Organotin derivatives of 4-acyl-5-pyrazolones. Crystal structure of *trans*-di(t-butyl)bis(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)tin(IV)

Claudio Pettinari, Giovanni Rafaiani, Giancarlo Gioia Lobbia, Adriana Lorenzotti, Flavio Bonati *

Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino, 1-62032 Camerino (Italy)

and Bruna Bovio *

Dipartimento di Chimica Generale, Università di Pavia, viale Taramelli 12, 27100 Pavia (Italy)

(Received August 8th, 1990)

Abstract

Stable, six-coordinated Q_2SnRX compounds have been prepared where QH is 1-phenyl-3-methyl-4-$R'C(=O)$-pyrazol-5-one (R' = Me, Ph) X = Cl or R, and R = Cl, Me, Et, i-Pr, n- and t-Bu, vinyl, benzyl or phenyl. They are not fluxional when X = Cl or Ph or X = R = t-Bu. The ^{119}Sn NMR chemical shift is a function of the number of chloride groups. Owing to crowding of the ligands, in the title molecule the C–Sn–C axis is bent (150.0(5)°) and the Sn–C bonds and two of the four Sn–O bonds are long: 2.20(1) for the Sn–C, 2.381(7) and 2.461(6) vs. 2.145(5) and 2.135(6) Å for Sn–O.

Introduction

4-Acyl-5-pyrazolones (Fig. 1) are a family of enolizable β-diketones that have been used as metal extracting agents, originally by Jensen [1] and later by many others, e.g. [2]. Derivatives of the most common members of the family, 1-phenyl-3-methyl-4-(RCO)-5-pyrazolone (QH; R = alkyl or aryl) with many metals, were isolated and characterized [1–4]. Nevertheless, although the resulting chelates seem
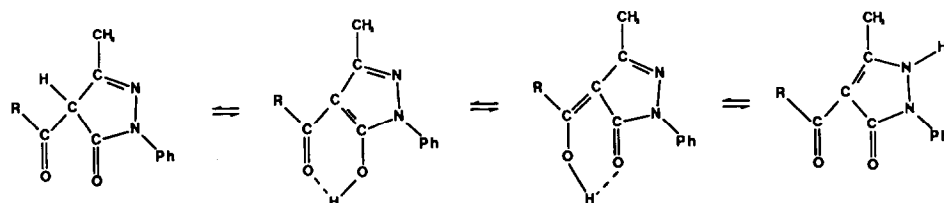

Fig. 1. Tautomeric structures possible for the ligand Q'H; the last one is found in the crystal [17].

to be more stable than the very common acetylacetonates, probably because of the presence of the fused pyrazole ring, there is no mention of them or of the parent ligands in several reviews dealing with inorganic or metal–organic β-diketonates [5]. Furthermore, apart from dicarbonylrhodium(I) or dicarbonyliridium(I) derivatives [4], no organometal cation has been treated with QH, so that, following our interest in the field of β-diketonates [4,6] and of tin chemistry [7], we decided to investigate organotin(IV) derivatives of 1-phenyl-3-methyl-4-(RCO)-5-pyrazolone, abbreviated Q'H when R = Ph, and Q"H when R = methyl. An additional reason for preparing organotin(IV) derivatives of these stable but sterically demanding ligands is the ability of the cation to undergo severe distortion from octahedral environment while maintaining six-coordination [8].

Results and discussion

The reaction between Q'H or Q"H and $R_{4-n}SnX_n$ (R = methyl, ethyl, i-propyl, n-butyl, t-butyl, vinyl, benzyl or phenyl; X = Cl or Br; n = 2, 3 or 4) in methanol containing potassium hydroxide readily afforded almost all the compounds listed in Table 1 (see the Experimental section for additional details). They are colourless or pale yellow solids and were identified from the analytical data in Table 1 and their infrared spectra (Sn–Cl stretching frequencies are reported in Table 1). They are insoluble in water but soluble in chlorinated solvents or in acetone in which they are non-electrolytes, thus ruling out ionic structures, e.g. $[Q_2(solvent)_xSn][X]_2$ or $[Q_3Sn]_2[SnX_6]$ for Q_2SnX_2.

Details of the electronic spectra (in all cases recorded in chloroform and some also in acetonitrile) are given in Table 2. The spectra of several compounds (**1, 2, 4, 6, 8, 9**) are unchanged after a few days, reflecting the stability of the samples. There is no evidence of equilibria involving bidentate and monodentate $[Q^-]$ ligands since Lambert–Beer law is obeyed, at least in the case of **2, 4** and **9**. While the starting ligand Q'H shows maxima at 246 and 288 nm [3a], in the tin derivatives there is a displacement to higher wavelength, namely 294 in $Q_2'Sn(CH_3)_2$ and 310 in $Q_2'SnCl_2$. This band tails into the visible part of the spectrum, which accounts for the colour of the compounds. The extinction coefficient for the band at higher wavelength is approximately twice that found for the corresponding ligand, Q'H (18,110 cm^{-1}), that is: ca. 28,600 cm^{-1} for $Q_2'Sn(CH_3)_2$ and ca. 45,500 cm^{-1} for $Q_2'SnCl_2$.

^{1}H-, ^{13}C- and ^{119}Sn NMR data, listed in Tables 3–7 support the formulae given and, in addition, allow some other conclusions to be reached. If it is assumed that in all the tin(IV) compounds under consideration the tin atom is in an approximately octahedral or a skewed trapezoidal bipyramidal environment [8], then the two *trans* isomers shown in the Fig. 2 and six *cis* isomers are possible in the case of Q_2SnX_2. In most of the compounds the presence of more than one isomer is revealed by the presence of three or more methyl groups in the ^{1}H- or ^{13}C-NMR spectra of several derivatives of Q'H (compounds **6, 9–12**) or of more than two methyl groups in the spectra of the derivatives of Q"H (compounds **18, 21–24**). In the first case additional supporting evidence is provided by the ^{119}Sn spectra reported in Table 7: several signals are found, and they are very near to one another, as expected for the six *cis* steric isomers, which have the same arrangement of donor atoms around tin(IV). Attempts to separate the isomers by fractional crystallization or by TLC have so far failed. Heating the compound **10** above the melting point did not

Table 1

Analytical and other data

Compound [a]	Yields %	M.p. °C	Elemental analyses (Found (calc.) (%)) [b]			IR data [c]
			C	H	N	
$Q_2'Sn(CH_3)_2$ **1**	61	193–199	61.92 (61.48)	4.60 (4.59)	7.76 (7.97)	
$Q_2'Sn(C_2H_5)_2$ **2**	93	165–168	62.70 (62.40)	4.99 (4.96)	7.46 (7.66)	
$Q_2'Sn(i-C_3H_7)_2$ **3**	51	161–163	64.02 (63.26)	5.34 (5.31)	7.18 (7.38)	
$Q_2'Sn(t-C_4H_9)_2$ **4**	80	211–212	64.12 (64.06)	5.70 (5.63)	6.94 (7.11)	
$Q_2'Sn(n-C_4H_9)_2$ **5**	19	132–134	63.87 (64.06)	5.72 (5.63)	6.97 (7.11)	
$(Q')_2Sn(C_6H_5)_2$ **6**	89	186–188	66.21 (66.77)	4.37 (4.39)	6.89 (6.77)	
$(Q')_2Sn(C_6H_5CH_2)_2$ **7**	26	115–116	66.72 (67.39)	4.71 (4.71)	6.12 (6.54)	
$(Q')_2Sn(C_2H_3)_2$ **8**	41	148–151	62.57 (62.75)	4.49 (4.43)	7.58 (7.70)	
$(Q')_2SnCl_2$ **9**	90	282–286	54.31 (54.87)	3.52 (3.52)	7.27 (7.53)	340m
$(Q')_2SnCH_3Cl$ **10**	64	196–199	58.05 (58.08)	3.91 (4.04)	7.34 (7.74)	330m
$(Q')_2SnC_6H_5Cl$ **11**	82	140–142	60.66 (61.14)	4.01 (3.98)	6.97 (7.13)	320m
$(Q')_2Sn(n-C_4H_9)Cl$ **12**	36	80–92 dec	60.08 (59.6)	4.59 (4.61)	6.98 (7.32)	310 broad
$(Q'')_2Sn(CH_3)_2$ **13**	83	230–233	53.46 (53.91)	4.87 (4.87)	9.45 (9.67)	
$(Q'')_2Sn(C_2H_5)_2$ **14**	80	197–200	55.70 (55.38)	5.37 (5.31)	9.01 (9.23)	
$(Q'')_2Sn(i-C_3H_7)_2$ **15**	36	193–196	57.36 (56.72)	5.80 (5.71)	8.59 (8.82)	
$(Q'')_2Sn(t-C_4H_9)_2$ **16**	51	226–227	57.60 (57.94)	6.22 (6.08)	8.27 (8.45)	
$(Q'')_2Sn(n-C_4H_9)_2$ **17**	51	142–144	58.21 (57.94)	6.37 (6.08)	8.76 (8.46)	
$(Q'')_2Sn(C_6H_5)_2$ **18**	88	188–192	61.21 (61.48)	4.52 (4.59)	7.89 (7.97)	
$(Q'')_2Sn(C_6H_5CH_2)_2$ **19**	40	141–142	61.95 (62.4)	4.90 (4.96)	7.37 (7.66)	
$(Q'')_2Sn(C_2H_3)_2$ **20**	72	158–169 dec.	55.32 (55.75)	4.66 (4.68)	9.10 (9.29)	
$(Q'')_2SnCl_2$ **21**	67	244–246	45.94 (46.49)	3.50 (3.58)	8.61 (9.04)	340s
$(Q'')_2SnCH_3Cl$ **22**	83	170–172	50.15 (50.08)	4.24 (4.20)	9.29 (9.34)	305m
$(Q'')_2SnC_6H_5Cl$ **23**	58	178–180	54.40 (54.45)	4.10 (4.11)	8.29 (8.47)	310m
$(Q'')_2Sn(n-C_4H_9)Cl$ **24**	45	165–167	52.55 (52.41)	4.91 (4.87)	8.73 (8.62)	300s

