 2.5827(0.0065), C=O(13)···H(31)_{arom} 2.2576(0.0088), C=O(9)···H(281)_{methynic}, 2.5862(0.0101), C=O(15)··· H(121)_{methynic} 2.5252(0.0158) and C=O(13)···H(81)_{vinylic} 2.3372(0.0077) Å. Besides the intermolecular contacts,



Fig. 5. FAB mass spectra for compounds 2a-2d.



Fig. 6. Molecular structure of $C_{40}H_{50}N_2O_{16}Sn$ and crystallographic numbering scheme.

Table 5 Bond distances selected (Å) for $C_{40}H_{50}N_2O_{16}Sn$ (2d)

Sn(1)–O(1)	2.112(4)	C(1)–C(8)	1.387(9)		
Sn(1)–O(2)	2.292(5)	C(8)–C(9)	1.396(10)		
Sn(1)–O(3)	2.115(4)	C(9)–O(2)	1.261(9)		
Sn(1)–O(4)	2.349(4)	O(3)–C(17)	1.289(7)		
Sn(1)–C(33)	2.133(9)	C(17)–C(24)	1.380(9)		
Sn(1)–C(37)	2.134(8)	C(24)–C(25)	1.416(9)		
O(1)–C(1)	1.307(7)	O(4)–C(25)	1.257(8)		

there are the following intramolecular contacts: NO(6)... H(41)_{arom} 2.4553(72), NO(5)...H(61)_{arom} 2.3962(72), C-O(7)...H(121)_{methynic} 2.4265(84), NO(11)...H(221)_{arom} 2.4682(65), NO(12)...H(201)_{arom} 2.4576(74), C=O(15)... H(281)_{methynic} 2.5368(101) and C-O(14)...H(271)_{methylenic} 2.5674(61) Å, which are significantly shorter than the sum of van der Waals radii of oxygen and hydrogen (2.70 Å) [40].

The six-membered ring Sn(1), O(1), C(1), C(8), C(9), O(2) adopts an intermediate between envelope and screw-boat conformation, while the ring Sn(1), O(3), C(17), C(24), C(25), O(4) adopts an intermediate envelop and twist conformation, from their puckering parameters calculated according to Cremer and Pople [41,42], which are: Q = 0.261, $\theta = 60.35^{\circ}$, $\phi = 10.56^{\circ}$ and Q = 0.241, $\theta = 62.06^{\circ}, \phi = 10.64^{\circ},$ respectively. Therefore the out of-plane displacements calculated for the atoms of each ring are: Sn(1), -0.178(3); O(1), 0.091(6); C(1), 0.034(8); C(8), -0.073(8); C(9), -0.014(9); O(2), 0.139(7) and Sn(1), -0.166(3); O(3), 0.122(6); C(17), -0.001(8); C(24), -0.075(8); C(25), 0.030(8); 0(4), 0.090(6) A, which give evidence that the six-membered rings do not lie in a plane [43]. In addition, the equatorial plane made by the four O atoms has the oxygen atoms associated with the primary bonds, O(1) and O(3), closer to each other than those associated with the secondary bond, O(2) and O(4), as shown by the corresponding angles O(3)-Sn(1)- $O(1) = 79.51(16)^{\circ}$ and $O(4)-Sn(1)-O(2) = 118.60(17)^{\circ}$, as well as O(1)-O(3) and O(2)-O(4) intramolecular distances of 2.7034(63) and 3.9915(74) Å, respectively. Therefore, bond angle values for C(33)–Sn(1)–O(1), C(33)–Sn(1)–O(3), C(37)–Sn(1)–O(1), C(37)–Sn(1)–O(3) are 99.80(3)°, 97.10(3)°, 99.90(2)° and 97.90(2)°, which are bigger than those of C(33)-Sn(1)-O(2) 85.20(3)°, C(33)-Sn(1)-O(4) 84.50(3)°, C(37)-Sn(1)-O(2) 86.40(3)° and C(37)–Sn(1)–O(4) 80.90(2)°, indicating that the *n*-Bu groups are folded towards the side of the secondary bonds.

3. Conclusion

The new diorganotin(IV) compounds 2a-2d were obtained as enolate derivatives. The tin atom is hexacoordinated in a skewed trapezoidal bipyramidal (STB) geometry according to their spectroscopic data in solution. Their ¹¹⁹Sn variable-temperature NMR studies provide information of the existence of *anti* and *syn* trans isomers, the *syn* isomer being in the major proportion at low temperature. The same result was observed in the solid state ¹³C and ¹¹⁹Sn NMR for compound **2d**, while its X-ray diffraction study at 168 K shows only the *syn* species, which exhibits interesting intermolecular contacts, NO(6)…H(191)_{arom}, C=O(13)…H(31)_{arom}, C=O(13)… H(121)_{methynic}, C=O(9)…H(281)_{methynic} and C=O(13)… H(81)_{vinylic}.

