

Tin(IV) and organotin(IV) derivatives of anionic 4-acyl-5-pyrazolonato ligands: synthesis, spectroscopic characterization (IR, far-IR,  $^{119}\text{Sn}$  Mössbauer,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR) and behavior in solution  
Crystal and molecular structure of *trans*-diphenylbis[1-phenyl-3-methyl-4-(4-bromobenzoyl)-pyrazolon-5-ato]tin(IV)

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## Abstract

Stable six-coordinate tin(IV) and organotin(IV) derivatives  $\text{X}_2\text{SnQ}_2$  ( $\text{X} = \text{Me}$ ,  $\text{Ph}$ ,  $\text{benzyl}$ ,  $\text{cyclohexyl}$ ,  $\text{Cl}$  or  $^t\text{Bu}$ ) ( $\text{QH} = 1\text{-R}'\text{-3-methyl-4-R}''(\text{C}=\text{O})\text{-pyrazol-5-one}$  in general; in detail  $\text{Q}'\text{H}$ :  $\text{R}' = \text{C}_6\text{H}_5$ ,  $\text{R}'' = \text{C}_6\text{H}_5$ ;  $\text{Q}''\text{H}$ :  $\text{R}' = \text{C}_6\text{H}_5$ ,  $\text{R}'' = \text{CH}_3$ ;  $\text{Q}_\text{A}\text{H}$ :  $\text{R}' = \text{C}_6\text{H}_5$ ,  $\text{R}'' = p\text{-CH}_3\text{O-C}_6\text{H}_4$ ;  $\text{Q}_\text{Br}\text{H}$ :  $\text{R}' = \text{C}_6\text{H}_5$ ,  $\text{R}'' = p\text{-Br-C}_6\text{H}_4$ ) have been synthesized and characterized by analysis and spectral (IR and far-IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR,  $^{119}\text{Sn}$  Mössbauer) data. Structural predictions were derived from  $^{119}\text{Sn}$  NMR parameters such as  $^1J_{(^{119}\text{Sn}-^{13}\text{C})}$ ,  $^2J_{(^{119}\text{Sn}-^1\text{H})}$  and  $\delta(^{119}\text{Sn})$ . The diffraction study of the complex  $[\text{Ph}_2\text{Sn}(\text{Q}_\text{Br})_2]$  shows the metal to be six-coordinate in a skewed trapezoidal bipyramidal geometry; Sn–O distances are 2.12(1) and 2.143(7) Å, and 2.223(8) and 2.26(1) Å and the Ph–Sn–Ph bond angle is 173.0(7)°.

**Keywords:** Tin;  $^{119}\text{Sn}$  Mössbauer spectra; X-ray structure; IR; NMR; Pyrazolonato complexes

## 1. Introduction

Diorganotin(IV) derivatives of bidentate O-donor ligands play an important role in many industrial and biological applications [1]: for example carboxylate complexes are known as PVC stabilizers [2] and as catalysts for transesterification reactions [3], polyurethane polymerizations [3] and RTV silicone curing reactions [4], while derivatives of acetylacetone [5], of salicylic acid [6] and the above-mentioned carboxylate compounds [7] possess antitumor properties. The latter are presumably because tin–oxygen bonds can be easily hydrolyzed, giving rise to intermediates that are be-

lieved to link as  $\text{R}_2\text{Sn}^{2+}$  moieties to biocellular macromolecules like DNA [8].

We have recently synthesized organotin(IV) derivatives of 4-R(C=O) pyrazolones [9], a family of heterocyclic enolizable bidentate O-donors (Fig. 1), analogous to 2,4-pentanedione and widely used to extract metal ions and as complexing agents in trace elements spectrophotometric analysis [10].

The crystal structures of three  $\text{R}_2\text{Sn}(\text{Q})_2$  derivatives (where  $\text{R} = \text{Me}$ ,  $^t\text{Bu}$  and  $\text{QH}$  is 4-aryl-1-phenyl-3-methylpyrazol-5-one) were also determined [9a,c,f]: the tin atom was always found in a strongly distorted octahedral environment, with the two alkyl groups in *trans* configuration ca. 150–155° and the pyrazolonato ligands linked to the tin atom through two different sets of Sn–O bonds. This kind of configuration, known as skewed trapezoidal bipyramidal (STB), is relatively

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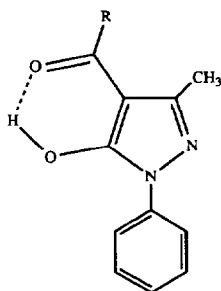


Fig. 1. Q'H: R = C<sub>6</sub>H<sub>5</sub>; Q''H: R = CH<sub>3</sub>; Q<sub>Br</sub>H: R = *p*-Br-C<sub>6</sub>H<sub>4</sub>; Q<sub>A</sub>H: R = *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>.

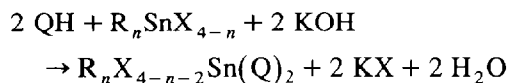
common for organotin(IV) compounds and, in accordance with Kepert's theoretical model [11], it is generally possible to ascribe the distortion to the small bite of the ligands [12]. In fact, in our compounds the bite of the acylpyrazolonates ranges from 78 to 80°, while in several diorganotin(IV)bis(acetylacetonato) derivatives, which adopt a regular octahedral geometry, the ligand bite is found in the range 83–86° [13].

In this paper we report the crystal structure of a Ph<sub>2</sub>Sn(Q)<sub>2</sub> derivative which shows surprisingly a more regular trans octahedral environment around tin. The axial angle (C–Sn–C) is 173.0(7)°, the four Sn–O bonds are essentially equivalent and the bite (O–Sn–O) is increased to 84.5(4) and 85.1(3)°.

In this context it seemed interesting to carry out a more detailed study on a series of R<sub>2</sub>SnQ<sub>2</sub> derivatives (where R = Me, <sup>1</sup>Bt, Ph, benzyl (Bz), cyclohexyl (Cy), Cl and QH = Q'H, Q''H, Q<sub>Br</sub>H, Q<sub>A</sub>H), some of which were synthesized for the first time, to establish the response of <sup>119</sup>Sn Mössbauer, far-IR, <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra parameters to the structure and bonding in these complexes. In particular, we have been tried to correlate the electronegativity and the steric hindrance of R groups and (Q<sup>-</sup>) proligands to the geometry of our derivatives.

