

**INFRARED,  $^{119}\text{Sn}$ ,  $^{13}\text{C}$  AND  $^1\text{H}$  NMR,  $^{119}\text{Sn}$  AND  $^{13}\text{C}$  CP/MAS NMR AND MÖSSBAUER SPECTRAL STUDY OF SOME TRIBUTYLSTANNYL CITRATES AND PROPANE-1,2,3-TRICARBOXYLATES**

Jaroslav HOLEČEK<sup>a1,\*</sup>, Antonín LYČKA<sup>b</sup>, David MICÁK<sup>a</sup>, László NAGY<sup>c</sup>, György VANKÓ<sup>d</sup>, Jiří BRUS<sup>e</sup>, S. Shanmuga Sundara RAJ<sup>f</sup>, Hoong Kun FUN<sup>g1</sup> and Seik Weng NG<sup>g</sup>

<sup>a</sup> Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic; e-mail: <sup>1</sup> jaroslav.holecek@upce.cz,

<sup>b</sup> Research Institute for Organic Syntheses, 532 18 Pardubice-Rybitví, Czech Republic; e-mail: antonin.lycka@vuosas.cz

<sup>c</sup> Department of Inorganic and Analytical Chemistry, Attila József University, H-6701 Szeged, Hungary; e-mail: laci@chem.u-szeged.hu

<sup>d</sup> Department of Nuclear Chemistry, Lóránt Eötvös University, 1518, Budapest, Hungary; e-mail: vank@para.chem.elte.hu

<sup>e</sup> Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic, 162 06 Prague 6, Czech Republic; e-mail: brus@imc.cas.cz

<sup>f</sup> X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM Penang, Malaysia; e-mail: <sup>1</sup> hkfun@usm.my

<sup>g</sup> Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia; e-mail: h1nswen@umcsd.um.edu.my

Received March 19, 1999

Accepted June 8, 1999

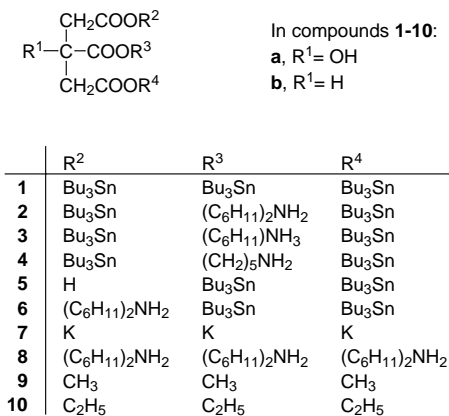
*Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday.*

Six tributylstannyl citrates and three tributylstannyl propane-1,2,3-tricarboxylates of the formula  $\text{R}^1\text{C}(\text{CH}_2\text{COOR}^2)(\text{COOR}^3)(\text{CH}_2\text{COOR}^4)$  ( $\text{R}^1 = \text{OH}$  or  $\text{H}$ ,  $\text{R}^2, \text{R}^3, \text{R}^4 = \text{H}, \text{Bu}_3\text{Sn}, \text{C}_6\text{H}_{11}\text{NH}_3, (\text{C}_6\text{H}_{11})_2\text{NH}_2$  or  $(\text{CH}_2)_5\text{NH}_2$ ) have been synthesised, and their solution and solid-state structures studied by infrared,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  CP/MAS NMR and  $^{119}\text{Sn}$  Mössbauer spectroscopies. In non-coordinating solvents, the compounds exist as isolated molecules or ionic-pairs with their tin atoms in pseudotetrahedral environments. In coordinating solvents, the tin atoms in the compounds are five-coordinate owing to the participation of the solvent in bonding; and their *trans*-trigonal bipyramidal coordination spheres consist of the *ipso*-carbon atoms of the butyl substituents in equatorial plane, and the solvent molecule and the oxygen atom of the monodentate carboxyl group in axial positions. A part of tributylstannyl groups together with some bidentate bridging carboxylate groups form polymeric chains in the solid state of citrates and propane-1,2,3-tricarboxylates. Also dioxastanna-rings with the participation  $\alpha$ -hydroxycarboxylate fragments

and one of the tributylstannyl groups occur probably in some citrates in the solid state. The spectroscopic assignment for the citrate has been confirmed by crystal structure analysis.

**Key words:** Stannanes; Organotin compounds; Citrates; Propane-1,2,3-tricarboxylates; IR spectroscopy; NMR spectroscopy,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$ ; CP/MAS NMR spectroscopy,  $^{13}\text{C}$  and  $^{119}\text{Sn}$ ; Mössbauer spectroscopy; Crystal structure.

Among organyltin(IV) compounds, the triorganyltin(IV) monocarboxylates have been the most well-studied in terms of synthesis, properties, structures and reactivities<sup>1</sup>, this class of compounds commanding more attention owing to their industrial applications. To a lesser extent, the analogous triorganyltin(IV) derivatives of dicarboxylic and polycarboxylic acids have also been studied, and for the dicarboxylic acids, a number of dicyclohexylammonium triorganylstannyl dicarboxylates have been crystallographically authenticated<sup>2-4</sup>. For the tricarboxylic acids in particular, in addition to the neutral tris[triorganyltin(IV)] carboxylates that result from the condensation between the triorganyltin hydroxides/hemioxides and the tricarboxylic acids, mixed esters and even ionic salts of mixed esters can also be synthesized. To date, compounds derived from tricarboxylic acids have not been studied, except for the tributylstannyl derivative of nitrilotriacetic acid<sup>5</sup>. The present study reports the spectroscopic features of selected tributylstannyl citrates and propane-1,2,3-tricarboxylates (Scheme 1), (where  $\text{R}^1$  is OH (series **a**, the citrates) or H (series **b**, the propane-1,2,3-tricarboxylates),  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  are the same or different H,  $\text{Bu}_3\text{Sn}$ ,  $(\text{C}_6\text{H}_{11})_2\text{NH}_2$ ,  $\text{C}_6\text{H}_{11}\text{NH}_3$  or  $(\text{CH}_2)_5\text{NH}_2$ ) in solution and in the solid state by using infrared,  $^{119}\text{Sn}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR,  $^{119}\text{Sn}$  and  $^{13}\text{C}$  CP/MAS NMR and Mössbauer spectroscopies.