The solid state NMR data, as well as low-temperature NMR studies should mirror more closely the structure deduced from the X-ray crystal structure analysis at 168 K where the molecules are effectively locked into place by intermolecular forces, therefore it is possible determine that the major product corresponds to the *trans-syn* isomer and the minor to the *trans-anti* isomer.

4. Experimental

4.1. General procedure and measurements

The reagents were purchased from Aldrich Co. 1,3-Diketone malonates **1a–1d** were prepared according to the literature [33,34]. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on Jeol GLX-270, Jeol Eclipse-400 and Bruker Avance 300-DPX spectrometers, CDCl₃ was used as solvent. The solid state ¹¹⁹Sn and ¹³C CP-MAS NMR spectra for compound **2d** were obtained on a Bruker ASX300 at 10.7 and 10.73 KHz, respectively. High resolution mass spectra (FAB) were obtained with a Jeol JMS-AX 505 mass spectrometer, and infrared spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrometer. The melting point for compound **2d** was measured in an open capillary tube on a Gallemkamp MFB-595 apparatus and it was uncorrected.

4.2. Preparation of compounds 2a-2d

The procedure outlined below is general for the preparation of compounds 2a-2d.

4.2.1. Synthesis of di-n-butyl[bis{dimethyl-2-(3-oxo-5-phenylpenten-5-ato) malonate}]tin(IV) (2a)

A solution of 63.6 mg (0.20 mmol) of **1a** in 10 ml of benzene was placed in a flask equipped with a magnetic stirrer and Dean-Stark trap and 25.7 mg (0.1 mmol) of di-*n*-butyltin(IV) oxide were added. The suspension was refluxed for 8 h. After being cooled to room temperature, the solvent was evaporated under vacuum. The residue was treated with chloroform, the solution was filtered and the solvent was evaporated under vacuum to yield 41 mg (49%) of compound 2a as a yellow oil.

4.2.2. Synthesis of di-n-butyl[bis{dimethyl-2-(5-[4-tertbutylphenyl]-3-oxo-penten-5-ato)malonate}]tin(IV) (2b)

57 mg (0.16 mmol) of compound **1b** and 20.3 mg (0.08 mmol) of di-*n*-butyltin(IV) oxide gave 60 mg (78%) of compound **2b** as a yellow oil.

4.2.3. Synthesis of di-n-butyl[bis{dimethyl-2-(5-[4-trifluoromethylphenyl]-3-oxo-penten-5-ato)malonate}]tin(IV) (2c)

81.7 mg (0.22 mmol) of compound 1c and 27.3 mg (0.11 mmol) of di-*n*-butyltin(IV) oxide gave 95 mg (88%) of compound 2c as a yellow oil.

4.2.4. Synthesis of di-n-buty[bis{dimethyl-2-(5-[4-nitropheny]-3-oxo-penten-5-ato)malonate}]tin(IV) (2d)

131.2 mg (0.37 mmol) of compound 1d and 46.6 mg (0.19 mmol) of di-*n*-butyltin(IV) oxide gave a solid, which was recrystallized from methanol to yield 95 mg (54%) of compound 2d, m.p. 93–94 °C.

4.3. Crystal structure determination of compound 2d

Diffraction data from compound 2d were collected on an Enraf-Nonius Kappa CCD diffractometer at 168 K. Compound 2d, C₄₀H₅₀N₂O₁₆Sn (MW 933.53), crystallized in the space group $P\overline{1}$, triclinic, from methanol as yellow light rectangular prisms, size: $0.45 \times 0.33 \times 0.21$ mm³ with a = 10.0920(2), b = 13.0880(4), c = 17.3920(2) Å, $V = 2142.38(17) \text{ Å}^3, \ \alpha = 75.432(10^\circ), \ \beta = 86.744(15^\circ),$ $\gamma = 74.502(11^{\circ}); \quad \rho = 1.447 \text{ g/cm}^3, \quad Z = 2, \quad \mu = 0.668$ mm^{-1} , $F(0\ 0\ 0) = 964$. Data collection: a total of 32 417 reflections were measured ($2^{\circ} > \theta > 26^{\circ}$), 9831 were independent and of these 3885 were considered observed $[F_{o} > 4.0\sigma(F_{o})]$. Solution and refinement: direct methods, all non hydrogen atoms were refined anisotropically, R = 0.0606, Rw = 0.0570, $w = 1/\sigma^2$, GoF = 1.1308, largest residual electron density peak/hole in the final difference map: $0.79/-0.50 \text{ e} \text{ Å}^{-3}$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [44]. Data reduction were performed by Denzo [45]. All calculations were carried out using the CRYSTALS program package [46] and the molecular graphics by the CAMERON program [47,48].

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Appendix A. Supplementary data

Crystallographic data for **2d** has been deposited at the Cambridge Crystallographic Data Center, CCDC No. 223635. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-366-033; e-mail: deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version at doi:10.1016/j.poly.2005.02.024.

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