## 2. Results and discussion

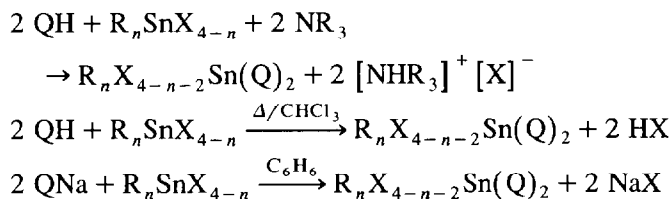
The compounds 1–24 listed below are obtained in good yields according to the following displacement reaction carried out generally in methanol or ethanol and alkali:



The reactions are rapid at room temperature, except those involving olibenzyltin(IV) derivatives which require a longer reaction time.

Relevant analytical data of the new derivatives 4, 10, 16, 21, 22 and 24 are reported in the Experimental section, whereas the spectral and analytical data of 1–3, 5–9, 11–15, 17–20 and 23 agree with those described in previous papers [9a,d,f].

As an alternative to the use of KOH, which may form oxides with R<sub>n</sub>SnX<sub>4-n</sub> such as (R<sub>2</sub>SnO)<sub>x</sub> or (R<sub>2</sub>SnX)<sub>2</sub>O, we have also employed the following procedures:



In all cases the complexes have been purified by dissolving the crude products in chloroform and by adding to the filtered solutions diethyl ether or petroleum ether.

All the complexes, air- and thermally-stable, are soluble in chlorinated and acetone solutions. In the former they are stable for a long time, while upon prolonged standing in acetone solution they are found to decompose somewhat, producing insoluble products for which the IR spectra (see below) and the analytical data suggest an oxide nature.

### 2.1. IR spectra

The IR (Table 1) and far-IR spectra (Table 2) of the ligands employed and of the derivatives 1–24 have been recorded both in nujol mull and in chloroform solutions. Several assignments for our complexes have been proposed on the basis of the previous reports on tin(IV) and organotin(IV) derivatives containing O-donor ligands [14] and of a comparison with the spectra of the starting tin(IV) and organotin(IV) acceptors and of the neutral 4-acyl-5-pyrazolonates.

The main changes observed in the spectra of the complexes with respect to those of the neutral free donors are: the disappearance of the broad absorption due to strongly hydrogen-bonded ν(OH); a slight shift of the carbonyl stretching frequencies; a different pattern for the bands in the 1500–1600 cm<sup>-1</sup> region due to ν(C=C) and ν(C=N). These changes suggest deprotonation of the ligand, involvement of both the carbonyl groups in the coordination of the tin(IV) atom, and formation of the six-membered chelate ring Sn–O–C–C–C–O.

In the spectra carried out in chloroform solution it is also possible to observe several vibrations in the regions 3060–3020 and 3000–2880 cm<sup>-1</sup> assignable to ν(C–H)<sub>aromatic</sub> and ν(C–H)<sub>aliphatic</sub> respectively.

The compound 14 shows the ν(C=O) at ca. 1588 cm<sup>-1</sup>: this value is lower than those of all the other complexes and indicates a greater Sn–O interaction. This fact is also supported by crystal data (see the diffraction study).

In the far-IR region the dimethyltin(IV)bis(4-acyl-5-pyrazolonate) complexes exhibit a single strong band at

ca. 590  $\text{cm}^{-1}$  assignable to  $\nu_{\text{asym}}(\text{Sn}-\text{C})$  [15]. The X-ray crystal structure determinations carried out previously on dimethyltin(IV) derivatives **1** and **13** [9a,c] indicated a non-linear C–Sn–C skeleton; however, in these compounds the  $\nu_{\text{sym}}(\text{Sn}-\text{C})$  cannot be assigned because it is hidden under some ligand vibrations. In the diphenyltin(IV) complexes **2**, **8**, **14** and **20** we assigned the strong absorptions at ca. 290 and ca. 245  $\text{cm}^{-1}$  to  $\nu_{\text{asym}}(\text{Sn}-\text{C})$  and  $\nu_{\text{sym}}(\text{Sn}-\text{C})$  respectively; these assignments are in agreement with those reported for the analogous (phenyl)<sub>2</sub>bis( $\beta$ -diketonate)tin(IV) [14] and for other diphenyltin(IV) compounds [16].

In the spectra of di(*t*-butyl)- and dicyclohexyltin(IV) derivatives, we assigned the respective strong sharp absorptions at ca. 420 and 425  $\text{cm}^{-1}$  to  $\nu_{\text{sym}}(\text{Sn}-\text{C})$  [17]. This is similar to those observed in the starting diorganotin(IV) halides and absent in the spectra of the free donors. It was not possible to identify with certainty the  $\nu_{\text{asym}}(\text{Sn}-\text{C})$  because of the presence of several overlapped ligand and Sn–O vibrations. The dibenzyltin(IV) complexes exhibit two bands at ca. 540 and 455  $\text{cm}^{-1}$  due to  $\nu_{\text{asym}}(\text{Sn}-\text{C})$  and  $\nu_{\text{sym}}(\text{Sn}-\text{C})$  [18].

All the diorganotin(IV) complexes show at least two bands in the region 380–450  $\text{cm}^{-1}$ , most likely due to  $\nu(\text{Sn}-\text{O})$  stretching vibrations [14b,18,19]. These absorptions are shifted downfield with respect to those observed (ca. 490–470 and 440–420  $\text{cm}^{-1}$ ) in the spectra of dihalotin(IV)bis( $\beta$ -diketonato) compounds **5**, **11**, **17** and **23**. This behaviour is explicable by the inductive effect due to substitution of the two organyl with two halide groups. It has been noted [14c,20] that a powerful electron-withdrawing group generally increases the strength of the Sn–O bonds.

The  $\nu(\text{Sn}-\text{Cl})$  for **5**, **11**, **17** and **23** were detected at ca. 330–350  $\text{cm}^{-1}$ : some differences have been found between the spectra recorded in solid-state (nujol mull) and those in chloroform solutions. The former spectra generally exhibit a multiplicity of broad bands due to the presence of different cis- and trans-isomers [14d], whereas the latter spectra show only two strong sharp absorptions. The existence of both cis and trans configurations in the solid-state is likely; only one isomer seems to be present in  $\text{CHCl}_3$  solution, which probably adopts the cis configuration generally found in this class of dihalotin(IV) compounds [14c,21].