SCHEME 1

## EXPERIMENTAL

### Preparation of Compounds

Compound **1a** was prepared by heating anhydrous citric acid (0.34 g, 1.8 mmol) and tributylstannyl methanolate (1.70 g, 5.3 mmol) in a benzene–ethanol mixture (1 : 1, 50 ml) for 3 h at 50 °C. The solvent was then reduced to *ca* 20 ml. The pure compound was obtained as a white solid (1.52 g, 81%) after recrystallisation of the crude product from chloroform. Compound **1b** was synthesised by the same procedure from the reaction of propane-1,2,3-tricarboxylic acid (0.58 g, 3.3 mmol) and tributylstannyl methanolate (3.18 g, 9.9 mmol) in benzene (30 ml) (3.13 g, 91% yield). Compound **5** was prepared from citric acid monohydrate (1.0 g, 4.7 mmol) and hexabutyldistannoxane (2.8 g, 4.7 mmol) in benzene; the water from the condensation was removed azeotropically. Under the same conditions, compounds **2a–4a** and **2b** were prepared from the corresponding acids, amines and hexabutyldistannoxane (molar ratio 1 : 1 : 1), as were compounds **6a** and **6b** (molar ratio 1 : 2 : 1/2) in benzene–ethanol (1 : 1). For example, citric acid monohydrate (2.0 g, 9.5 mmol), dicyclohexylamine (1.7 g, 9.5 mmol) and hexabutyldistannoxane (5.7 g, 9.9 mmol) were heated in 60 ml of benzene–ethanol and the water was azeotropically removed. The volume of the solution was reduced to about a third; slow cooling of the solution afforded compound **2a** as a white solid. For all syntheses, the crude products were dried *in vacuo* at moderately elevated temperatures (*i.e.*, below the melting points of the compounds) to the constant mass. The composition of the new compounds were elucidated by the chemical elemental analysis (Table I) before the compounds were subjected by <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy (Tables II and III).

### Infrared Spectra

Infrared spectra (Table IV) were recorded in chloroform solutions and as paraffin suspensions on a Perkin–Elmer 684 instrument connected to a DS data station.

### Solution and Solid-State NMR Spectra

<sup>1</sup>H (360.13 MHz), <sup>13</sup>C (90.566 MHz) and <sup>119</sup>Sn (134.29 MHz) NMR spectra were measured on a Bruker AMX 360 spectrometer in 5 mm tuneable probes as 5–30% solutions or as saturated solutions in deuterochloroform, hexadeuteriodimethyl sulfoxide or tetradeuteriomethanol at 300 K. The <sup>13</sup>C chemical shifts were referenced to the solvent signals and these were recalculated to the  $\delta$ -scale ( $\delta(^{13}\text{C})$  77.00 (CDCl<sub>3</sub>), 39.60 (CD<sub>3</sub>)<sub>2</sub>SO and 48.12 ppm (CD<sub>3</sub>OD)). The  $\delta(^1\text{H})$  and  $\delta(^{119}\text{Sn})$  chemical shifts were referenced to the internal hexamethyldisiloxane ( $\delta$  0.05 ppm) and external tetramethylstannane ( $\delta$  0.0 ppm) standards. An unambiguous assignment of the <sup>1</sup>H and <sup>13</sup>C NMR signals was carried out by a combination of one-dimensional (selective INEPT, differential NOE) and two-dimensional (H,H-COSY, H,C-COSY) techniques.

<sup>13</sup>C (50.3 MHz) and <sup>119</sup>Sn (74.6 MHz) NMR CP/MAS spectra were recorded at 300 K on a Bruker DSX 200 spectrometer in a 4 mm ZrO<sub>2</sub> rotor at a MAS frequency of 4–8 kHz. The  $\delta(^{13}\text{C})$  and  $\delta(^{119}\text{Sn})$  chemical shifts were referred to the carbonyl signal of glycine ( $\delta$  176.0 ppm) and tetracyclohexyltin ( $\delta$  –97.35 ppm).

## Mössbauer Spectra

The  $^{119\text{m}}\text{Sn}$  Mössbauer spectra (Table V) were recorded at 77 K on a RANGER spectrometer in the constant-acceleration mode with a source activity of 0.4 Gbq. The isomer shift (*IS*) and quadrupole splitting (*QS*) values were derived by fitting the spectra as Lorentzian lines. The reproducibility of the Mössbauer parameters was  $\pm 0.02 \text{ mm s}^{-1}$  (*IS*) and  $0.04 \text{ mm s}^{-1}$  (*QS*) in each measurement. The *IS* values are referenced to that of  $\text{CaSnO}_3$ . To determine the steric arrangement of the coordination sphere in the tributylstannyl citrates, the experimental *QS* values were compared with those calculated on the basis of a simple but general molecular orbital model, according to the partial quadrupole splitting approach<sup>6,7</sup> for symmetries of

TABLE I  
Analytical and physical data of compounds **1a**, **1b**-**6a**, **6b**

Compound <sup>a</sup>	M.p., °C	Formula M.w.	Calculated/Found			
			% C	% H	% Sn	% N
<b>1a</b>	58-59	$\text{C}_{42}\text{H}_{86}\text{O}_7\text{Sn}_3$	47.63	8.18	33.62	
		1 059.21	47.45	8.13	33.53	
<b>1b</b>	49-50	$\text{C}_{42}\text{H}_{86}\text{O}_6\text{Sn}_3$	48.36	8.31	34.13	
		1 043.21	49.22	8.38	33.93	
<b>2a</b>	122-124	$\text{C}_{42}\text{H}_{83}\text{NO}_7\text{Sn}_2$	53.02	8.79	24.95	1.47
		951.50	53.30	8.74	25.07	1.43
<b>2b</b>	63-64	$\text{C}_{42}\text{H}_{83}\text{NO}_6\text{Sn}_2$	53.92	8.94	25.37	1.50
		935.50	54.76	8.90	24.78	1.65
<b>3a</b>	103-106	$\text{C}_{36}\text{H}_{73}\text{NO}_7\text{Sn}_2$	49.74	8.46	27.31	1.61
		869.36	50.33	8.68	28.04	1.58
<b>4a</b>	120-122	$\text{C}_{35}\text{H}_{70}\text{NO}_7\text{Sn}_2$	49.21	8.26	27.79	1.64
		854.32	49.88	8.59	27.53	1.95
<b>5a</b>	53-55	$\text{C}_{30}\text{H}_{60}\text{O}_7\text{Sn}_2$	46.79	7.85	30.82	
		770.18	47.03	7.88	30.50	
<b>6a</b>	124-130	$\text{C}_{42}\text{H}_{80}\text{N}_2\text{O}_7\text{Sn}$	59.78	9.56	14.07	3.32
		843.80	61.08	9.95	14.36	3.32
<b>6b</b>	81-82	$\text{C}_{42}\text{H}_{80}\text{N}_2\text{O}_6\text{Sn}$	60.94	9.74	14.34	3.38
		827.80	60.82	9.88	14.19	3.43

four and five coordinated tin(IV) atoms bonded to three alkyl groups and two oxygen atoms (belonging to monodentate or bidentate carboxyl, and hydroxyl groups). The following *PQS* values were used for the calculation of *QS*:  $\{\text{butyl}\}_{\text{tetr}} = -1.37$ ,  $\{\text{butyl}\}_{\text{tbpe}} = -1.13$ ,  $\{\text{butyl}\}_{\text{tbpa}} = -0.94$ ,  $\{\text{COO}\}_{\text{tbpe}(\text{bidentate})} = 0.293$ ,  $\{\text{COO}\}_{\text{tbpa}} = 0.075$ ,  $\{\text{COO}\}_{\text{tetr}(\text{monodentate})} = 0.11$ ,  $\{\text{OH}\}_{\text{tbpa}} = -0.13$  and  $\{\text{OH}\}_{\text{tbpe}} = 0.02 \text{ mm s}^{-1}$ .