[a] Q'H is 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and Q''H is 1-phenyl-3-methyl-4-acetyl-5-pyrazolone. [b] Calculated values in parentheses. [c] Sn–Cl stretching frequencies.

Table 2

Electronic spectra in chloroform

Compound	Λ_{max}[a]	ϵ_{max}	Λ_{max}	ϵ_{max}
Q'H	244	16940	290	18110
$Q_2'Sn(CH_3)_2$ **1**	248	33875	294	28600
$Q_2'Sn(C_2H_5)_2$ **2**	250	47893	294	36860
$Q_2'Sn(i-C_3H_7)_2$ **3**	250	38241	294	27023
$Q_2'Sn(t-C_4H_9)_2$ **4**	248	47663	296	31149
$Q_2'Sn(C_6H_5)_2$ **6**	250	44809	302	38257
$Q_2'Sn(CH=CH_2)_2$ **8**	250	44074	300	37097
$Q_2'SnCl_2$ **9**	244	36353	310	45524
$Q_2'SnCH_3Cl$ **10**	248	36010	306	39470
$Q_2'SnC_6H_5Cl$ **11**	246	32788	308	35753

[a] Λ in nm.

produce any change in the infrared (Nujol mull) or ^{1}H NMR spectrum of the cooled sample; similarly no significant change could be detected in the ^{1}H NMR spectrum of the same compound in chloroform up to 50°C or in dimethylsulphoxide up to 100°C.

It thus seems, that isomers when present are stable enough to be detected but not (so far) isolated. They are present when the acceptor ability of tin(IV) is enhanced by electronegative substituents, such as at least one halide. Indeed, isomers have not been detected only in cases in which the tin(IV) atom bears two methyl, i-propyl, n-butyl, or benzyl groups (**1**, **3**, **5** or **7**) in the case of Q', or the same plus ethyl groups in the case of Q'' (compounds **13**, **14**, **15**, **17**, **19**). Thus the presence of only one 3-Me and only one acetyl group in the NMR spectra is likely to be due to
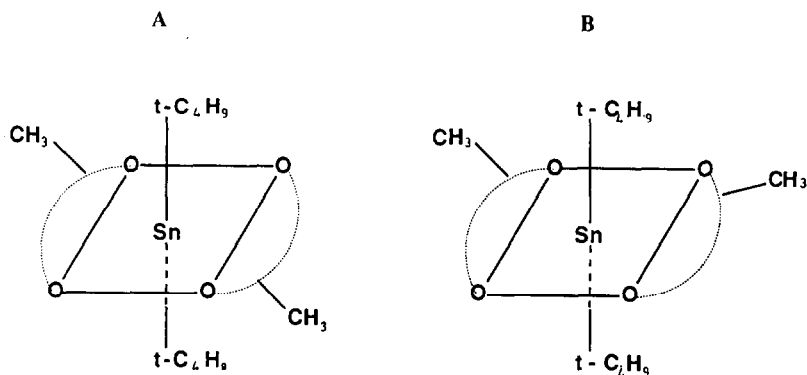
A   B

Fig. 2. The two *trans*-isomers for the compound $Q_2'Sn(t-C_4H_9)_2$.

Table 3

^{1}H NMR data ^{a} for Q' derivatives (in CDCl$_3$)

Compound	C–H aromatic	3-CH$_3$	R–Sn	Other data ^{b}
Q'H	7.25–7.34 m	2.11 s		10.2–10.7 broad O–H
	7.42–7.68 m			
	7.86–7.93 m			
1	7.15–7.31 m	1.82 s	1.02 s	^2J(Sn–H) = 99
	7.43–7.59 m			
	7.94–7.98 m			
2	7.15–7.29 m	1.82 s	1.24 t (7.8)	^2J (Sn–H) = 94.9
	7.42–7.58 m		1.70 q	^3J (Sn–H) = 161.9
	7.97–8.02 m			
3	7.12–7.28 m	1.83 s	2.17 sept	^3J (Sn^{117}–H) = 144.5
	7.46–7.61 m		133 d (7.7)	^3J (Sn^{119}–H) = 153.6
	8–8.07 m			
4	7.12–7.26 m	1.82 s	1.29 s [9]	^3J (Sn–H) = 133.3
	7.44–7.66 m		1.30 s [1]	
	8.02 d			
5	7.15–7.30 m	1.82 s	0.85 t (7.62)	^2J (Sn–H) = 124.9
	7.43–7.60 m		1.28 m	
	7.98 d		1.5–1.75 m	
6	7.14–7.52 m	1.66 broad	7.14–7.92 m	
	7.75–7.78 m			
	7.87 d			
7	6.78–7.05 m	1.62	6.78–7.05 m	^2J (Sn–H) = 120.5
	7.18–7.60 m		7.18–7.60 m	
	7.90 d		3.14 s	
8	7.18–7.59 m	1.77 s	5.92 dd	J_{gem} = 2.14; J_{cis} = 12.72;
	7.90–7.96 m		6.12 dd	J_{trans} = 19.74; ^2J (Sn–H) = 191.3;
			6.58 dd	^3J (Sn–H) = 163.7;
9	7.18–7.73 m	1.7 s [1]		
	7.93–7.99 m	1.79 s [1]		
		1.89 s [1.1]		
		1.98 s [1]		
9	7.20–7.74 m	1.68 s; 1.77 s		in CD$_2$Cl$_2$
	7.75 d	1.89 s; 1.96 s		
10	6.9–8.1 m broad	1.6–2.1 m	1.28s	^2J = 133.2
11	7.05–8.05 m	1.5 s; 1.58 s;	7.05–8.05 m	
		1.62 s; 1.64 s;		
		1.78 s; 1.90 s;		
		1.91 s; 1.99 s		
12	7.0–7.8 m	1.5–2.2 m	0.9 t (7.31)	
	7.85–8.1 m		1.46 s; 1.5–2.2 m	

^{a} δ in ppm from internal TMS. ^{b} J in Hz.

fluxionality around the coordination center rather than to the absence of isomers. In addition, when the alkyl groups are bulky, as in the two t-butyl derivatives **4** and **16**, there is no fluxionality: the ^{1}H and ^{119}Sn NMR spectra show that two isomers, in a ca. 9 : 1 ratio, are present in which the alkyl groups must be *trans*, and the isomerism is attributed to a different arrangement of the two Q ligands, as shown in formulae **A** and **B** (Fig. 2).