The medium or strong absorption generally found at ca. 170–180  $\text{cm}^{-1}$  (compounds **1**, **3–4**, **6–7**, **9–10**, **12–13**, **15–16**, **18–19**, **21–22** and **24**) and at ca. 220  $\text{cm}^{-1}$  (**2**, **8**, **14** and **20**) could be assigned to  $\delta(\text{C}-\text{Sn}-\text{C})$  [16,22]. Moreover, the strong bands observed at ca. 220  $\text{cm}^{-1}$  in the spectra of **5**, **11**, **17** and **23** are characteristic of the  $\delta(\text{Cl}-\text{Sn}-\text{Cl})$  [14a].

## 2.2. NMR spectra

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the new derivatives **4**, **10**, **16**, **21**, **22** and **24** in  $\text{CDCl}_3$  solution are listed in the

Experimental section and were assigned according to Ref. [9]. The data corroborate the conclusions previously reported [9]; in the  $^1\text{H}$  spectra the 3- $\text{CH}_3$  proton resonance in the free ligands shifts upfield upon complexation, whereas in the  $^{13}\text{C}$  spectra the carbon atom of the same group shifts downfield. A displacement for both the carbonyl groups was observed upon coordination: an upfield for C(O), and a downfield displacement for C(5) with the same order of magnitude of the C(3) and C(4) displacement; this trend can be correlated with the formation of Sn–O bonds, which generate a decrease of electron density on the heterocyclic ring.

The main  $^{119}\text{Sn}$  NMR parameters ( $^nJ_{(^{119}\text{Sn}-^1\text{H})}$ ,  $^nJ_{(^{119}\text{Sn}-^{13}\text{C})}$  and  $^{119}\text{Sn}$  chemical shift) of derivatives **1–24** in  $\text{CDCl}_3$  solution are listed in Table 3.

The coupling constants observed are of the same order as those reported in the literature for hexacoordinate diorganobis(chelate)tin(IV) derivatives [23].

The  $\theta(\text{C}-\text{Sn}-\text{C})$  can be correlated to the magnitude of  $^1J_{(^{119}\text{Sn}-^{13}\text{C})}$  and  $^2J_{(^{119}\text{Sn}-^1\text{H})}$  and structural predictions can be derived by applying the Lockhart [24] and Howard equations [25] (Table 3). The values of  $\theta$  obtained for compounds **1** and **13**, by using the Eq. (I) (also reported in Table 3) are significantly different from those previously observed for the same compounds in the solid state [9a,f]. The best results are obtained from Eq. (II) which gives  $\theta$  values nearer to those found in the crystals. Eq. (III) has been utilized to derive the  $\theta$  values for the dibenzyl-, the dicyclo and the di-*t*-butyl. In all cases the data are indicative of a strongly distorted trans-octahedral or STB configuration.

The amount of s character in Sn–C bonds can be related to tin–proton coupling constants through the well-known Holmes–Kaeszy correlation [26]. In our dimethylbis( $\beta$ -diketonate)tin(IV) complexes **1**, **7**, **13** and **19**, it would appear that the Sn–C bonds have 47%, 48%, 43% and 46% s character respectively. On this basis we can conclude that, similar to  $\text{Me}_2\text{Sn}(\text{acac})_2$  ( $\text{acacH} = 2,4\text{-pentanedione}$ ), in  $\text{CDCl}_3$  solution the bonds in the C–Sn–C moieties of **1**, **7**, **13** and **19** are essentially  $\text{sp}_2$  hybrids, whereas the  $5p_x$  and  $5p_y$  orbitals are likely to be involved in the four tin–oxygen bonds.

In the  $^{13}\text{C}$  spectra of dibenzyl- and dicyclohexyltin(IV) compounds the  $^nJ_{(^{119}\text{Sn}-^{13}\text{C})}$  ( $n \geq 1$ ) have also been detected. The poor solubility of the diphenyl compounds prevented observation of the tin satellites; however, the tin hexacoordination is confirmed by the magnitude of the values of  $^{2/3/4}J_{(^{119}\text{Sn}-^{13}\text{C})}$  consistent with octahedral tin(IV) species [23].

The following trends, in accordance with that previously described in literature [27], have always been observed:

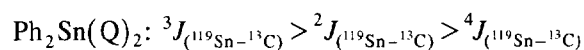


Table 1  
IR data ( $\text{cm}^{-1}$ ) for the ligands and compounds 1–24

Compound	State	Concentration ( $\mu\text{g cm}^{-3}$ )	$\nu(\text{C-H})$	1600–1450	Other data <sup>a</sup>
Q'H	Nujol			1599s, 1570sh, 1560s, 1554s, 1536m, sh, 1498s	3500–2700br
1 ( $\text{CH}_3$ ) <sub>2</sub> Sn(Q') <sub>2</sub>	CHCl <sub>3</sub>	4.0	3037s, 3020m, 3012m, 2993w	1608s, 1563s, 1525sh, 1518m, 1500m	2800–2700br
	Nujol		3079w, 3060w, 3039w, 3021w	1604s, 1594s, 1582s, 1569s, 1531s, 1494s	
	CHCl <sub>3</sub>	4.0	3067sh, 2996m, 2935w	1601s, 1586s, 1570s, 1560sh, 1532s, 1528s, 1523sh, 1507sh, 1500s	
	Nujol		3063w, 3047w, 3026w	1606s, 1598s, 1586s, 1573s, 1555m, 1532s, 1498s	
2 ( $\text{C}_6\text{H}_5$ ) <sub>2</sub> Sn(Q') <sub>2</sub>	CHCl <sub>3</sub>	5.0	3018m, 2989w	1607s, 1587m, 1574m, 1560m, 1529m, 1527m, 1505sh, 1500m	
	Nujol		3081w, 3050w, 3039w, 3022w	1598s, 1593s, 1586sh, 1562s, 1528s, 1503m, 1492s	
3 ( $\text{C}_7\text{H}_7$ ) <sub>2</sub> Sn(Q') <sub>2</sub>	CHCl <sub>3</sub>	3.3	3033m, 2986w, 2933w	1600s, 1594s, 1584m, 1527m, 1552s, 1531m, 1523m, 1519m	
	Nujol		3078w, 3054w, 3044w, 3025w	1599s, 1592s, 1581s, 1567s, 1564s, 1532s, 1497m	
4 ( $\text{C}_6\text{H}_{11}$ ) <sub>2</sub> Sn(Q') <sub>2</sub>	CHCl <sub>3</sub>	4.0	2995m, 2930m, 2852m	1604s, 1597s, 1585m	
	Nujol		3080sh, 3064w, 3048w, 3032w	1598sh, 1594s, 1556s, 1548sh, 1522s, 1500s, 1483s	
5 Cl <sub>2</sub> Sn(Q') <sub>2</sub>	CHCl <sub>3</sub>	4.0	2997m, 2933w, 2850w	1600s, 1586s, 1575s, 1552s, 1513sh, 1500s	
	Nujol		3073sh, 3057m	1614m, 1602s, 1593s, 1582s, 1567sh, 1562s, 1538s, 1527s, 1495m	
6 ( $\text{C}_4\text{H}_9$ ) <sub>2</sub> Sn(Q') <sub>2</sub>	CHCl <sub>3</sub>	4.5	3035m, 2983w	1601s, 1595s, 1584m, 1568s, 1540m, 1526m, 1521m, 1507m, 1500m	
	Nujol			1622s, 1614s, 1609s, 1592s, 1580s, 1574s, 1567s, 1557s, 1538m, 1494s	3530–2250br
Q''H	CHCl <sub>3</sub>	4.0	2993m, 2930m, 2882w	1623s br, 1596s, 1568s br	
	Nujol		3081w, 3064w, 3044w	1600s, 1589s, 1573s, 1534s, 1501sh, 1488s	
	CHCl <sub>3</sub>	4.5	2984m, 2884w	1606s, 1594s, 1582s, 1539m	
	Nujol		3085w, 3066w, 3050w, 3041w, 3023w	1601s, 1590s, 1575s, 1564s, 1558sh, 1545s, 1534s, 1500sh, 1483s	
8 ( $\text{C}_7\text{H}_7$ ) <sub>2</sub> Sn(Q'') <sub>2</sub>	CHCl <sub>3</sub>	4.0	2991m, 2930m	1619s, 1597s, 1575s, 1535s, 1500sh	
	Nujol		3078w, 3061w, 3049w, 3022w	1611s, 1600s, 1591s, 1573s, 1539s, 1529s, 1503sh, 1482s	
9 ( $\text{C}_6\text{H}_{11}$ ) <sub>2</sub> Sn(Q'') <sub>2</sub>	CHCl <sub>3</sub>	4.5	3060sh, 3037m, 3011m, 2988m, 2929w	1611s, 1578s, 1535s, 1518m, 1500sh	
	Nujol		3077w, 3058w, 3045w	1597s, 1592s, 1566s, 1544s, 1530s, 1507sh, 1487s	
	CHCl <sub>3</sub>	4.5	3034m, 3022m, 3013m, 2983w, 2921w	1607s, 1595s, 1583s, 1532s	
	Nujol		3076w, 3064w, 3047w	1598s, 1592s, 1566s, 1544s, 1530s, 1507sh, 1487s	
11 Cl <sub>2</sub> Sn(Q'') <sub>2</sub>	CHCl <sub>3</sub>	4.0	3037m, 3012m, 2996w, 2882w	1606s, 1596s, 1586s, 1563s, 1540s, 1522m, 1511m, 1495m	
	Nujol		3077w, 3063w, 3043w, 3028w	1606s, 1592s, 1580s, 1545s, 1533s, 1492s	
12 ( $\text{C}_4\text{H}_9$ ) <sub>2</sub> Sn(Q'') <sub>2</sub>	CHCl <sub>3</sub>	3.9	3034m, 3018m, 2995m, 2890w, 2885w	1608s, 1595s, 1583s, 1532s	
	Nujol			1637sh, 1617s, 1591s, 1583s, 1565s, 1555s, 1515s, 1498s	3300–2000br
	Q <sub>Br</sub> H				
(CH <sub>3</sub> ) <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	CHCl <sub>3</sub>	4.2	3037m, 3029m, 3022m, 3014m, 2993w	1607s, 1591s, 1559s, 1523w, 1518m, 1514m, 1500m	
	Nujol		3078w, 3062w, 3042w	1604s, 1596s, 1587s, 1580s, 1560s, 1529s, 1498sh, 1489s	