TABLE II  
 $^1\text{H}$  NMR data ( $\delta(^1\text{H})$  values) of compounds **1–6** in  $\text{CDCl}_3$

Compound <sup>a</sup>	$\delta(^1\text{H})$ , ppm									
	H(1)	H(3)	H(2)	H(4)	CH <sub>2</sub>	CH	H(1')	H(2')	H(3')	H(4')
<b>1a</b>	1.17–1.33		1.55	0.86	2.82 2.75	–				
<b>1b</b>	1.23	1.30	1.57	0.88	2.69 2.52	3.13				
<b>2a</b>	1.21	1.31	1.58	0.89	2.81 2.78	–	2.88	1.95	1.74	1.64 1.26
<b>2b</b>	1.19 <sup>b</sup>	1.29 <sup>b</sup>	1.56	0.87	2.66 2.42	3.07	2.93	1.97 1.35 <sup>b</sup>	1.78 1.16 <sup>b</sup>	1.61 1.30 <sup>b</sup>
<b>3a</b>	1.22	1.28	1.53	0.85	2.75 2.68	–	2.92	1.99	1.71	1.63
<b>4a</b>	1.22	1.30	1.57 <sup>b</sup>	0.89	2.78 2.71	–	1.75	2.05	1.57 <sup>b</sup>	
<b>5a</b>	1.26	1.32	1.58	0.89	2.87 2.78	–	–	–	–	–
<b>6a</b>	1.18	1.38	1.65	0.93	2.68 2.72	–	3.12	2.08 1.04	1.72 1.36	
<b>6b</b>	1.19	1.35	1.62	0.89	2.64 2.38	3.05	2.86	2.01		

<sup>a</sup> Scheme 1. <sup>b</sup> Overlapped signals.

TABLE III  
 $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data of compounds 1-10

Com- pound <sup>a</sup>	Solvent	$\delta(^{119}\text{Sn})$ ppm (b)	$\delta(^{13}\text{C})$ , ppm/( $^{119}\text{Sn}$ , $^{13}\text{C}$ ), Hz																		
			C(1)	C(2)	C(3)	C(4)	CH <sub>2</sub>	C or CH	COO	C(1')	C(2')	C(3')	C(4')								
<b>1a</b>	CDCl <sub>3</sub>	121.0(1) 111.4(2) -10.8(1)	16.39	27.70	26.95	13.53	43.60	73.66	178.68(1)												
			(357.7)	(19.0)	(64.4)					175.55(2)											
			18.21	27.69	26.59	13.66	44.10	73.64	177.88(1)												
(s)		-9.8(2) 99.8(1) 3.7(1)	(467.0)	(26.8)	(75.0)				174.90(2)												
			18.24	28.26	27.56	13.70	43.82	74.49	181.27(1)												
									173.89(1)												
<b>1b</b>	CDCl <sub>3</sub>	106.0(1) 106.7(2) -1.3(1)	16.37	27.81	27.02	13.61	36.69	39.45	179.42(1)												
			(359.0)	(19.2)	(65.4)					177.24(2)											
			17.68			13.20				178.21(1)											
DMSO-d <sub>6</sub>		-12.9(2)	(439.0)						175.86(2)												
			and																		
			18.24							13.76											
(s)		92.4(1) -5.7(1) -26.2(1)																			
<b>2a</b>	CDCl <sub>3</sub>	109.7	16.31	27.69	26.93	13.51	43.89	73.66	178.85(1)	52.60	30.26	24.87	25.32								
			(358.2)	(18.8)	(65.0)							175.79(2)									
			18.33	27.80	26.70	13.75						179.02(1)	52.19	31.00	24.28	25.31					
DMSO-d <sub>6</sub>		-22.6	(472.61)	(26.7)	(75.35)																
			17.82(2)	28.09(2)		13.25(2)	44.75	73.78	180.31(1)	51.60	30.46	25.50	27.00								
			19.45(1)	27.67(1)		14.27(1)			175.65(1)												
(s)		-70.5(1)	20.54(1)	27.18(1)		15.42(1)															
<b>2b</b>	CDCl <sub>3</sub>	105.6	16.34	27.27	26.98	13.57	38.03	39.81	179.07(1)	52.96	29.67	24.77	25.14								
			(359.8)	(19.0)	(63.5)																

TABLE III  
(Continued)

Com- pound <sup>a</sup>	Solvent	$\delta(^{119}\text{Sn})$ ppm <sup>b</sup>	$\delta(^{13}\text{C})$ , ppm/( $^{119}\text{Sn}$ , $^{13}\text{C}$ ), Hz											
			C(1)	C(2)	C(3)	C(4)	CH <sub>2</sub>	C or CH	COO	C(1')	C(2')	C(3')	C(4')	
<b>3a</b>	CDCl <sub>3</sub>	110.9 (356.8)	16.42 (18.8)	27.72 (18.8)	26.96 (64.3)	13.54	43.92	73.90	179.01(1)	49.89	32.02	24.58	24.98	
	DMSO-d <sub>6</sub>	-20.3	18.38 (472.6)	27.80 (26.7)	26.70 (75.4)	13.75	44.71	73.32	178.02(1)	45.59	32.11	24.24	24.98	
<b>4a</b>	(s)	1.2(1) -50.8(1)	16.43(1) 18.20(1)	29.27(1) 28.61(1)	27.94(1) 27.79(1)	12.66(1) 14.07(1)	44.95	75.34	181.27(1)	51.16	33.26	22.04	20.17	
	CDCl <sub>3</sub>	105.3	16.37 (361.4)	27.70 (19.05)	26.93 (64.7)	13.52	44.71	74.07	179.96(1)	44.10	22.71			
<b>5a</b>	(s)	-57.7(1) -65.2(1)	20.82(1) 19.09(1)	29.28(1) 29.74(1)	28.34(1) 27.83(1)	13.31(1) 13.75(1)	44.56	74.71	179.98(1)	44.56	20.82	19.04		
	CDCl <sub>3</sub>	134.3(1) 121.2(1)	16.53 (352.9)	27.63 (18.8)	26.90 (64.3)	13.50	43.22	73.31	177.65(1)					
<b>6a</b>	DMSO-d <sub>6</sub>	-11.4(1) -16.4(1)	18.27 (496.2)	27.64 (25.5)	26.52 (74.8)	13.60	43.62	73.10	176.44(1)					
	(s)	43.1(1) -31.5(1)	17.53(1) 18.37(1)	28.02(1) 29.50(1)	27.40(1) 27.83(1)	13.73(1) 14.11(1)	43.67(1) 44.20(1)	75.19	177.98(1)					
<b>6a</b>	CD <sub>3</sub> OH	17.4	18.61 (446.5)	29.34 (25.9)	28.38 (75.5)	14.46	46.26	75.98	182.07(1)					
	DMSO-d <sub>6</sub>	-16.3	18.25	27.61	26.51	13.62	45.06	72.06	177.46(1)	52.22	31.15	24.30	25.35	
<b>6a</b>	(s)	-90.6	18.60(1) 20.96(1) 21.53(1)	29.69(1) 29.07(2)	28.27(1) 27.64(1)	13.49(1) 14.01(1)	43.10	76.01	182.24(1)	51.80	30.60	22.24	23.24	
					26.86(1)	14.36(1)			175.25(1)					

TABLE III  
(Continued)