The foregoing NMR evidence thus suggests that the coordination number around tin(IV) is likely always to be six; further support comes from the observation that,

Table 4

^{1}H NMR data for Q'' derivatives (in CDCl$_3$)

	C–H aromatic	CH$_3$	R–Sn	Other data [a]
Q''H	7.26–7.32 m	2.46 s		11.6–12.6 br O–H
	7.41–7.48 m	2.48 s		
	7.8–7.86 d			
13	7.15–7.30 m	2.42 s	0.83 s	^2J (Sn–H) = 105
	7.8–7.86 d	2.45 s		
14	7.14–7.27 m	2.42 s	1.15 t	^2J (Sn–H) = 94.3
	7.88–7.94 m	2.44 s	1.5 q	^3J (Sn–H) = 158.3
15	7.12–7.29 m	2.47 s	1.98 sept	^3J (Sn–H) = 151.4
	7.90–7.98 m	2.47 s	1.27 d (7.5)	^3J (Sn–H) = 144.5
16	7.10–7.36 m br	2.44 s	1.21 s [9]	^3J (Sn–H) = 132.9
	7.85–8.08 m br	2.46 s	1.42s [1]	
17	7.13–7.27 m	2.42 s	0.75 t (7.5)	^2J (Sn–H) = 125.4
	7.90 d	2.44 s	1.2–1.4 m; 1.49 t	
18	7.0–7.43 m	2.32 s br	7.0–7.43 m	
	7.50–8.0 m	2.35 s br	7.50–8.0 m	
19	6.78–7.03 m	2.23 s	2.86 s	^2J (Sn–H) = 122.9
	7.15–7.36 m	2.26 s	7.15–7.36 m	
	7.70–7.86 m		7.70–7.86 m	
			6.78–7.03 m	
20	7.16–7.38 m	2.2 s	5.8 dd	J_{gem} = 2.30; J_{cis} = 12.7
	7.84 d	2.2 s	6.08 dd	J_{trans} = 19.30
			6.24 dd	^2J (Sn–H) = 188.9
				^3J (Sn–H) = 175.6
21	7.14–7.50 m	2.36 s; 2.42 s		
	7.60–7.70 m	2.47 s; 2.51 s		
		2.59 s; 2.67 s		
22	7.0–8.05 m br	2.0–2.70 m	1.0 s [1]	^2J (Sn–H) = 129.1
			1.17 s [4]	
23	7.0–8.05 m	2.1–2.65 m	7.0–8.05 m	
24	6.98–8.02 m br	1.98–2.70 m br	0.95 t; 1.42 s	
			1.6–1.9 m	

[a] J in Hz.

as far as ^{119}Sn chemical shifts are concerned, effects of substitution of each chloride by one methyl or phenyl group is roughly additive, as shown in Fig. 3 and already found also with organotin(IV) tris- or tetrakis(pyrazolyl)borates [7].

X-Ray crystal structure of compound 4

The crystal structure of the title compound consists of discrete molecules and corresponds to one of the two isomers seen in solution, although we cannot say whether it is the more or the less abundant. An ORTEP view [9] of the compound with the numbering scheme is given in Fig. 4. Bond distances and bond angles are listed in the Tables 8 and 9. Though the molecule exhibits no real crystallographic symmetry and all atoms occupy general positions, a virtual C_{2v} symmetry is probable with a mirror plane passing through Sn,C(22),C(22a) and the midpoints of the segments O(14)–O(14a) and O(15)–O(15a), the other mirror plane coinciding with the four oxygen atoms. The shortest intermolecular approaches between the

Table 5

^{13}C NMR data for Q′ derivatives (in CDCl$_3$)

Compound	CH$_3$	Phenyl rings	CO,C(5)	C(3),C(4)	C–Sn	Other data [a]
Q′H	15.8	120.8; 126.7; 127.9; 128.3	192.0	148.0		
		129.1; 131.9; 137.3; 137.6	162.5	103.6		
1	16.5	121.1; 125.7; 127.8; 128.4	190.7	149.5	9.3	
		129.0; 131.2; 138.2; 139.5	162.0	104.8		
2	16.5	120.8; 125.4; 127.7; 128.4	191.8	149.4	9.6	^1J(Sn–C) = 852.8, 897.6
		129.0; 131.1. 138.4; 139.7	162.9	104.9	22.4	^2J(Sn–C) = 51.9
3	16.6	120.6; 125.3; 127.7; 128.3	191.9	149.3	20.2	^1J(Sn–C) = 815.2, 861.6
		129.0; 131.1; 138.5; 139.8	163.1	105.2	36.3	^2J(Sn–C) = 32.3
4	16.6	120.4; 125.2; 127.6; 128.3	192.1	149.1	29.4	
		129.0; 131.0; 138.6; 140.0	163.0	106.0	51.2	
5	16.5	120.8; 125.4; 127.7; 128.4	191.6	149.4	13.62; 26.0	^1J(Sn–C) = 831.4,869.7
		128.9; 131.1; 138.4; 139.8	162.9	104.8	27.1; 29.4	^2J(Sn–C) = 46.4
						^3J(Sn–C) = 137
6	16.2	120.7; 125.9; 127.5; 127.9	191.2	149.5	see the	
		128.1; 128.2; 128.5; 128.6	164.0	148.2	third	
		128.7; 128.9; 131.4; 135.3		105.4	column	
		137.7; 138.5				
7	15.9	120.8; 125.5; 127.6; 128.2	191.0	149.3	36.8;124.5	^1J(Sn–C) = 817.1
		128.8; 131.2; 138.5; 139.1	162.6	105.0	127.9;129.2	^1J(Sn–C) = 772.2
					138.1	^2J(Sn–C) = 36.4
8	16.4	120.9; 125.8; 127.9; 128.3	191.3	149.5	133.2	
		128.9; 131.3; 138.0; 139.0			143.9	
9	16.1	121.0; 121.3; 121.7; 127.0	n.o.	n.o.	n.o.	
	16.3	121.1; 127.3; 127.3; 128.4	n.o.	n.o.	n.o.	
	16.4	128.5; 128.5; 128.6; 128.8				
	16.5	128.9; 129.0; 129.1; 132.5				
		132.6; 132.8; 133.0; 136.5				
		136.6; 136.8				
9	16.4	121.2; 121.5; 122.0; 127.4	n.o.	n.o.	n.o.	in CD$_2$Cl$_2$
	16.5	127.4; 127.7; 127.7; 128.7	n.o.	n.o.	n.o.	
	16.6	128.8; 128.9; 129.0; 129.2				
		129.3; 129.5; 129.5; 133.0				
		133.1; 133.2; 133.4				
10	16.2	120.2; 121.1; 121.5; 126.4	n.o.	149.6	12.2	
		128.4; 128.8; 132.1; 137.1	n.o.	n.o.		
		137.4				
11	16.2 br	120.2; 120.9; 121.1; 121.5	n.o.	n.o.	see the	
	16.2	126.4; 126.5; 126.7; 128.0	n.o.	n.o.	third	
	16.3	128.2; 128.4; 128.4; 128.6			column	
	16.32	128.8; 128.9; 129.0; 129.1				
	16.4	129.8; 131.9; 132.1; 132.3				
		132.5; 134.4; 134.6; 134.8				
12	16.2	120.2; 121.5; 126.3; 128.4	191.1	149.9	13.7; 25.7	^2J(Sn–C) = 66.4
		128.8; 132.1; 137.2; 137.6	163.0	105.4	27.4; 32.1 br	

[a] J in Hz.

molecule x, y, x, and the equivalent $1 + x$, y, z; x, y, $1 + z$ are normal Van der Waals contacts.