<b>13</b>	$(C_6H_5)_2Sn(Q_{Br})_2$	CHCl <sub>3</sub> Nujol	3.6	3036m, 3012m, 2988w, 2882w 3080w, 3066w, 3058w, 3034w, 3020w	1601s, 1577s, 1558s, 1531m, 1491m 1588s, 1574s, 1568s, 1564s, 1556s, 1548s, 1538s, 1532s, 1527s, 1500s
<b>14</b>	$(C_7H_7)_2Sn(Q_{Br})_2$	CHCl <sub>3</sub> Nujol	3.4	3068w, 3038m, 3033m, 3012m, 2989w 3079w, 3058w, 3022w	1608s, 1590s, 1576s, 1557s, 1531s, 1493m 1597sh, 1589s, 1580s, 1574s, 1555s, 1537s, 1527sh, 1490s
<b>15</b>	$(C_6H_{11})_2Sn(Q_{Br})_2$	CHCl <sub>3</sub> Nujol	3.3	3034m, 3021m, 3017m, 3013m, 2988w 3084w, 3062w, 3052w, 3026w, 3020w	1600sh, 1591s, 1576s, 1557s, 1531s, 1493m 1620m, 1600s, 1592s, 1580s, 1568s, 1557s, 1537s, 1520s, 1504s, 1488s
<b>16</b>	$Cl_2Sn(Q_{Br})_2$	CHCl <sub>3</sub> Nujol	6.0	3036m, 3012m, 2988w, 2931m, 2851w 3078w, 3066w, 3048w	1592s, 1578s, 1558s, 1531m, 1490m 1593s, 1588s, 1567s, 1544s, 1513s, 1497s
<b>17</b>	$(C_4H_9)_2Sn(Q_{Br})_2$	CHCl <sub>3</sub> Nujol	3.8	3030m, 3026m, 3015m, 2993w 3082w, 3064w, 3042w, 3020w	1600sh, 1590s, 1569s, 1548s, 1530sh 1594s, 1588s, 1574s, 1558s, 1532s
<b>18</b>	$Q_AH$	CHCl <sub>3</sub> Nujol	6.0	2980m, 2946m, 2882m, 2853m	1603sh, 1593s, 1579s, 1559s, 1530s, 1499sh 1608s, 1560s, 1515s, 1500m
	$(CH_3)_2Sn(Q_A)_2$	CHCl <sub>3</sub> Nujol	4.5	3069w, 3036m, 3011m, 2989w, 2937w 3060w, 3046w, 3032w, 3020w, 3012w	1608s, 1560s, 1515s, 1500m 1605s, 1591s, 1581s, 1568s, 1558s, 1540s, 1521s, 1506s, 1500s, 1490s
<b>19</b>	$(C_6H_5)_2Sn(Q_A)_2$	CHCl <sub>3</sub> Nujol	4.4	3037m, 3033m, 3030m, 3015s, 2982w 3067w, 3048w, 3020w, 3009w	1602s, 1596s, 1578s, 1560s, 1525s br 1609s, 1604s, 1595s, 1586s, 1575s, 1566s, 1555s, 1532s, 1518s, 1497s
<b>20</b>	$(C_7H_7)_2Sn(Q_A)_2$	CHCl <sub>3</sub> Nujol	4.4	3067w, 3036s, 3011m, 2986w, 2940w 3078w, 3050w, 3019w	1606s, 1587s, 1578m, 1568m, 1556s, 1527br 1597s, 1592s, 1578s, 1557s, 1529s, 1518s, 1491s
<b>21</b>	$(C_6H_{11})_2Sn(Q_A)_2$	CHCl <sub>3</sub> Nujol	4.4	3068m, 3033s, 3026m, 3017m, 3012m 3060w, 3041w, 3034w, 3007w	1603s, 1594s, 1581m, 1557s, 1427br, 1491m 1605s, 1598s, 1592s, 1576s, 1568s, 1556s, 1532s, 1527s, 1514s, 1504s
<b>22</b>	$Cl_2Sn(Q_A)_2$	CHCl <sub>3</sub> Nujol	4.0	2982m, 2938m, 2856m 3073w, 3043w	1603s, 1594s, 1579m, 1560s, 1527br, 1518m, 1513m 1603s, 1595s, 1578s, 1560s, 1534s, 1516s
<b>23</b>	$(C_4H_9)_2Sn(Q_A)_2$	CHCl <sub>3</sub> Nujol	4.0	3060w, 3037m, 3030m, 3026m, 3021m 3075w, 3060w, 3043w, 3035w	1605s, 1599s, 1582s, 1565m, 1544br, 1530sh 1602s, 1592s, 1582s, 1572sh, 1557s, 1526s, 1510s
<b>24</b>		CHCl <sub>3</sub>	4.4	3060w, 3037m, 3012m, 2982m, 2940m	1603s, 1593s, 1582s, 1559s, 1527m, 1518br

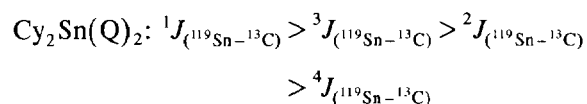
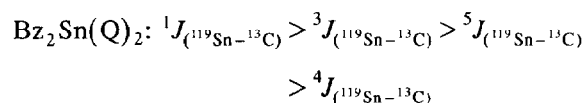
<sup>a</sup> (O–H) stretching.

Table 2  
Far-IR data ( $\text{cm}^{-1}$ ) for the ligands and compounds 1–24

Compound	State	$\nu(\text{Sn}-\text{C})$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{Cl})$	$\delta(\text{C}-\text{Sn}-\text{C})$	Other data
Q'H	Nujol					533m, 507m, 416w, 403w, 393w, 364m 329m, 297w, 280w, 255w, 215w
	$\text{CHCl}_3$					538m, 505m, 407m, 395sh, 360m, 326m 278br, 252w, 209w
1	Nujol	596m	441br, 394m		176m	546m, 510m, 494m, 414m, 403w, 364m 326w, 280w, 255w, 248w, 215m
	$\text{CHCl}_3$	586m	435m, 398s		174s	548m, 510m, 495m, 350m, 324w, 284w 224w
2	Nujol	289s, 252s	450s, 442s		225s	553s, 508s, 404w, 357m, 348m, 339m 292w, 185m
	$\text{CHCl}_3$	268s, 247s	448s br		220br	553s, 510s, 362w, 351m, 332w, 296m 179br
3	Nujol	454s	427m, 400s		168m	560m, 545m, 511m, 495m, 386w, 351m 325w, 283m, 247s, 211w, 196m
	$\text{CHCl}_3$	456s	430s, 400m br		175s	547s, 510s, 351m, 329w, 286w, 245s 225m
4	Nujol	423m, 390s	439m, 394m 378s		169m	550m, 540m, 509m, 326w, 282w, 266m 214m, 138m
	$\text{CHCl}_3$	422m	436m, 392s br		169s	547m, 510m, 349m, 327m, 283w, 266m 217m, 145m
5	Nujol		472m, 442m	355s, 349s 341s		560m, 513m, 398w, 263w, 244w, 217m 187m
	$\text{CHCl}_3$		462m, 444m	363s, 343s		559s, 508s, 398w, 279w, 247w, 225w 151w
6	Nujol	420w, 398s	430s, 398s		168m	545s, 508m, 351m, 327m, 303m, 280m 247m, 225m, 200br
	$\text{CHCl}_3$	392s	427s, 392s		169m	547s, 510s, 351m, 324w, 303w, 279m 247m, 226m
Q'H	Nujol					584m, 511m, 444w, 410w, 387w, 346m 315w, 281w, 255vw, 227w, 210w, 178w 588m, 507m, 374m, 325m, 311m, 281w 268w, 208w, 169w
	$\text{CHCl}_3$					553m, 542m, 512m, 496m, 292w, 267w 163w, 153w
7	Nujol	591m	446sh, 436m		188m	512m, 494m, 325m, 277m, 190sh, 150sh 561m, 510m, 463w, 420m, 280w, 247w 213w, 200w
	$\text{CHCl}_3$	587s	442s, 400s		178s	544w, 511m, 502m, 326m, 296m, 247m 225w, 153w
8	Nujol	290br	450s, 395s		183m	567m, 543m, 511m, 494m, 376w, 352w 325w, 303w, 247m, 225m, 202m, 195m
	$\text{CHCl}_3$	278s, 269s	448s, 403s		180w br	554w, 511m, 496m, 325m, 278m, 246w 555m, 543m, 509m, 495m, 329m, 280m 265m, 244w, 206w
9	Nujol	457m	444m, 419m 399m		177m	587w, 552w, 511m, 493m, 326m, 271m 214m
	$\text{CHCl}_3$	456sh	441m, 400m		179s br	543m, 511m, 398w, 385w, 376w, 303w 280m, 247m, 225m, 202m, 177m, 152m
10	Nujol	420m, 390sh	436m, 394s		172s	586w, 508m, 278m, 222m, 196m 552w, 542w, 510m, 498w, 292w, 273w 187m, 162m
	$\text{CHCl}_3$	422m, 390sh	438m, 398s		172s	587w, 511m, 493m, 325w, 274m, 197m 150m
11	Nujol		487s, 419s 398s	353s, 337br 330sh		595m, 542m, 501m, 467m, 438m, 355m 286w, 225w
	$\text{CHCl}_3$		474s, 418s	350s br		553m, 502m, 445m, 388m, 334m, 317m 280w, 255w
12	Nujol	400s, 389vs	433m, 400sh		172s	508m, 527w, 384s, 352w, 328w, 302w 280m, 266w, 255w, 247w, 225w, 203w 152w
	$\text{CHCl}_3$	392vs	433m, 400s		172m	566w, 511w, 328w, 301w, 279w, 206w
Q <sub>Br</sub> H	Nujol					595m, 542m, 501m, 467m, 438m, 355m 286w, 225w
	$\text{CHCl}_3$					553m, 502m, 445m, 388m, 334m, 317m 280w, 255w
13	Nujol	592m	455s, 442s 407m, 399m		172s	508m, 527w, 384s, 352w, 328w, 302w 280m, 266w, 255w, 247w, 225w, 203w 152w
	$\text{CHCl}_3$	586m	443s, 387s		171s br	566w, 511w, 328w, 301w, 279w, 206w