Compound <sup>a</sup>	Solvent	$\delta(^{119}\text{Sn})$ ppm <sup>(b)</sup>	$\delta(^{13}\text{C})$ , ppm/ $(^{\circ}\text{J}(^{119}\text{Sn}, ^{13}\text{C})$ , Hz)											
			C(1)	C(2)	C(3)	C(4)	CH <sub>2</sub>	C or CH	COO	C(1')	C(2')	C(3')	C(4')	
<b>6b</b>	CDCl <sub>3</sub>	101.8 (368.5)	16.16	27.58	26.78	13.37	39.08	40.61	179.59(1)	50.45	29.81	24.65	25.07	
			(18.8)	(65.2)					177.34(2)					
<b>7a</b>	DMSO-d <sub>6</sub>	-22.6 (475.5)	18.38	27.17	26.75	13.79			177.78(1)	52.30	30.38	25.36	26.74	
			(475.5)	(26.9)	(74.2)				175.40(2)					
<b>8a</b>	D <sub>2</sub> O			46.45	75.49				181.86(1)					
									179.06(2)					
<b>9a</b>	CD <sub>3</sub> OD			47.41	76.60				183.25(1)	51.33	32.34	25.68	26.20	
									179.87(2)					
<b>10a</b>	(s)			47.57	77.54				179.26(1)	51.78	31.14	26.14	25.52	
									178.60(1)					
<b>9a</b>	CDCl <sub>3</sub>			42.77	72.96				173.41(1)	52.81(1)				
									169.81(2)	51.65(2)				
<b>10a</b>	DMSO-d <sub>6</sub>			43.08	73.15				173.19(1)	52.29(1)				
									169.79(2)	51.56(2)				
<b>10a</b>	(s)			43.44(1)	73.79				174.28(1)	54.52(1)				
									173.17(1)	53.08(1)				
<b>10a</b>	CDCl <sub>3</sub>			45.38(1)					170.36(1)	51.37(1)				
									172.40(1)	61.09(1)	13.02(1)			
				42.38	72.29				168.77(2)	59.79(2)	13.09(2)			

a Scheme 1. b Relative intensity. c

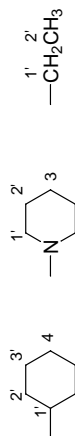




TABLE IV  
Values of  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  ( $\text{cm}^{-1}$ ) in IR spectra of compounds 1–9

Compound <sup>a</sup>	$\text{CHCl}_3$		Paraffine suspension	
	$\nu_{\text{as}}$	$\nu_{\text{s}}$	$\nu_{\text{as}}$	$\nu_{\text{s}}$
<b>1a</b>	1 654 vs	1 344 s, b	1 658 s	1 358 s
		1 379 s	1 624 sh	1 374 s
			1 608 vs	1 398 m
<b>1b</b>	1 642 vs	1 339 m, b	1 656 m	1 339 vw
		1 379 m	1 569 vs	1 379 s
<b>2a</b>	1 641 vs, b	1 360 m, b	1 664 vs	1 359 m, b
			1 630 vs	1 387 w
		1 566 vs	1 378 m	1 570 vs
<b>2b</b>	1 642 vs, b	1 378 s, b		
		1 570 vs		
<b>3a</b>	1 652 vs	1 356 m, b		
		1 577 s	1 378 m	1 596 vs, b
<b>4a</b>	1 647 vs	1 360 m, b		
		1 566 s	1 378 s	1 585 vs, b
<b>5a</b>	1 719 s		1 716 s	1 368 sh
		1 660 s	1 360 m, b	
		1 648 s	1 378 s	1 574 vs, b
<b>6a</b>			1 576 vs, b	1 378 s
<b>7a</b>			1 593 vs	1 392 s
<b>8a</b>			1 570 vs	1 365 vs
			1 555 vs	1 380 vs
<b>9a</b>	1 743 vs		1 758 vs	1 210 s
		1 730 sh	1 744 vs	1 228 s

<sup>a</sup> Scheme 1.

## Crystal Structure Determination of Dicyclohexylammonium Bis(tributylstannyl) Citrate

The specimen of **2a** that was used for crystal structure determination was the unexpected product that was obtained from the reaction of dicyclohexylamine, hexabutyl-distannoxane and citric acid monohydrate (molar ratio 2 : 1/2 : 1). The amine and the acid were heated in a small volume of ethanol until the reagents dissolved completely; the distannoxane was then added and the mixture briefly heated. Slow cooling of the filtered solution yielded colorless crystals of **2a**. Room-temperature diffraction measurements were performed on a Siemens CCD area-detector diffractometer; 9 075 independent reflections were used for solution<sup>8</sup> and refinement<sup>9</sup>. The structure is severely disordered; for the Sn2 atom, the three butyl groups are disordered in two positions, for the tributylstannyl group having the Sn1 atom, the entire tributylstannyl group is disordered in two positions. The refinements converged to a final *R* index of 11.5%. The disorder could not be resolved from diffraction data collected at low-temperature on a four-circle diffractometer. Crystal data: C<sub>42</sub>H<sub>83</sub>NO<sub>7</sub>Sn<sub>2</sub>, monoclinic, *C2/c*, *a* = 36.390(1), *b* = 14.5483(4), *c* = 22.7082(6) Å. The structure is shown in an ORTEP plot in Fig. 1.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-122742. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

TABLE V  
Experimental and calculated Mössbauer parameters of tributylstannyl citrates (mms<sup>-1</sup>) at 77 K

Compound <sup>a</sup>	<i>IS</i>	<i>QS</i> <sub>exp</sub>	<i>QS</i> <sub>calc</sub>	Live width
<b>1a</b>	1.31(2)	2.66	2.71	0.97
			2.96	
			2.48	
<b>2a</b>	1.33(1)	3.37	3.38	0.75
			2.95	
			2.17	
<b>3a</b>	1.29(1)	2.18	2.96	0.71
			2.95	
			2.06	
<b>5a</b>	1.26(1)	2.18	2.97	0.76
			2.97	
<b>6a</b>	1.32	3.12	2.97	0.90
			3.10	
<b>5a</b>	1.36(1)	3.10	2.97	1.00
			3.64	
<b>6a</b>	1.37(1)	3.64	3.55	0.77
			3.43	
<b>6a</b>	1.42	3.43	3.43	0.95
			3.43	

<sup>a</sup> Scheme 1.

## RESULTS AND DISCUSSION

*Identification of Compounds*

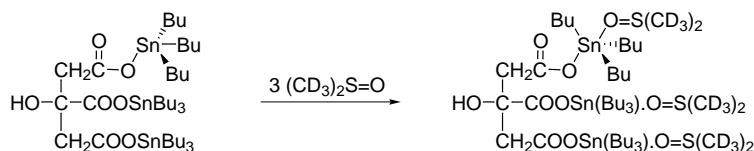
The elemental analyses (Table I) confirm the composition of the new compounds reported here. In the  $^1\text{H}$  NMR spectra, the signals are well resolved for the H(2), H(4), H(CH<sub>2</sub>), H(CH) and H(1') signals, and the intensities of the overlapping methylene protons signals (H(1) and H(3)) of the butyl substituents, as well as those of the cyclohexyl rings (H(2'), H(3') and H(4')) can be integrated to the proposed formulations of the compounds. The identities of the compounds have also been confirmed by the number of signals in the  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra.