The tin atom is surrounded by six donor atoms but, as in certain organotin(IV) derivatives [8], the environment is hardly octahedral, in contrast to typical tin(IV) derivatives of β-diketones: *trans*-Me$_2$Sn(acac)$_2$ [10], *trans*-Bu$_2$Sn(dbm)$_2$ [11], *cis*-Cl$_2$Sn(acac)$_2$ [12], or [(acac)Sn(O-i-Pr)$_2$(μ-O-i-Pr)]$_2$ [13], where acacH and dbmH indicate acetylacetone and dibenzoylmethane, respectively; in our compounds the

Table 6. ^{13}C NMR data for Q'' derivatives (in CDCl$_3$)

Q''H	CH$_3$	phenyl rings	CO,C(5)	C(3),C(4)	C–Sn	other data [a]
13	15.6 26.6	120.6; 126.5; 129.1; 137.2	194.3 160.4	147.7 104.2		
14	17.4 27.9	121.1; 125.5; 128.9; 138.3	192.7 161.8	149.0 104.6	8.9	$^1J(\mathrm{Sn\text{-}C}) = 918.8$
15	17.5 27.9	120.90; 125.33; 128.94; 138.45	193.2 161.8	148.9 104.8	9.4 21.8	$^1J(\mathrm{Sn\text{-}C}) = 960.8$ $^1J(\mathrm{Sn\text{-}C}) = 947$
16	17.5 27.9	120.7; 125.2; 128.9; 138.6	193.4 162.2	148.8 105.1	20.0 35.5	$^1J(\mathrm{Sn\text{-}C}) = 874.8,\,836$ $^2J(\mathrm{Sn\text{-}C}) = 31$
17	17.5 28.0	120.6; 125.1; 129.0; 138.6	193.9 162.4	148.6 106.0	29.3; 30.2 50.2	$^1J(\mathrm{Sn\text{-}C}) = 844.6/892$ $^2J(\mathrm{Sn\text{-}C}) = 44.4$
18	17.5 27.9	120.9; 125.3; 128.9; 138.5	193.1 162.0	148.9 104.8	13.6; 26.0 26.9; 28.7	$^2J(\mathrm{Sn\text{-}C}) = 56$
19	17.1 27.3	120.6; 120.9; 125.8; 127.6 128.1; 128.5; 135.3; 137.8	193.7 162.9	148.2; 149.1 104.0; 105.5	see the third column	
20	17.1 27.5	120.9; 125.4; 128.8; 138.2	193.2 n.o.	148.8 105.0	36.3; 124.3 127.5; 129.1 138.9	$^2J(\mathrm{Sn\text{-}C}) = 32$
21	17.3 27.6	120.9; 125.7; 128.8; 138.1	193.4 162.2	149.1 103.0	132.9 144.0	
22	17.0; 17.1 27.1; 27.1	121.1; 121.6; 127.0; 127.2 127.3; 128.9; 128.9; 129.1 129.1; 136.5; 136.7; 136.7 136.8	195.2; 195.1 194.6; 194.4 162.0	150.1; 150.2 150.3; 105.9 105.7; 105.5		
23	16.9; 17.2 27.2	120.2; 121.2; 121.4; 126.4 128.7; 137.2	195.0 162.2	149.4 105.6	10.4 br 11.6	
24	16.7; 16.9 17.0; 17.1 17.2; 26.8 27.1; 27.2 27.4	120.2; 121.0; 121.1; 121.4 121.5; 126.3; 126.5; 126.6 126.6; 128.6; 128.7; 128.8 128.9; 129.0; 129.5; 129.7 129.8; 129.9; 130.0; 134.2 134.3; 134.5; 134.8; 137.1 137.3; 137.3; 137.5	192.8; 193.5 194.1; 194.9 195.5; 162.4	149.3; 149.5 149.6; 149.6 149.7; 145.8 146.1; 105.7 106.0	see the third column	
	16.9; 17.3 27.1	120.2; 120.2; 121.1; 121.3 121.4; 126.3; 128.8; 137.2br	194.6 br 162.1br	149.3 br 105.7br	13.6 25.7 27.2	$^2J(\mathrm{Sn\text{-}C}) = 65.8$ $^3J(\mathrm{Sn\text{-}C}) = 12.9$

[a] J in Hz.

Table 7

^{119}Sn NMR data [a]

No.	Compound	$-\delta$ (ppm)	No.	Compound	$-\delta$ (ppm)
1	$Q'_2Sn(CH_3)_2$	318.5	13	$Q''_2Sn(CH_3)_2$	320.6
2	$Q'_2Sn(C_2H_5)_2$ [b]	356.4	14	$Q''_2Sn(C_2H_5)_2$	357.6
3	$Q'_2Sn(i\text{-}C_3H_7)_2$	410.6	15	$Q''_2Sn(i\text{-}C_3H_7)_2$	411.8
4	$Q'_2Sn(t\text{-}C_4H_9)_2$	456.2	16	$Q''_2Sn(t\text{-}C_4H_9)_2$	455.7
		468.4			463.4
5	$Q'_2Sn(n\text{-}C_4H_9)_2$	355.0	17	$Q''_2Sn(n\text{-}C_4H_9)_2$	355.6
6	$Q'_2Sn(C_6H_5)_2$	480.9	18	$Q''_2Sn(C_6H_5)_2$	483.1
		486.0			487.1
		500–503			
7	$Q'_2Sn(C_6H_5CH_2)_2$	451.3	19	$Q''_2Sn(C_6H_5CH_2)_2$	448.7
8	$Q'_2Sn(C_2H_3)_2$	495 br	20	$Q''_2Sn(C_2H_3)_2$	493.9 br
9	Q'_2SnCl_2	629.6	21	Q''_2SnCl_2	630.7
		632.5			632.6
		634.9			635.5
10	Q'_2SnCH_3Cl	491.4	22	Q''_2SnCH_3Cl	490.9
		491.7			492.3
		494.2			
		495.5			
11	$Q'_2SnC_6H_5Cl$	563.9	23	$Q''_2SnC_6H_5Cl$	560.7
		564.4			562.9
		564.9			565.3
12	$Q'_2Sn(n\text{-}C_4H_9)Cl$	509.6	24	$Q''_2Sn(n\text{-}C_4H_9)Cl$	508.7
		510.0			509.6
		512.3			510.3
		513.8			

[a] All spectra in $CDCl_3$ solution (except 9, in CD_2Cl_2). [b] 3.5 ppm broad.

cis- or trans-angles range from 74.1(2) to 127.4(2)° or from 150.0(5) to 153.1(2)°. The least square-planes of the regions expected to be planar, the displacements of the atoms from the best plane, the χ^2 values with the probability P that the regions are not planar, and the angles between the planes are given in Table 10. In particular, the four oxygens and the tin atom do not lie in a plane; similarly the six-membered C(4), C(13), O(14), Sn, O(15), C(5) and C(4a), C(13a), O(14a), Sn, O(15a), C(5a) rings adopt a twist-boat conformation with the following puckering parameters $Q = 0.180$, $\theta = 87.0$, $\phi = 29.5°$ and $Q = 0.170$, $\theta = 80.7$, $\phi = 33.5°$, resp. [14], to be compared with $\theta = 90$ and $\phi = 30°$ for an ideal twist-boat.

The marked distortion of the molecule from the expected octahedral symmetry is due to the presence of the two bulky butyl groups: there is a separation of only 3.04–3.25 Å between O(14) and C(22), C(22a), C(23), C(23a), C(24) and C(24a) and between O(14a) and C(22), C(22a), C(23a), C(25) and C(25a). Indeed, the two butyl groups are nearly eclipsed, and the C–Sn–C axis is bent on one side (150.0(5)°); this allows methyl groups to occupy the space left between the O(14) and O(14a), which are 4.340(9) Å apart, while on the other side the distance between the remaining two oxygens, O(15) and O(15a), is only 2.579(8) Å; correspondingly the angles O(14)–Sn–O(14a) and O(15)–Sn–O(15a) are very different (127.4(2) and 74.1(2)°, respectively), while the "bite" of the two Q ligands remains the same i.e.: 79.8(2)° for O(14)–Sn–O(15) and 79.3(2)° for O(14a)–Sn–O(15a).