Table 2 (continued)

Compound	State	$\nu(\text{Sn}-\text{C})$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{Cl})$	$\delta(\text{C}-\text{Sn}-\text{C})$	Other data
14	Nujol	300m, 292m	453m, 442m		225m 203m	553br, 542s, 395m, 385m, 354w, 324w 280m, 247m
	CHCl <sub>3</sub>	297m, 285br	460s br, 449s		225m 200br	575m, 510m, 389m, 337w, 247m, 171vw
15	Nujol	456br, 432s	450s, 387s		174m	572w, 556w, 512m, 330w, 282w, 265m 213m, 197m
	CHCl <sub>3</sub>	456br, 440br	440br, 388br		171m	595w, 567w, 552w, 510m, 329m, 279m 244m, 211m
16	Nujol	421s, 382s	434s, 370s		171m	554m, 542m, 511m, 334w, 332w, 290m 273m, 203m
	CHCl <sub>3</sub>	442s, 385br	440s, 385s		168m	552s, 511m, 326m, 285m, 269m, 247w 218m
17	Nujol		482s, 465m 396m	357s, 338m		581w, 544w, 512m, 385sh, 298w, 282w 230m, 206w
	CHCl <sub>3</sub>		479s, 395s	353br, 340sh		583m, 517m, 508m, 278m, 224m, 221m 201m
18	Nujol	430sh, 400s	436s, 486s		169m	511m, 352w, 326w, 279w, 267w, 255w 247w, 203w
	CHCl <sub>3</sub>	440br, 390br	443s, 394s		165s	564w, 511m, 327w, 302w, 279m, 254m 226sh, 213m
Q <sub>A</sub> H	Nujol					543w, 530w, 512w, 501w, 445m, 327m 280w, 266w
	CHCl <sub>3</sub>					540br, 533w, 519w, 506w, 443w, 420w 326w, 280w
19	Nujol	589s	462s, 434s 386s		179m	541m, 535m, 518m, 511m, 349m, 329s 310s, 281m, 260w, 247vw, 225m, 204m
	CHCl <sub>3</sub>	585m	448br, 398m		171s	539s, 511s, 342m, 325m, 302m, 280m 247m, 224m
20	Nujol	279s, 266s 255m	470br, 463s 446s, 419w		225m	538m, 383m, 339m, 303m, 203m, 176m
	CHCl <sub>3</sub>	278s, 267s	449s, 419w		225m	539s, 510s, 498w, 384w, 247m, 200br
21	Nujol	443m	456s, 396s		170m	547m, 514m, 480w, 351w, 326w, 303w 260m, 247m
	CHCl <sub>3</sub>	420sh	456s, 397m		169m	538m, 510m, 481m, 347m, 316m, 302m 279m, 244m
22	Nujol	420m, 390s	440s, 390s		168m	538m, 510m, 275m, 240w, 215m
	CHCl <sub>3</sub>	421m, 385w	449s, 396m		169s	537s, 510s, 478m, 320br, 305br, 268m 247m, 214s
23	Nujol		474m, 420m	352s, 334s		549s, 525w, 501m, 398w, 375m, 280m 247m, 225m
	CHCl <sub>3</sub>		474m, 420m	340s br		550s, 542s, 500s, 279m, 225s br
24	Nujol	420m, 398s	430s, 398s		160s	540m, 509m, 302m, 278m, 242w
	CHCl <sub>3</sub>	434s, 395s	450s, 395s		165s	534s, 510s, 478m, 342m, 302m, 279m 248m, 225m



The <sup>119</sup>Sn NMR data, consistent with the hexacoordinate structure proposed in Ref. [28], also give further information. For example, when more sterically-hindered groups, such as *t*-butyl, or more electron-withdrawing groups, such as the phenyls or halogens, are linked to the metal center, the existence of isomers

is suggested by the presence of more than one <sup>119</sup>Sn resonance.

In the <sup>1</sup>H NMR spectra of the dihalotin(IV) derivatives, four different signals for the 3-CH<sub>3</sub> groups were observed, probably due to the four geometrical isomers shown in Fig. 2.