*Structure of Compounds*Tris(tributylstannyl) Esters **1a** and **1b**

Two  $^{119}\text{Sn}$  signals ( $\delta(^{119}\text{Sn})$  121.0, 111.4 ppm) in a 1 : 2 intensity ratio are observed in the  $^{119}\text{Sn}$  NMR spectra of tris(tributylstannyl) citrate (compound **1a**) in non-coordinating deuteriochloroform. As the chemical shifts are typical of four-coordinate tributylstannyl compounds having the central tin atom in a tetrahedral or (pseudo)tetrahedral geometry<sup>10</sup>, compound **1a** probably exists as discrete molecules in solution, and any interaction of its carbonyl or hydroxyl oxygen atoms with central tin atom is marginal. The value of the  $\delta(^{119}\text{Sn})$  121.0 ppm signal corresponds to the tin atom bonded to the central carboxyl group, *i.e.*, the C(OH)(CO<sub>2</sub>Sn), whereas the  $\delta(^{119}\text{Sn})$  111.4 ppm corresponds to the tin atoms bonded to the terminal carboxyl groups, *i.e.*, the C(OH)(CH<sub>2</sub>CO<sub>2</sub>Sn). This assignment is corroborated by the presence of two signals in the high-frequency region of the  $^{13}\text{C}$  NMR spectrum ( $\delta(^{13}\text{C})$  178.68, 175.55 ppm in approximately 1 : 2 integral intensity). However, only one set of butyl signals is found in the  $^{13}\text{C}$  NMR spectrum, which implies that the two types of tributylstannyl groups must be exchanging rapidly on the NMR time scale. From the one-bond coupling constant  $^1J(^{119}\text{Sn},^{13}\text{C})$  of 357.7 Hz, the C-Sn-C angle is calculated<sup>11</sup> to be *ca* 110°.

In deuteriochloroform, the  $^{119}\text{Sn}$  and  $^{13}\text{C}$  NMR chemical shifts of compound **1b** are similar to those of compound **1a**, which suggests that the two compounds adopt similar structures in solution despite the absence of the hydroxyl group. When compound **1a** is dissolved in DMSO-*d*<sub>6</sub>, a coordinating solvent, two signals ( $\delta(^{119}\text{Sn})$  -10.8, -9.8 ppm, intensity ratio approxi-

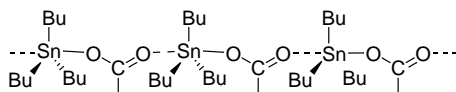
mately 1 : 2) appear in the  $^{119}\text{Sn}$  NMR spectrum. The lower-intensity signal is assigned to the tin atom bonded to central carboxylic group whereas the higher-intensity signal is assigned to the tin atom bonded to terminal carboxylic group. The upfield shift of both values of  $\delta(^{119}\text{Sn})$  by *ca* 120–130 ppm in changing from a non-coordinating to a coordinating solvent brings the chemical shifts to values typical of five-coordinate tributylstannyl compounds<sup>10</sup>. These signals imply that existence of a donor–acceptor complex with three molecules of DMSO- $d_6$  for each molecule of tris(tributylstannyl) citrate. The two carboxyl signals in the  $^{13}\text{C}$  NMR spectra of the DMSO- $d_6$  solution of compound **1a** ( $\delta(^{13}\text{C})$  177.88, 174.90 ppm; intensity ratio approximately 1 : 2) are slightly shifted upfield compared with those in non-polar chloroform.



Solvent effects in causing an upfield shift cannot be excluded, as suggested by the exchange of the  $\delta(^{13}\text{C})$  values for the COO group in compounds **9a** and **10a** in the two solvent systems (Table III). Only one set of signals for the butyl carbon atoms is observed in the  $^{13}\text{C}$  NMR spectrum of compound **1a** in DMSO- $d_6$ . The relevant one-bond coupling constant  $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 467.0$  Hz yields an estimated<sup>11</sup> C–Sn–C angle of about  $121^\circ$  in a trigonal bipyramidal arrangement of the ligands surround the tin atom. The donor oxygen atom of the solvent and the esteryl oxygen atom of the monodentate carboxyl groups occupy the apical positions in the universally axially-most-electronegative configuration.

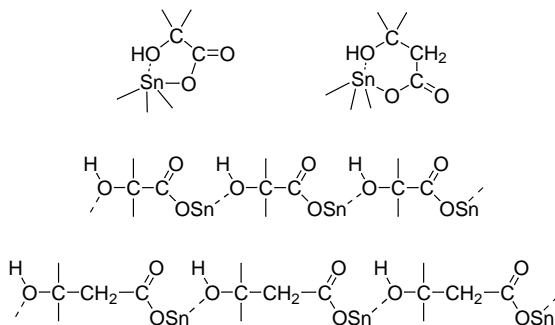
In the  $^{119}\text{Sn}$  CP/MAS NMR spectrum, compound **1a** displays three signals ( $\delta(^{119}\text{Sn})$  99.8, 3.7,  $-31.2$  ppm) of approximately the same intensity. The 99.8 ppm signal belongs to the range that is typical of four-coordinate tributylstannyl compounds, whereas the other two signals fall within the range for five-coordinated tributylstannyl compounds<sup>10</sup>. Interestingly, for the trialkylstannyl monocarboxylates, no crystallographic example is known of a tetrahedral trialkylstannyl system, with the possibly exception of the tricyclohexylstannyl carboxylates, whose tetrahedral nature can be attributed to the combined steric bulk of the three cyclohexyl rings<sup>12,13</sup>. Three signals ( $\delta(^{13}\text{C})$  181.27, 173.89, 172.22 ppm, intensity ratio approximately 1 : 1 : 1) are also seen in the  $^{13}\text{C}$  CP/MAS NMR spectrum of this

compound. The  $\delta(^{13}\text{C})$  181.27 ppm signal is markedly shifted downfield in comparison with all  $\delta(^{13}\text{C})(\text{COO})$  values of other compounds in solution. On the other hand, the other two signals are shifted somewhat upfield. The downfield shift is promoted by the change of the carboxyl group denticity<sup>14-17</sup>. The  $\delta(^{13}\text{C})$  181.27 ppm can be assigned to a carboxyl group that is monodentate in deuteriochloroform solution but is bridging in the solid state. The other two carboxylic groups are evidently monodentate in the solid state (compare also the  $\delta(^{13}\text{C})(\text{COO})$  values of organic esters **9a** and **10a** as a prototypes of monodentate carboxyl groups on the one hand, and the same parameters for the ionic (**7a**) and pseudoionic (**8a**) citrates as a prototypes of bridging carboxyl groups on the other in Table III). The bridging carboxyl group links adjacent tributylstannyl girdles into a polymeric chain:



in the arrangement found in most triorganotin(IV) carboxylates<sup>13,18</sup>.