Other effects of the bulkiness of the t-butyl groups can be seen in the lengthening of the Sn–C bonds and of two Sn–O distances. The Sn–C bonds are 2.20(1) Å, that
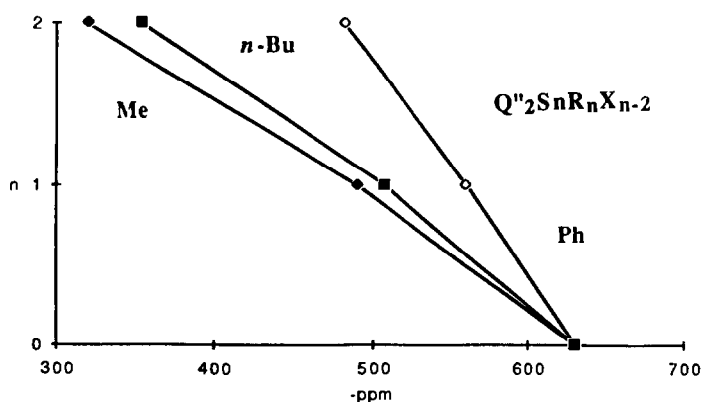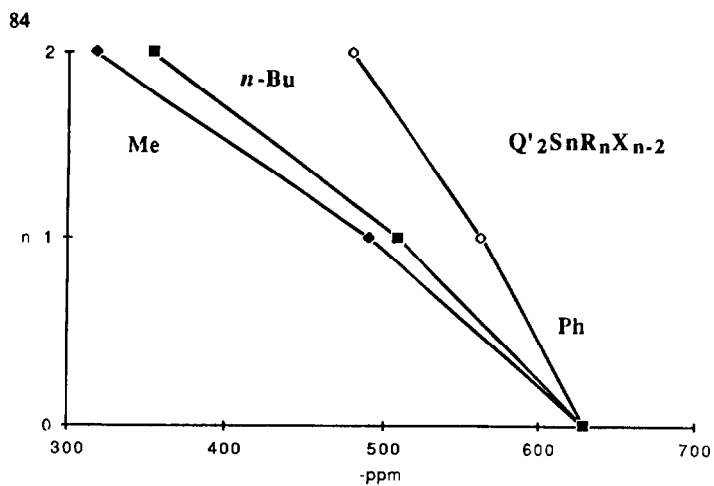
Fig. 3. Effects of the substitution on the ^{119}Sn chemical shift of $Q'_2SnR_nX_{n-2}$ and of $Q''_2SnR_nX_{n-2}$ complexes.
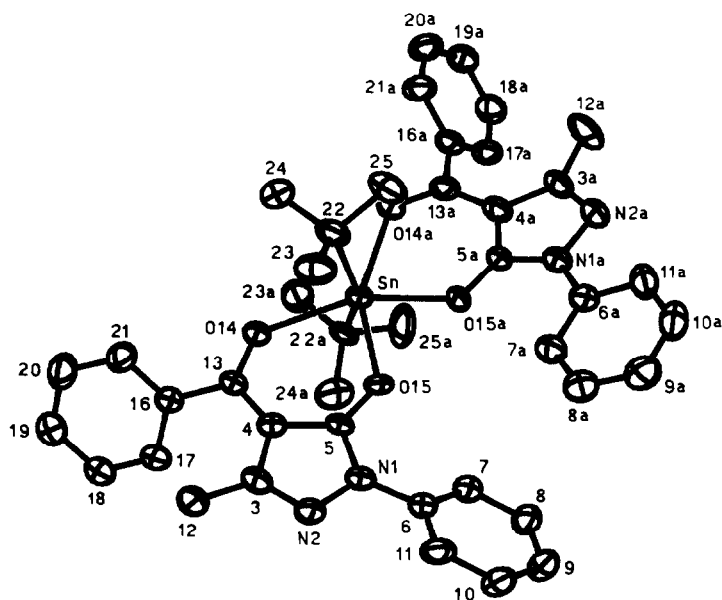

Fig. 4. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 30% of the electron density. Hydrogen atoms are omitted for clarity.

Table 8

Interatomic distances (Å) and bond angles (deg) with e.s.d.'s in parentheses

In the coordination sphere:			
Sn–O(14)	2.381(7)	Sn–O(14a)	2.461(6)
Sn–O(15)	2.145(5)	Sn–O(15a)	2.135(6)
Sn–C(22)	2.204(11)	Sn–C(22a)	2.196(17)
O(14)–Sn–O(15)	79.8(2)	O(14a)–Sn–O(15a)	79.3(2)
O(14)–Sn–C(22)	82.9(4)	O(14a)–Sn–C(22)	84.9(3)
O(14)–Sn–C(22a)	83.6(6)	O(14a)–Sn–C(22a)	82.3(5)
O(14)–Sn–O(15a)	153.1(2)	O(14a)–Sn–O(15)	152.1(2)
O(15)–Sn–C(22)	106.9(3)	O(15a)–Sn–C(22)	98.4(4)
O(15)–Sn–C(22a)	96.8(4)	O(15a)–Sn–C(22a)	105.6(6)
O(14)–Sn–O(14a)	127.4(2)	C(22)–Sn–C(22a)	150.0(5)
O(15)–Sn–O(15a)	74.1(2)		
In the bidentate-5-pyrazolonate ligands:			
N(1)–N(2)	1.39(1)	N(1a)–N(2a)	1.40(1)
N(2)–C(3)	1.31(1)	N(2a)–C(3a)	1.31(1)
C(3)–C(4)	1.44(1)	C(3a)–C(4a)	1.44(1)
C(4)–C(5)	1.42(1)	C(4a)–C(5a)	1.42(1)
C(5)–N(1)	1.37(1)	C(5a)–N(1a)	1.34(1)
N(1)–C(6)	1.42(1)	N(1a)–C(6a)	1.42(1)
C(3)–C(12)	1.50(1)	C(3a)–C(12a)	1.50(2)
C(4)–C(13)	1.41(1)	C(4a)–C(13a)	1.41(1)
C(5)–O(15)	1.292(9)	C(5a)–O(15a)	1.286(9)
C(13)–O(14)	1.26(1)	C(13a)–O(14a)	1.27(1)
C(13)–C(16)	1.48(1)	C(13a)–C(16a)	1.50(1)
N(2)–N(1)–C(5)	111.6(7)	N(2a)–N(1a)–C(5a)	111.1(8)
N(2)–N(1)–C(6)	118.7(7)	N(2a)–N(1a)–C(6a)	117.9(8)
C(5)–N(1)–C(6)	129.4(7)	C(5a)–N(1a)–C(6a)	130.8(8)
N(1)–N(2)–C(3)	106.0(7)	N(1a)–N(2a)–C(3a)	105.9(8)
N(2)–C(3)–C(4)	112.0(8)	N(2a)–C(3a)–C(4a)	112.1(9)
N(2)–C(3)–C(12)	119.0(9)	N(2a)–C(3a)–C(12a)	117.9(9)
C(4)–C(3)–C(12)	128.6(9)	C(4a)–C(3a)–C(12a)	129.9(1.0)
C(3)–C(4)–C(5)	103.7(7)	C(3a)–C(4a)–C(5a)	103.2(8)
C(3)–C(4)–C(13)	132.5(8)	C(3a)–C(4a)–C(13a)	131.5(9)
C(5)–C(4)–C(13)	123.6(7)	C(5a)–C(4a)–C(13a)	124.6(8)
C(4)–C(5)–N(1)	106.4(7)	C(4a)–C(5a)–N(1a)	107.7(7)
C(4)–C(5)–O(15)	131.7(7)	C(4a)–C(5a)–O(15a)	130.2(8)
N(1)–C(5)–O(15)	121.9(7)	N(1a)–C(5a)–O(15a)	122.0(8)
N(1)–C(6)–C(7)	121.1(8)	N(1a)–C(6a)–C(7a)	122.8(9)
N(1)–C(6)–C(11)	119.2(9)	N(1a)–C(6a)–C(11a)	116.7(1.0)
C(4)–C(13)–O(14)	121.1(8)	C(4a)–C(13a)–O(14a)	123.0(8)
C(4)–C(13)–C(16)	120.7(7)	C(4a)–C(13a)–C(16a)	120.3(8)
O(14)–C(13)–C(16)	118.1(8)	O(14a)–C(13a)–C(16a)	116.7(8)
Sn–O(14)–C(13)	132.0(6)	Sn–O(14a)–C(13a)	128.7(6)
C(13)–C(16)–C(17)	120.4(9)	C(13a)–C(16a)–C(17a)	120.2(7)
C(13)–C(16)–C(21)	120.1(9)	C(13a)–C(16a)–C(21a)	119.4(9)
Sn–O(15)–C(5)	129.1(5)	Sn–O(15a)–C(5a)	130.5(5)
In the t-butyl ligands:			
C(22)–C(23)	1.53(2)	C(22a)–C(23a)	1.51(3)
C(22)–C(24)	1.51(2)	C(22a)–C(24a)	1.51(3)
C(22)–C(25)	1.53(2)	C(22a)–C(25a)	1.54(3)