In the <sup>119</sup>Sn NMR spectra, only three signals were found, with intensity ratio of ca. 1:2:1, probably indicating the coincidence of two *cis* isomers and a statistical distribution of all four isomers.

It is well known [23,28] that the extent of the chemical shift  $\delta(^{119}\text{Sn})$  of complexes having the same coordination number depends primarily on the types of sub-

Table 3

<sup>119</sup>Sn NMR data (CDCl<sub>3</sub> solution) <sup>a</sup> of derivatives 1–24 and structural predictions by the Lockhart [24] and Howard equations

Compound	<sup>2</sup> J(Sn–H)	<sup>3</sup> J(Sn–H)	<sup>1</sup> J(Sn–C)	<sup>2</sup> J(Sn–C)	<sup>3</sup> J(Sn–C)	<sup>4</sup> J(Sn–C)	θ(C–Sn–C) (deg)			<sup>119</sup> Sn δ (–ppm)
							Eq. (I)	Eq. (II)	Eq. (III) <sup>b</sup>	
Me <sub>2</sub> Sn(Q') <sub>2</sub>	1	103	938				168.2	159	178.3	319
Ph <sub>2</sub> Sn(Q') <sub>2</sub>	2			60	90	19				481, 486, 501br
Bz <sub>2</sub> Sn(Q') <sub>2</sub>	3	124	817		50	31			160.3	451
Cy <sub>2</sub> Sn(Q') <sub>2</sub>	4		791	35	130	< 5			155.5	431
Cl <sub>2</sub> Sn(Q') <sub>2</sub>	5									630, 633, 635
<sup>t</sup> Bu <sub>2</sub> Sn(Q') <sub>2</sub>	6		133	819					160.5	456, 469
Me <sub>2</sub> Sn(Q'') <sub>2</sub>	7	104	960				170.3	161.0	175.4	321
Ph <sub>2</sub> Sn(Q'') <sub>2</sub>	8			59	89	19				483, 487
Bz <sub>2</sub> Sn(Q'') <sub>2</sub>	9	125	819		53	31			160.5	449
Cy <sub>2</sub> Sn(Q'') <sub>2</sub>	10		780	35	130	< 5			155.0	433
Cl <sub>2</sub> Sn(Q'') <sub>2</sub>	11									631, 633, 636
<sup>t</sup> Bu <sub>2</sub> Sn(Q'') <sub>2</sub>	12		133	835					163.4	456, 463
Me <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	13	93	944				149.9	159.6	178.2	316
Ph <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	14			59	93	18				481, 484, 486
Bz <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	15	122	797		51	31			156.6	451
Cy <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	16		816	35	128	< 5			160.0	428
Cl <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	17									629, 633, 636
<sup>t</sup> Bu <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	18		135	790					155.4	453
Me <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	19	101	943				164.3	159.5	177.4	321
Ph <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	20			59	90	18				484, 493
Bz <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	21	124	796		52	31			156.4	457
Cy <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	22		801	36	133	< 5			157.3	432
Cl <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	23									634, 638, 641
<sup>t</sup> Bu <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	24		135	820					160.7	457

<sup>a</sup> *J* in Hz; <sup>b</sup> Eq. (I): θ(C–Sn–C) = 0.0161[<sup>2</sup>*J*(<sup>119</sup>Sn–<sup>1</sup>H)]<sup>2</sup> – 1.32[<sup>2</sup>*J*(<sup>119</sup>Sn–<sup>1</sup>H)] + 133.4 [24];Eq. (II): θ(C–Sn–C) = ([<sup>1</sup>*J*(<sup>119</sup>Sn–<sup>13</sup>C)] + 875)/11.4 [24]; Eq. (III): θ(C–Sn–C) = 0.178[<sup>1</sup>*J*(<sup>119</sup>Sn–<sup>13</sup>C)] + 14.74 [25].

stituent on the tin atom. The trend observed in our derivatives 1–24 is

$$-\delta_{\text{Cl}_2\text{SnQ}_2} > -\delta_{\text{Ph}_2\text{SnQ}_2} > -\delta_{\text{Bz}_2\text{SnQ}_2} > -\delta_{\text{Bu}_2^t\text{SnQ}_2} \\ > -\delta_{\text{Cy}_2\text{SnQ}_2} > -\delta_{\text{Me}_2\text{SnQ}_2}$$

and agrees perfectly with most of the trends described in literature [23].

### 2.3. <sup>119</sup>Sn Mössbauer data

Some complexes have been investigated by Mössbauer spectroscopy. The isomer shift (IS) quadrupole

splitting, (QS) average linewidth at half maximum *I* ± and calculated C–Sn–C bond angle are reported in Table 4.

The IS value decreases on going from four to six-coordination species and increases with the covalent character of the tin–ligand bonds. For the compounds examined, the IS value is typical of quadrivalent tin in inorganic and organometallic derivatives. The complexes reported here are all potentially octahedral with four oxygen atoms bonded to the tin. The two complexes Cl<sub>2</sub>Sn(Q)<sub>2</sub> 5 and 23 (Q = Q' or Q<sub>A</sub>) show IS values (0.24 mm s<sup>–1</sup>) less positive than the average

Table 4

<sup>119</sup>Sn Mössbauer data

Compound	No.	IS <sup>a,b</sup> (mm s <sup>–1</sup> )	QS <sup>b</sup> (mm s <sup>–1</sup> )	<i>I</i> ± <sup>b</sup> (mm s <sup>–1</sup> )	C–Sn–C <sup>c</sup> (deg)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn(Q') <sub>2</sub>	2	0.81	2.42	0.98	117
Cl <sub>2</sub> Sn(Q') <sub>2</sub>	5	0.24	0	1.10	
( <sup>t</sup> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(Q') <sub>2</sub>	6	1.60	3.87	0.80	157
(CH <sub>3</sub> ) <sub>2</sub> Sn(Q') <sub>2</sub>	7	1.24	4.14	0.78	180
(C <sub>7</sub> H <sub>7</sub> ) <sub>2</sub> Sn(Q'') <sub>2</sub>	9	1.29	3.45	0.89	141
(CH <sub>3</sub> ) <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	13	1.32	3.97	0.83	162
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	14	1.15	3.78	0.92	173
(C <sub>7</sub> H <sub>7</sub> ) <sub>2</sub> Sn(Q <sub>Br</sub> ) <sub>2</sub>	15	1.40	3.42	1.02	140
(CH <sub>3</sub> ) <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	19	1.26	3.91	1.00	159
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	20	0.84	2.37	0.82	116
(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	22	1.53	3.90	0.86	158
Cl <sub>2</sub> Sn(Q <sub>A</sub> ) <sub>2</sub>	23	0.24	0	1.23	