One of the monodentate carboxylic groups forms, together with the four-coordinate tributylstannyl group, pseudotetrahedral environment similar to that in isolated molecules. The other monodentate carboxylic group is bonded to the second of the five-coordinated tin atom. The fifth position completing this five-coordinate arrangement must be occupied in this case by the oxygen atom of hydroxyl group forming, with high probability, dioxastanna ring by intramolecular donor-acceptor interaction or an intermolecular bridge:



Metalladioxa rings involving the participation of the  $\alpha$ -hydroxycarboxyl moieties of citric acid are found in some transition and main group metal

citrates<sup>19-21</sup>, and also in some tin(II) citrates<sup>22</sup>. Also the structural motif with bridging hydroxyl group was found more times in crystals of different organotin hydroxycarboxylates<sup>13</sup>.

Changes in the character of carboxyl groups in compound **1a** in solution and in the solid state are observed in the infrared spectra of the compound. The infrared spectrum in chloroform has one intense asymmetric  $\nu_{\text{as}}(\text{COO})$  stretching at  $1\,654\text{ cm}^{-1}$  and two symmetric  $\nu_{\text{s}}(\text{COO})$  stretchings at  $1\,344$  and  $1\,379\text{ cm}^{-1}$ . The asymmetric band is split into three bands of approximately the same intensities, with  $\nu_{\text{as}}$  of  $1\,658$ ,  $1\,624$  and  $1\,608\text{ cm}^{-1}$ , for the compound in the paraffin suspension. Three bands are also present in the  $\nu_{\text{s}}(\text{COO})$  region at  $1\,358$ ,  $1\,374$  and  $1\,398\text{ cm}^{-1}$ . The bands at  $\nu_{\text{as}} = 1\,658\text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1\,358\text{ cm}^{-1}$  are assigned to a monodentate COO group, whereas the bands at  $\nu_{\text{as}} = 1\,608\text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1\,398\text{ cm}^{-1}$  are assigned to the bridging carboxyl group (compare the infrared stretching frequencies of compound **1a** with those of potassium citrate **7a** as a prototype of a bidentate carboxyl group). The bands at  $\nu_{\text{as}} = 1\,624\text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1\,374\text{ cm}^{-1}$  are assigned to the five-membered dioxastanna rings comprising the tin atom and  $\alpha$ -hydroxycarboxyl moiety, by comparison with the bands found in tin(II) citrate<sup>22</sup>. This assignment is supported indirectly by the absence of similar bands in infrared spectra of compound **1b** (Table IV).

The Mössbauer spectrum of the compound **1a** consists of two doublets with  $IS = 1.31\text{ mm s}^{-1}$ ,  $QS = 2.66\text{ mm s}^{-1}$  and  $IS = 1.33\text{ mm s}^{-1}$ ,  $QS = 3.37\text{ mm s}^{-1}$  in the expected 2 : 1 intensity ratio. For the  $QS = 3.37\text{ mm s}^{-1}$  doublet, the  $QS/IS$  ratio exceeds 2.1, which implies higher-than-four coordination<sup>23</sup>. The quadrupole splitting as calculated by the point-charge model ( $QS_{\text{calc}} = 3.38\text{ mm s}^{-1}$ ) agrees with the experimental value, so that one tin atom must be bridged through the carboxyl entities in the solid state. The more intensive doublet belonging to tributylstannyl groups with the coordination of  $4 + 1$ .

As suggested by the NMR and infrared measurements, compound **1b** consists of polymeric chains of *trans*-trigonal bipyramidal  $\text{Bu}_3\text{SnO}_2$  groups ( $\delta(^{119}\text{Sn}) -5.7, -26.2\text{ ppm}$ ) that are linked by bridging carboxylic groups ( $\delta(^{13}\text{C})(\text{COO}) 180.66, 179.74\text{ ppm}$ ;  $\nu_{\text{as}} = 1\,569\text{ cm}^{-1}$ ,  $\nu_{\text{s}} = 1\,379\text{ cm}^{-1}$ ). The third tributylstannoxycarbonyl group ( $\delta(^{119}\text{Sn}) 92.4\text{ ppm}$ ;  $\delta(^{13}\text{C})(\text{COO}) 176.45\text{ ppm}$ ;  $\nu_{\text{as}} = 1\,656\text{ cm}^{-1}$ ,  $\nu_{\text{s}} = 1\,339\text{ cm}^{-1}$ ) does not participate in bonding.

Bis(tributylstannyl) Esters **2a–5a** and **2b**

Only one signal ( $\delta(^{119}\text{Sn})$  105.3–110.9 ppm) is found in the  $^{119}\text{Sn}$  NMR spectra of the bis(tributylstannyl) citrates **2a–4a** in deuterochloroform solution. The range of values is nearly that for compound **1a**, and the values are interpreted in terms of four-coordinate tributylstannyl units<sup>10</sup>, as implied by the magnitude of the coupling constants ( $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 356.8\text{--}361.4$  Hz). Two signals (intensity ratio *ca* 2 : 1) are found in the high-frequency part of  $^{13}\text{C}$  NMR spectra. The  $\delta(^{13}\text{C})$  values (175.79–176.50 ppm) of more intensive signals are very similar those in compound **1a**. They correspond to carbon atoms of monodentate terminal carboxylic groups in compounds **2a–4a**. The less intensive signal is shifted something downfield compared to that of compound **1a**, to the region typical of ionic citrates (*cf.*  $\delta(^{13}\text{C})(\text{COO})$  values for compounds **7a** and **8a**, Table III).

Two bands of asymmetric ( $\nu_{\text{as}}$ ) and two bands of symmetric stretching vibration ( $\nu_{\text{s}}$ ) were found in the carbonyl region of IR spectra of compound **2a–4a** in chloroform solutions. The values  $\nu_{\text{as}}$  of very strong bands  $\nu_{\text{as}}$  (1 641–1 652  $\text{cm}^{-1}$ ) and of strong or medium broad bands  $\nu_{\text{s}}$  (1 356–1 360  $\text{cm}^{-1}$ ) are practically identical with those found in infrared spectra of chloroform solutions of the compound **1a** and belong to monodentate terminal carboxylic groups bonded with tributylstannyl moieties. The values of strong bands  $\nu_{\text{as}}$  (1 566–1 577  $\text{cm}^{-1}$ ) and of medium relatively narrow band  $\nu_{\text{s}}$  (1 378  $\text{cm}^{-1}$ ) are in accord with the idea of an “ionic” character of central carboxylic group of the citrate<sup>24</sup> (see also IR spectra of compounds **7a** and **8a**).

It seems that ionic or pseudoionic pairs are present in chloroform solutions of compounds **2a–4a**. The anionic part is formed by particles of citric acid in which hydrogen atoms of terminal carboxyl groups were substituted by two pseudotetrahedral tributylstannyl moieties. Hydrogen atom of the central carboxyl group is linked up with the nitrogen atom of amines by the hydrogen bond and/or it is completely transferred as proton to this amine molecule (formation of ammonium ions). Virtually full agreement of IR and  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR parameters of compounds **2a** and **2b** excludes all consideration about the participation of hydroxy-group oxygen atom of compound **2a** (and with high probability also **3a** and **4a**) on the intra- or intermolecular interaction with some tin atoms.