Table 8 (continued)

In the t-butyl ligands:			
Sn–C(22)–C(23)	107.8(8)	Sn–C(22a)–C(23a)	107.9(1.2)
Sn–C(22)–C(24)	107.6(1.0)	Sn–C(22a)–C(24a)	113.1(1.5)
Sn–C(22)–C(25)	110.0(9)	Sn–C(22a)–C(25a)	110.0(1.5)
C(23)–C(22)–C(24)	112.0(1.3)	C(23a)–C(22a)–C(24a)	109.3(1.8)
C(23)–C(22)–C(25)	109.0(1.3)	C(23a)–C(22a)–C(25a)	108.5(1.7)
C(24)–C(22)–C(25)	110.4(1.0)	C(24a)–C(22a)–C(25a)	107.9(1.8)
In the phenyl rings (Weighted average of bond distances and endocyclic angles):			
C(joint)–C(*ortho*)	1.389(5)	∢ C(*ipso*)	119.9(5)
C(*ortho*)–C(*meta*)	1.382(7)	∢ C(*ortho*)	119.8(4)
C(*meta*)–C(*para*)	1.384(8)	∢ C(*meta*)	120.3(5)
		∢ C(*para*)	119.8(7)

is longer than in *trans*-Me$_2$Sn(acac)$_2$ (2.14(2) Å) [10] or in *trans*-Bu$_2$Sn(dbm)$_2$ [11], 2.115(10) Å. Similarly, in the case of the Sn–O distances, in our compound there are two sets of values: one set, which is normal, includes the shorter ones (namely: Sn–O(15) 2.145(5) and Sn–O(15a) 2.135(6) Å) and is comparable with the Sn–O distances reported for other tin(IV) β-diketonates, such as: *trans*-Me$_2$Sn(acac)$_2$ [10] (2.18(1) and 2.20(1) Å), *trans*-Bu$_2$Sn(dbm)$_2$ [11] (2.189(8) and 2.199(8) Å), *cis*-Cl$_2$Sn(acac)$_2$ [12] (2.051(2) and 2.064(2) Å), or [(acac)Sn(O-i-Pr)$_2$(μ-O-i-Pr)]$_2$ [13] (2.106 or 2.112 Å). The other set includes the longer distances (namely: Sn–O(14) 2.381(7) and Sn–O(14a) 2.461(6) Å). The exceptional lengthening of these two bonds can be attributed to the need to accomodate the two t-butyl groups and to the asymmetry of β-diketonato ring in the Q$^-$ ligand as found in (Q$'$)$_2$UO$_2$(OSMe$_2$) [15]. In any case, in our compound the shorter Sn–O bonds are near to the longer C–O bonds and vice versa, as expected if the contribution of one of the two enolate forms were higher, which was previously established from stronger evidence in the case of bis(benzoylacetonato-O,O')tin(II) [16]. In addition, the "bite" of our ligand (79.3(2) or 79.8(2)°) is bigger than in the seven-coordinated complex (Q$'$)$_2$UO$_2$(OSMe$_2$) (71.8(2)° or 72.0(2)° [15]) but is the smallest among the series of octahedral tin(IV) β-diketonates: *trans*-Me$_2$Sn(acac)$_2$ [10] (86(1)°), *trans*-Bu$_2$Sn(dbm)$_2$ [11] (83.2(2) or 83.8(2)°), *cis*-Cl$_2$Sn(acac)$_2$ [12] (87.3(1)°), or [(acac)Sn(O-i-Pr)$_2$(μ-O-i-Pr)]$_2$ [13] (83.4(2)°). Comparison with the crystal structure of the parent ligand Q$'$H [17] (see Fig. 1), shows that inside the chelate rings of the tin complex the C–O bond order is lower and the C–C bond order higher than in the starting β-diketone.

Inside both the pyrazole rings the rules [18] about the pattern of values for the angles apply, here and in (Q$'$)$_2$UO$_2$(OSMe$_2$) [15], although the value of the C(3)–C(4) distances (as defined in ref. 18) lie in the highest part of the range of distances reported up to now.

Experimental

The usual procedures and instruments were employed [7b]. ^{1}H, ^{13}C, ^{119}Sn NMR and electronic spectra (HP 8452A Diode Array Spectrophotometer) were recorded in CDCl$_3$ and CHCl$_3$ solution unless stated otherwise.

Table 9

Average bond distances (Å) and angles (deg) with e.s.d.'s in parentheses [a]

	N	x_m	σ_m	σ_m'
Sn–O(14)	2	2.422	0.040	0.005
Sn–O(15)	2	2.141	0.005	0.004
Sn–C(22)	2	2.202	0.004	0.009
N(1)–N(2)	2	1.393	0.006	0.008
N(1)–C(6)	2	1.419	0.004	0.009
N(2)–C(3)	2	1.310	0.004	0.010
C(3)–C(4)	2	1.442	0.002	0.009
C(3)–C(12)	2	1.498	0.000	0.011
C(4)–C(5)	2	1.423	0.001	0.008
C(4)–C(13)	2	1.413	0.001	0.009
C(5)–N(1)	2	1.359	0.014	0.008
C(5)–O(15)	2	1.289	0.003	0.007
C(13)–O(14)	2	1.267	0.002	0.008
C(13)–C(16)	2	1.492	0.009	0.009
C(22)–C(met)	6	1.522	0.005	0.010
O(14)–Sn–O(15)	2	79.6	0.2	0.2
O(15)–Sn–C(22)	4	101.9	2.6	0.2
N(2)–N(1)–C(5)	2	111.4	0.2	0.5
N(2)–N(1)–C(6)	2	118.4	0.4	0.5
C(5)–N(1)–C(6)	2	130.1	0.7	0.5
N(1)–N(2)–C(3)	2	106.0	0.1	0.5
N(2)–C(3)–C(4)	2	112.1	0.1	0.6
N(2)–C(3)–C(12)	2	118.5	0.5	0.7
C(4)–C(3)–C(12)	2	129.2	0.6	0.7
C(3)–C(4)–C(5)	2	103.5	0.3	0.5
C(3)–C(4)–C(13)	2	132.0	0.5	0.6
C(5)–C(4)–C(13)	2	124.0	0.5	0.6
C(4)–C(5)–N(1)	2	107.0	0.6	0.5
C(4)–C(5)–O(15)	2	131.1	0.7	0.5
N(1)–C(5)–O(15)	2	121.9	0.1	0.5
N(1)–C(6)–C(7)	2	121.8	0.8	0.6
N(1)–C(6)–C(11)	2	118.1	1.2	0.7
C(4)–C(13)–O(14)	2	122.0	1.0	0.6
C(4)–C(13)–C(16)	2	120.5	0.2	0.5
O(14)–C(13)–C(16)	2	117.4	0.7	0.4
Sn–O(14)–C(13)	2	130.3	1.7	0.4
C(13)–C(16)–C(17)	2	120.3	0.1	0.6
C(13)–C(16)–C(21)	2	119.7	0.4	0.6
Sn–O(15)–C(5)	2	129.7	0.7	0.4
Sn–C(22)–C(met)	6	108.9	0.7	0.4
C(met)–Sn–C(met)	6	109.8	0.6	0.6

[a] All values were calculated according to A. Domenicano, A. Vaciago and C.A. Coulson, Acta Crystallogr., B31 (1975) 221.

$Q_2'Sn(CH_3)_2$, **1**. To a methanol solution (100 mL) of Q'H (2 mmol) [1] were added potassium hydroxide (2 mmol) and dimethyldichlorotin(IV) (1 mmol). A precipitate was formed. The mixture was set aside overnight and the precipitate, then filtered off, washed with methanol (ca. 10 mL), and dried to constant weight, and shown to be compound **1**, which was recrystallized from methanol/water.