As observed for compound **1a**, the  $\delta(^{119}\text{Sn})$  values of compounds **2a–4a** in coordinating solvents are markedly shifted upfield compared with those in deuterochloroform solutions. The shifts are attributed to donor–acceptor interaction between the tributylstannyl groups and the solvent molecules.

Two signals with integral intensity ratio approximately 2 : 1 are found in the carboxyl region of  $^{13}\text{C}$  NMR spectra of compounds **2a–4a**; the more intense signal is assigned to the terminal carboxylic groups and the less intense one to the central carboxyl group.

In contrast to the solution  $^{119}\text{Sn}$  NMR spectra of compounds **2a–4a**, the  $^{119}\text{Sn}$  CP/MAS NMR spectra consist of two signals with an approximately 1 : 1 intensity ratio. The  $\delta(^{119}\text{Sn})$  values of compound **2a** (86.4,  $-70.5$  ppm) indicate the presence of tin atoms of tributylstannyl moiety in four-coordination ( $\delta(^{119}\text{Sn})$  86.4 ppm) and five-coordination ( $\delta(^{119}\text{Sn})$   $-70.5$  ppm)<sup>10</sup>. The solid-state spectra also show the presence of three different signals in the carboxyl region, which arises from the three differently substituted carboxyl groups. The  $\delta(^{13}\text{C})(\text{COO})$  values of compounds having an ammonium cation in the formula are probably not suitable for structural assignment because the assignments are influenced by various factors. Besides solvent effects and the presence of negative charges on tin-bearing unit, a downfield shift of about 5 or more ppm units on going from COOH to COO<sup>-</sup> and virtually the same upfield shift as a consequence of hydrogen bond formation (and its bond length) in the arrangement COO $\cdots$ HNR<sub>3</sub> (refs<sup>14–17</sup>) must be considered as the most important.

Three bands at  $\nu_{\text{as}} = 1\,664$ ,  $1\,630$  and  $1\,570\text{ cm}^{-1}$  and another three at  $\nu_{\text{s}} = 1\,359$ ,  $1\,387$  and  $1\,397\text{ cm}^{-1}$  are found in the infrared spectrum of compound **2a**. A comparison of the bands of compounds **1a** and **2a** shows that the bands at  $1\,664$  and  $1\,359\text{ cm}^{-1}$  must belong to carboxyl group that is bonded to a tetrahedral tributylstannyl group, whereas the pair at  $1\,570$  and  $1\,397\text{ cm}^{-1}$  must belong to the ionic carboxyl group. The pair  $1\,630$  and  $1\,387\text{ cm}^{-1}$  corresponds to the bridging carboxylic group forming probably together with trigonal bipyramidal tributylstannyl group one unit of the polymeric chain.

The existence of two doublets of approximately the same intensity in Mössbauer spectrum of the compound **2a** confirms the presence of two differently coordinated tin atoms. The doublet with  $IS = 1.29\text{ mm s}^{-1}$  and  $QS = 2.95\text{ mm s}^{-1}$  ( $QS_{\text{calc}} = 2.96\text{ mm s}^{-1}$ ) corresponds to a *trans*-trigonal bipyramidal tributylstannyl group in polymeric chain, whereas the doublet with  $IS = 1.26\text{ mm s}^{-1}$  and  $QS = 2.18\text{ mm s}^{-1}$  corresponds to a pseudotetrahedral tributylstannyl.

The structural assignments for compound **2a** is confirmed by crystal structure analysis. The compound crystallizes as an ion-pair, and can be also formulated as dicyclohexylammonium di(carboxytributylstannylmethyl)hydroxyacetate (Fig. 1). Of the two tributylstannyl groups in the compound, one have the tin atom in a tetrahedral geometry; there are no



Sn...O interactions less than 3.5 Å involving the Sn2 tin atom. The other tin atom, Sn1, is linked to an adjacent symmetry-related Sn1 atom through the one terminal carboxyl group to form an infinite chain structure. The chain structure is stabilized by hydrogen bonding with the dicyclohexylammonium cation.

Both signals in  $^{119}\text{Sn}$  CP/MAS NMR spectrum of the compound **4a** ( $\delta(^{119}\text{Sn})$  -57.7 and -65.2 ppm) are shifted to the  $\delta(^{119}\text{Sn})$  region typical of five-coordinated tin atom in tributylstannyl compounds<sup>10</sup>. The  $\delta(^{13}\text{C})(\text{COO})$  values in the  $^{13}\text{C}$  CP/MAS NMR spectrum (179.98, 176.83 and 176.07 ppm) are in agreement with bridging or ionic carboxylic groups. The spectral values suggest that unlike in compound **2a**, the monomeric units of the compound **4a** are bonded into chains by both terminal tributylstannoxycarbonyl groups. The value of  $\delta(^{119}\text{Sn})$  1.2 ppm in the  $^{119}\text{Sn}$  CP/MAS NMR spectrum of compound **3a** lies between regions typical of the four- and five-coordinated tin atoms in tributylstannyl compounds, so that coordination environment of the tin atom is formed by four strongly bonded and one less strongly bonded partners. The other signal ( $\delta(^{119}\text{Sn})$  -50.8 ppm) corresponds to five-coordinate tin. The structural arrangement of the anion of compound **3a** is similar to that of **4a**. Two pairs of signals (intensity ratio 1 : 1) are observed for the carbon atoms of the butyl substituents in  $^{13}\text{C}$  CP/MAS NMR spectra of compounds **3a** and **4a**.

The IR and Mössbauer spectra confirm the assignment of the structure of compounds **3a** and **4a** in the solid state. The primary broad bands at  $\nu_{\text{as}} = 1\ 652$  and  $1\ 647\ \text{cm}^{-1}$  (see infrared spectra of compounds **3a** and **4a** in chlo-

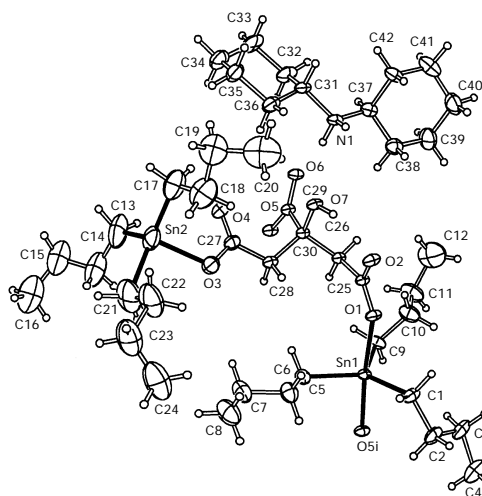


FIG. 1  
Crystal structure of compound **2a**

reform solution) corresponding to monodentate carboxyl groups bonded to the four-coordinate tin atoms of the tributylstannyl group are absent in the IR spectra of the paraffin suspension. Only broad and strong bands ( $\nu_{\text{as}} = 1\,596$  and  $1\,585\text{ cm}^{-1}$ ) belonging to both the bridging and "ionic" carboxylic groups are observed. The symmetric bands in paraffin suspension are shifted to the higher wavenumbers compared with the analogous values in chloroform solutions. Only one doublet with  $IS = 1.32\text{ mm s}^{-1}$  and  $QS = 3.12\text{ mm s}^{-1}$  corresponding to the *trans*-trigonal bipyramidal arrangement of both tributylstannyl groups ( $QS_{\text{calc}} = 2.97\text{ mm s}^{-1}$ ) in polymeric chain is found in Mössbauer spectrum of compound **3a**. The nature of the donor-acceptor interaction in both polymeric chains could not be distinguished from the Mössbauer measurements.