88

Table 10

Planarity of molecular regions

Plane	Equation [a], χ^2, P	Atoms	Displacements (Å)
I	$0.1225X' - 0.5423Y' - 0.8312Z' - 0.0876 = 0$	Sn	−0.0008(6)
		O(14)	−0.056(7)
		O(15)	0.139(6)
	$\chi^2 = 1275.5\ (n = 2)\ P > 99\%$	O(14a)	0.124(7)
		O(15a)	−0.126(7)
II	$0.0778X' - 0.5221Y' - 0.8493Z' + 0.0177 = 0$	Sn	−0.0006(6)
		O(14)	0.044(7)
		O(15)	0.089(6)
	$\chi^2 = 639.1\ (n = 3)\ P > 99\%$	C(5)	−0.034(8)
		C(13)	0.092(9)
		C(4)	−0.139(8)
III	$0.1788X' - 0.6267Y' - 0.7585Z' - 0.6637 = 0$	Sn	−0.0001(5)
		O(14a)	−0.035(7)
		O(15a)	0.073(7)
	$\chi^2 = 468.3\ (n = 3)\ P > 99\%$	C(5a)	−0.124(9)
		C(4a)	−0.007(9)
		C(13a)	0.095(9)
IV	$-0.0541X' - 0.6126Y' - 0.7885Z' - 1.2282 = 0$	N(1)	0.024(7)
		N(2)	−0.015(8)
		C(3)	−0.003(9)
	$\chi^2 = 31.6\ (n = 2)\ P > 99\%$	C(4)	0.020(8)
		C(5)	−0.025(7)
V	$0.3355X' - 0.6933Y' - 0.6378Z' - 1.5918 = 0$	N(1a)	−0.003(9)
		N(2a)	0.004(10)
		C(3a)	−0.002(10)
	$\chi^2 = 0.46\ (n = 2)\ P = 20.4\%$	C(4a)	−0.001(9)
		C(5a)	0.002(8)
VI	$-0.3960X' - 0.6965Y' - 0.5984Z' - 3.6517 = 0$	C(6)	0.004(8)
		C(7)	−0.004(10)
		C(8)	0.000(13)
	$\chi^2 = 0.87\ (n = 3)\ P = 16.7\%$	C(9)	0.001(14)
		C(10)	0.004(13)
		C(11)	−0.006(11)
VII	$0.3757X' + 0.2514Y' - 0.8920Z' + 6.2660 = 0$	C(16)	−0.002(11)
		C(17)	−0.001(19)
		C(18)	0.009(21)
	$\chi^2 = 0.42\ (n = 3)\ P = 6.6\%$	C(19)	−0.006(20)
		C(20)	−0.003(23)
		C(21)	0.006(17)
VIII	$0.4293X' - 0.7016Y' - 0.5687Z' - 2.2149 = 0$	C(6a)	0.007(10)
		C(7a)	−0.004(11)
	$\chi^2 = 2.00\ (n = 3)\ P = 42.2\%$	C(8a)	−0.005(15)
		C(9a)	0.014(19)
		C(10a)	−0.002(22)
		C(11a)	−0.015(18)
IX	$-0.7118X' - 0.2413Y' - 0.6596Z' + 1.4190 = 0$	C(16a)	0.008(9)
		C(17a)	−0.018(10)
		C(18a)	0.029(12)
	$\chi^2 = 12.19\ (n = 3)\ P > 99\%$	C(19a)	−0.020(13)
		C(20a)	0.008(15)
		C(21a)	−0.005(13)

Table 10 (continued)

Dihedral angles (deg)					
II/IV	9.82	II/VII	49.03	IV/VI	23.08
III/V	11.98	III/IX	58.37	V/VIII	6.68

[a] Transformation matrix from triclinic X, Y, Z to orthogonal X', Y', Z' coordinates:

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^{\star} \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^{\star} \end{pmatrix}$$

The remaining compounds were prepared similarly, with the following variations: 7 and 13 were crystallized from chloroform/petrol ether; 4, 19 and 23 from chloroform/methanol; crude 12 was extracted with dichloromethane and then evaporated extract was crystallized from methanol/water. Compound 9 was obtained from hydrated tin(IV) chloride as well as from ammonium hexachlorostannate(IV).

X-Ray analysis

A prismatic pale yellow crystal with approximate dimensions $0.15 \times 0.15 \times 0.40$ mm was used for data collection and mounted on an Enraf Nonius CAD-4 diffractometer with graphite-monochromated Cu-K_{α} radiation.

Table 11

Crystal data, data collection, and refinement of the structure

Formula	$C_{42}H_{44}N_4O_4Sn$
Formula weight	787.5
Space group	$P\bar{1}$
Color	pale yellow
a, Å	11.051(1)
b, Å	20.827(5)
c, Å	8.7155(6)
α, deg	98.160(9)
β, deg	97.071(8)
γ, deg	101.974(9)
V_c, Å^3	1918.2(2)
Z	2
D(calcd) g cm^{-3}	1.36
Crystal size, mm	$0.28 \times 0.56 \times 0.07$
μ(Cu-K_{α}), cm^{-1}	58.7
Data collection instrument	Enraf–Nonius CAD4
Radiation (monochromated)	Cu-K_{α} ($\lambda = 1.5418$ Å)
T of data collection, K	293
Scan mode	$\omega/2\theta$
Data collection range	$4 \leqslant 2\theta \leqslant 70$
standards (measured every 300 min)	$5 - 9 - 5, -7 - 8 1, 5 2 - 6$
No. of unique reflections measured	7196($\pm h$, $\pm k$, l)
No. of data with $F_o^2 \geq 3\sigma(F_o^2)$	6573
No. of parameters refined	460
R^a and R_w^b	0.065, 0.042

[a] $R = (\Sigma \| F_o | - k | F_c \|)/\Sigma | F_o |$. [b] $R_w = [\Sigma w(| F_o | - k | F_c |)^2/\Sigma w | F_o |^2]^{1/2}$.

Table 12

Final coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

Atom	x	y	z	B (Å^2)
Non-hydrogen atoms				
Sn	−0.06036(5)	−0.22616(2)	0.35168(7)	4.46(1)
N(1)	−0.1275(7)	−0.3910(3)	0.6171(9)	4.8(2)
N(2)	−0.2360(8)	−0.4195(3)	0.6702(9)	5.4(2)
C(3)	−0.3253(9)	−0.3950(4)	0.6030(11)	5.6(2)
C(4)	−0.2789(8)	−0.3484(3)	0.5043(10)	5.0(2)
C(5)	−0.1479(7)	−0.3454(3)	0.5237(9)	4.7(2)
C(6)	−0.0184(8)	−0.4150(3)	0.6529(10)	4.7(2)
C(7)	0.0758(8)	−0.4082(4)	0.5598(13)	5.4(2)
C(8)	0.1779(10)	−0.4359(5)	0.5932(17)	6.5(3)
C(9)	0.1883(12)	−0.4697(6)	0.7180(19)	6.9(3)
C(10)	0.0937(13)	−0.4760(5)	0.8107(16)	6.6(3)
C(11)	−0.0079(12)	−0.4484(4)	0.7790(12)	5.7(2)
C(12)	−0.4532(10)	−0.4119(5)	0.6478(16)	7.1(3)
C(13)	−0.3398(7)	−0.3155(3)	0.3980(11)	5.0(2)
O(14)	−0.2789(6)	−0.2672(3)	0.3453(9)	5.6(2)
O(15)	−0.0573(6)	−0.3086(2)	0.4732(8)	5.1(1)
C(16)	−0.4752(8)	−0.3399(4)	0.3363(13)	5.1(2)
C(17)	−0.5240(12)	−0.4062(5)	0.2748(23)	7.3(4)
C(18)	−0.6479(13)	−0.4288(6)	0.2083(26)	7.7(5)
C(19)	−0.7250(13)	−0.3840(8)	0.2059(24)	7.1(4)
C(20)	−0.6768(12)	−0.3170(9)	0.2671(28)	8.3(5)
C(21)	−0.5520(12)	−0.2955(6)	0.3311(21)	6.5(3)
C(22)	−0.0891(11)	−0.1438(4)	0.5215(14)	5.6(2)
C(23)	−0.1363(22)	−0.1732(7)	0.6608(18)	7.9(5)
C(24)	−0.1833(15)	−0.1121(6)	0.4387(25)	7.7(5)
C(25)	0.0350(15)	−0.0926(7)	0.5805(22)	8.0(5)
N(1a)	0.3398(7)	−0.1693(3)	0.5223(11)	5.4(2)
N(2a)	0.4350(8)	−0.1217(4)	0.4831(13)	6.3(2)
C(3a)	0.3830(8)	−0.0991(5)	0.3656(13)	5.9(3)
C(4a)	0.2521(8)	−0.1308(4)	0.3205(11)	5.3(2)
C(5a)	0.2310(7)	−0.1759(3)	0.4275(11)	4.7(2)
C(6a)	0.3687(9)	−0.1989(4)	0.6556(14)	5.5(2)
C(7a)	0.2836(10)	−0.2486(5)	0.7005(14)	6.2(3)
C(8a)	0.3179(15)	−0.2748(6)	0.8318(18)	7.2(4)
C(9a)	0.4361(19)	−0.2528(8)	0.9189(22)	8.3(4)
C(10a)	0.5207(14)	−0.2022(10)	0.8763(29)	9.1(6)
C(11a)	0.4889(12)	−0.1738(8)	0.7446(23)	7.9(4)
C(12a)	0.4629(12)	−0.0455(7)	0.3006(18)	8.4(4)
C(13a)	0.1568(8)	−0.1161(4)	0.2168(11)	5.2(2)
O(14a)	0.0410(6)	−0.1374(3)	0.2198(8)	5.5(2)
O(15a)	0.1323(5)	−0.2199(3)	0.4352(8)	5.2(2)
C(16a)	0.1900(8)	−0.0731(4)	0.0969(11)	5.2(2)
C(17a)	0.2690(9)	−0.0894(4)	−0.0079(12)	5.8(3)
C(18a)	0.3002(12)	−0.0491(6)	−0.1165(13)	6.3(3)
C(19a)	0.2619(12)	0.0101(5)	−0.1108(15)	6.6(3)
C(20a)	0.1835(13)	0.0264(5)	−0.0073(18)	7.1(4)
C(21a)	0.1490(12)	−0.0143(4)	0.0991(15)	6.6(3)
C(22a)	−0.0977(20)	−0.2838(6)	0.1127(21)	5.3(3)
C(23a)	−0.1863(17)	−0.2541(10)	0.0129(27)	7.3(4)
C(24a)	−0.1546(25)	−0.3569(8)	0.1056(37)	7.0(3)
C(25a)	0.0245(25)	−0.2783(13)	0.0436(31)	6.9(4)

The SEARCH program was used to obtain 25 reflections, which were used in the program INDEX to derive approximate cell dimensions. Accurate lattice parameters, given in Table 11, were obtained by least-squares refinement of these reflections. The triclinic cell quoted was confirmed by the use of TRACER program [19].

A total of 7705 independent reflections ($4 \leq 2\theta \leq 70°$) were measured at room temperature using $\omega/2\theta$ scan. The intensities of three standard reflections were monitored every 60 min and showed no significant variation. A total of 6573 reflections with $I \geq 3\sigma(I)$ were regarded as observed. The intensities were corrected for Lorentz and polarization effects and for absorption (minimum and maximum absorption factors 0.8307 and 0.9985) [20]. An approximate absolute scale and a mean thermal factor of 3.793 $Å^2$ were determined by Wilson's method [21].

The statistical distribution of the normalized structure factors indicates the centrosymmetric space group $P\bar{1}$.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods. The position of tin atom was derived from a three-dimensional Patterson map. A difference electron density synthesis based upon the Sn signs revealed the positions of all non-hydrogen atoms. The positions of the hydrogen atoms were then calculated from the geometry of the compound and checked on a final difference Fourier map and were not refined. The final least-squares anisotropic refinement, including the hydrogen atoms with isotropic thermal parameters of their bonded atoms gave weighted R_w factor 0.049 ($R = 0.065$) with the maximum shift/esd ratio 0.77. The maximum and minimum $\Delta\rho$ values on the final difference Fourier map were 0.64 and -0.53 e$Å^{-3}$, both close the Sn atom. Unit weights were used in all stages.

All calculations were carried out with the Enraf–Nonius SDP crystallographic computing package [22] and with local programs. The final atomic coordinates for non-hydrogen atoms are given in Table 12.

Supplementary material

Tables .of anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom coordinates, bond distances and angles involving hydrogen atoms, and a list of structure factors can be obtained from one of the authors (B. Bovio).

References

1 B.S. Jensen, Acta Chem. Scand., 13 (1959) 1347; idem, ibid., 1668; idem, ibid., 1890.
2 S. Miyazaki, H. Mukai, S. Umetani, S. Kihara, and M. Matsui, Inorg. Chem., 28 (1989) 3014, and references therein.
3 (a) R. Morales, H. Nekimken, C.S. Bartholdi and P.T. Cunningham, Spectrochim. Acta, A44 (1988) 165 and references therein; (b) A. Terebenina, B. Iordanov, N. Iordanov, I. Bachvarova and G. Borisov, Izv. Khim., 20 (1987) 532 (Chem. Abstr. 109 103545e).
4 F. Bonati, L.A. Oro and M.T. Pinillos, Polyhedron, 4 (1985) 357, and reference therein.

5 S. Kawaguchi, Variety of coordination modes of ligands in metal complexes, Springer Verlag, Berlin, 1988, chapter 5 (pp. 75–119); S. Kawaguchi, Coord. Chem. Rev., 10 (1986) 51; A.R. Siedle, Diketones and related ligands, in Comprehensive Coordination Chemistry, Vol. 2, Pergamon Press, Oxford, 1987, Section 15.4 (pp. 365–412); R.C. Mehrotra, R. Bohra and D.P. Gaur, Metal β-diketonates and allied derivatives, Academic Press, New York, 1978.

6 F. Bonati, Organomet. Chem. Rev., (1966) 379; N.A. Bailey, E. Coates, G.B. Robertson, F. Bonati and R. Ugo, Chem. Comm., (1967) 1041; F. Bonati and G. Minghetti, Angew. Chem., 80 (1968) 664; idem, J. Organomet. Chem., 22 (1970) 5; F. Bonati and G. Minghetti, Synth. React. Inorg. Metal-Org. Chem., 5 (1975) 135.

7 (a) F. Bonati, and G. Wilkinson, J. Chem. Soc., (1964), 179; (b) G. Gioia Lobbia, F. Bonati, P. Cecchi, A. Cingolani, A. Lorenzotti, J. Organomet. Chem., 378 (1989) 139; G. Gioia Lobbia, F. Bonati, P. Cecchi, D. Leonesi, J. Organomet. Chem., 391 (1990) 155.

8 C. Wei, N.W. Kong, V.G.K. Das, G.B. Jameson and R.J. Butcher, Acta Crystallogr., Cryst. Struct. Commun., C45 (1989) 861 and references therein.

9 C.K. Johnson, ORTEP. Report ORNL-3793, Oak Ridge National Laboratory Tennessee, U.S.A., (1965).

10 G.A. Miller and E.O. Schlemper, Inorg. Chem., 12 (1973) 677.

11 G. Poli, C.J. Cheer and W.H. Nelson, J. Organomet. Chem., 306 (1986) 347.

12 G.A. Miller and E.O. Schlemper, Inorg. Chim. Acta, 30 (1978) 131.

13 C.D. Chandler, G.D. Fallon, A.J. Koplick and B.O. West, Austr. J. Chem., 40 (1987) 1427.

14 D. Cremer and J.A. Pople, J. Am. Chem. Soc., 97 (1975) 1354.

15 R.R. Ryan and G.D. Jarvinen, Acta Crystallogr., Cryst. Struct. Commun., C43 (1987) 1295.

16 P.F.R. Ewing, P.G. Harrison and T.J. King, J. Chem. Soc., Dalton Trans., (1975) 1455.

17 M.J. O'Connell, C.G. Ramsay and P.J. Steel, Austr. J. Chem., 38 (1985) 401.

18 F. Bonati and B. Bovio, J. Crystallogr. Spectr. Res., 20 (1990) 235; F. Bonati, Gazz. Chim. Ital., 119 (1989) 291.

19 S.L. Lawton, R.A. Jacobson, TRACER, a cell reduction program, Ames Laboratory, Iowa State University of Sciences and Technology, Ames, IA (1965).

20 A.C.T. North, D.C. Phillips and F.C. Mathews, Acta Crystallogr., Sect. A, 24 (1968) 351.

21 A.J.C. Wilson, Nature (London), 150 (1942) 152.

22 B.A. Frenz and Associates Inc., College Station, TX 77840 and Enraf–Nonius, Delft, 1985.