As confirmed by the presence of two signals ( $\delta(^{119}\text{Sn})$  134.3 and 121.2 ppm; intensity ratio 1 : 1) in  $^{119}\text{Sn}$  NMR spectrum of compound **5a** in deuteriochloroform solution, the constitution of its molecules differs considerably from other bis(tributylstannyl) compounds. Only two signals (177.65 and 175.07 ppm, intensity ratio 1 : 2) are found in the carboxyl region of the  $^{13}\text{C}$  NMR spectrum; the more intense signal is split. The signal with  $\delta(^{119}\text{Sn})$  121.2 ppm and  $\delta(^{13}\text{C})(\text{COO})$  177.65 ppm belongs to the tin and carbon atoms of the central tributylstannoxycarbonyl group, as deduced from similar  $\delta(^{119}\text{Sn})$  and  $\delta(^{13}\text{C})(\text{COO})$  values found for compound **1a**. The signals at  $\delta(^{119}\text{Sn})$  134.3 ppm and  $\delta(^{13}\text{C})$  175.07 ppm suggest a similar same terminal arrangement. The other part of the split signal belongs to the unsubstituted terminal COOH group. The band with  $\nu_{\text{as}} = 1\,719\text{ cm}^{-1}$  in the IR spectrum of compound **5a** in chloroform solution, which is partly occluded by the solvent band, belongs to the unsubstituted COOH group. Two pairs of bands with  $\nu_{\text{as}} = 1\,660, 1\,648\text{ cm}^{-1}$  and  $\nu_{\text{s}} = 1\,378, 1\,360\text{ cm}^{-1}$  are assigned to the central and one of the terminal carboxyl groups. Compound **5a** interacts with two molecules of DMSO- $d_6$ , as deduced from  $\delta(^{119}\text{Sn})$  -11.4 and -16.4 ppm,  $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 496.2\text{ Hz}$ .

The chemical shifts of  $\delta(^{119}\text{Sn})$  43.1, -31.5 ppm in  $^{119}\text{Sn}$  CP/MAS NMR spectrum and the Mössbauer  $QS = 3.10$  and  $3.64\text{ mm s}^{-1}$  ( $QS_{\text{calc}} = 2.97$  and  $3.55\text{ mm s}^{-1}$ ) of the compound **5a** correspond to the one tin atom with a coordination number equal to five and one with a coordination number 4 + 1. The molecular units in solid compound **5a** are linked into layers in a bonding scheme similar to that of compound **3a**. This assignment is supported by the fact the bands  $\nu_{\text{as}} = 1\,660, 1\,648\text{ cm}^{-1}$  in the IR spectrum in chloroform are absent in the solid state; additionally, an intense but broad band appears at  $\nu_{\text{as}} = 1\,574\text{ cm}^{-1}$  in paraffin suspension.

The differences in the architecture of compounds **2a–4a** and compound **5a** probably arise from the different acidities of the individual carboxyl groups in citric acid ( $pK_1$  (central COOH) = 3.128,  $pK_2$  = 4.761,  $pK_3$  = 6.396 at 25 °C)<sup>25</sup>. If the reaction of the carboxyl groups of citric acid with amines and hexabutylstannoxane (see Experimental) proceeds step-by-step in the order of decreasing group acidity, then the central carboxylic group in compounds **2a–4a** would be preferentially blocked by the amines, and therefore only the two terminal carboxyl groups could be substituted by tributylstannyl groups. On the other hand, the central carboxylic group is accessible for bonding with the tributylstannyl group if an amine is not present in the condensation reaction, so that compound **5a** is formed by the substitution of the central carboxyl and one of the terminal carboxyl groups.

### Mono(tributylstannyl) Esters **6a** and **6b**

A stepwise preferential blocking of the carboxyl groups by amines is suggested to account for the structural assignment of compound **6a**. Only one signal is found in the  $^{119}\text{Sn}$  CP/MAS NMR spectrum at  $\delta(^{119}\text{Sn})$  -90.6 ppm. This unusually upfield shifted signal is interpreted in terms of a trigonal bipyramidal geometry of the coordination environment of tin. Three signals of approximately the same intensity are found in the  $^{13}\text{C}$  CP/MAS NMR spectrum for the carboxyl carbon atoms (182.24, 178.38 and 175.25 ppm), and there are three sets of signals for the butyl carbon atoms. The Mössbauer  $IS = 1.42 \text{ mm s}^{-1}$  and  $QS = 3.43 \text{ mm s}^{-1}$  are consistent with a coordination number greater than four; the close agreement of the measured and calculated  $QS$  values suggests the existence of a polymeric chain structure (*vide supra*). The three different carboxyl signals in  $^{13}\text{C}$  CP/MAS NMR show that one of the terminal carboxyl group of the molecule participates in the formation of this polymeric chain. A pair of broad but very strong IR bands in the paraffin suspension of this compound ( $\nu_{\text{as}} = 1576 \text{ cm}^{-1}$ ,  $\nu_{\text{s}} = 1378 \text{ cm}^{-1}$ ) implicates the bridging or ionic character of all carboxylic groups.

Unlike the propane-1,2,3-tricarboxylate **6b**, compound **6a** is insoluble in common non-coordinating solvents. Compound **6b** probably exists as a pseudo ion-pair in deuteriochloroform solution, as suggested by their NMR spectra parameters ( $\delta(^{119}\text{Sn})$  101.8 ppm,  $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 368.5 \text{ Hz}$ ; two signals in carboxyl region at  $\delta(^{13}\text{C})$  179.59, 177.34 ppm with an intensity ratio *ca* 1 : 2) with the tributylstannyl group bonded to the central carboxylic group of the propane-1,2,3-tricarboxylate fragment in a pseudotetrahedral geometry. Both terminal carboxyl groups are blocked by the dicyclo-

hexylamine molecules as the acidic protons are transferred to the amino group. The carboxyl and ammonium groups must be linked by hydrogen bonds, as suggested by the relatively low  $\delta(^{13}\text{C})(\text{COO})$  value of 177.34 ppm. This compound forms a molecular complex with only one molecule of  $\text{DMSO-}d_6$  when dissolved in this solvent ( $\delta(^{119}\text{Sn}) -22.62$  ppm,  $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 475.5$  Hz). The  $\text{DMSO-}d_6$  complex of compound **6a** would have the same structural arrangement as the  $^{119}\text{Sn}$  and  $^{13}\text{C}$  spectra parameters of both mono(tributylstannyl) compounds are similar.

*The authors thank A. Szorcik and Prof. A. Vértés for the Mössbauer measurements. They also thank the Grant Agency of the Czech Republic (grant No.203/97/0502), Ministry of Education, Youth and Sports of the Czech Republic (the COST 8.20 programme), the Hungarian Research Foundation (T 022909), the National Science Council for R & D, Malaysia (IRPA 09-02-03-0371 and 190-9609-2801) for financial support.*

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