<sup>a</sup> With respect to a R.T. spectrum of CaSnO<sub>3</sub>. <sup>b</sup> ± 0.5 mm s<sup>–1</sup>. <sup>c</sup> Calculated by using the literature partial quadrupole splittings: [Ph] = –0.95 mm s<sup>–1</sup>; [Alk] = –1.03 mm s<sup>–1</sup>.



reviewed value 0.37 (0.08) mm s<sup>-1</sup> reported for octahedral Cl<sub>4</sub>SnO<sub>2</sub>-type complexes [29], in consonance with the increasing electronegativity of the oxygen with re-

spect to the chlorine. The decrease in the s-electron density at the tin nucleus is observable in the series R<sub>2</sub>Sn(Q<sub>A</sub>)<sub>2</sub> (R = Cl, Ph, Me, Cy) and in the pairs of

Table 5

Atomic coordinates and isotropic displacement parameters with their e.s.d.s in parentheses

Atom	x	y	z	B <sub>eq</sub>
Sn	0.3367(1)	0.13933(2)	0.4333(1)	3.37(3)
Br(1)	0.7200(3)	0.1458(1)	-0.0965(2)	9.0(1)
Br(51)	-0.2778(2)	0.30733(4)	-0.0776(2)	6.8(1)
O(1)	0.4723(8)	0.0985(2)	0.5528(8)	3.8(3)
O(2)	0.4427(9)	0.1304(2)	0.3090(8)	4.3(3)
O(51)	0.2400(8)	0.1446(2)	0.5592(8)	3.8(3)
O(52)	0.1914(8)	0.1840(2)	0.3165(9)	4.2(3)
N(1)	0.599(1)	0.0456(2)	0.581(1)	3.7(3)
N(2)	0.663(1)	0.0256(3)	0.521(1)	4.4(4)
N(51)	0.0300(9)	0.1444(3)	0.567(1)	3.6(3)
N(52)	-0.0987(9)	0.1612(3)	0.501(1)	4.2(4)
C(3)	0.647(1)	0.0440(3)	0.419(1)	4.1(5)
C(4)	0.570(1)	0.0777(3)	0.406(1)	3.4(4)
C(5)	0.540(1)	0.0760(3)	0.515(1)	3.3(4)
C(6)	0.609(1)	0.0319(3)	0.703(1)	3.8(4)
C(7)	0.571(2)	0.0530(4)	0.780(1)	5.2(6)
C(8)	0.586(2)	0.0385(4)	0.898(2)	5.9(6)
C(9)	0.635(2)	0.0036(4)	0.935(2)	5.6(6)
C(10)	0.671(2)	-0.0164(4)	0.858(2)	5.6(6)
C(11)	0.658(1)	-0.0030(3)	0.739(1)	4.6(5)
C(12)	0.700(2)	0.0284(4)	0.332(2)	6.2(7)
C(13)	0.527(1)	0.1050(3)	0.314(1)	3.9(4)
C(14)	0.575(1)	0.1101(3)	0.213(1)	4.4(5)
C(15)	0.485(2)	0.1216(4)	0.091(1)	5.0(5)
C(16)	0.525(2)	0.1317(4)	-0.002(2)	6.4(7)
C(17)	0.666(2)	0.1310(4)	0.032(2)	5.5(7)
C(18)	0.757(2)	0.1199(4)	0.150(2)	5.4(6)
C(19)	0.715(1)	0.1097(3)	0.243(1)	4.4(5)
C(20)	0.188(1)	0.1007(4)	0.319(2)	5.2(6)
C(21)	0.124(2)	0.1033(6)	0.184(2)	7.7(8)
C(22)	0.027(3)	0.0770(9)	0.111(3)	12(1)
C(23)	-0.006(3)	0.0495(9)	0.169(4)	13(1)
C(24)	0.057(2)	0.0462(6)	0.303(4)	11(1)
C(25)	0.154(2)	0.0723(4)	0.379(2)	6.7(7)
C(26)	0.477(1)	0.1820(3)	0.527(1)	3.6(4)
C(27)	0.438(1)	0.2134(3)	0.571(1)	4.3(4)
C(28)	0.529(2)	0.2409(4)	0.632(2)	5.4(6)
C(29)	0.666(1)	0.2377(4)	0.654(1)	4.7(5)
C(30)	0.704(1)	0.2068(4)	0.615(1)	5.1(5)
C(31)	0.615(1)	0.1794(4)	0.554(1)	4.0(4)
C(53)	-0.095(1)	0.1819(3)	0.411(1)	3.6(4)
C(54)	0.039(1)	0.1803(3)	0.411(1)	3.3(4)
C(55)	0.115(1)	0.1554(3)	0.513(1)	3.2(4)
C(56)	0.051(1)	0.1162(3)	0.657(1)	3.8(4)
C(57)	0.177(2)	0.1005(5)	0.731(2)	6.7(7)
C(58)	0.188(2)	0.0720(5)	0.810(2)	8.1(8)
C(59)	0.079(2)	0.0576(6)	0.822(2)	8.4(8)
C(60)	-0.043(2)	0.0736(8)	0.749(2)	11(1)
C(61)	-0.063(2)	0.1028(7)	0.669(2)	10(1)
C(62)	-0.222(1)	0.2016(3)	0.327(1)	4.7(5)
C(63)	0.084(1)	0.1948(3)	0.325(1)	3.2(4)
C(64)	0.002(1)	0.2234(3)	0.228(1)	3.4(4)
C(65)	-0.030(2)	0.2183(4)	0.099(1)	6.3(6)
C(66)	-0.110(2)	0.2432(5)	0.008(2)	7.5(7)
C(67)	-0.159(1)	0.2736(3)	0.048(1)	4.7(5)
C(68)	-0.117(1)	0.2809(3)	0.174(1)	4.2(5)
C(69)	-0.038(1)	0.2550(3)	0.266(1)	3.5(4)

$$B_{eq} = (4/3)\sum(ij)[\alpha(i)\alpha(j)b(ij)].$$

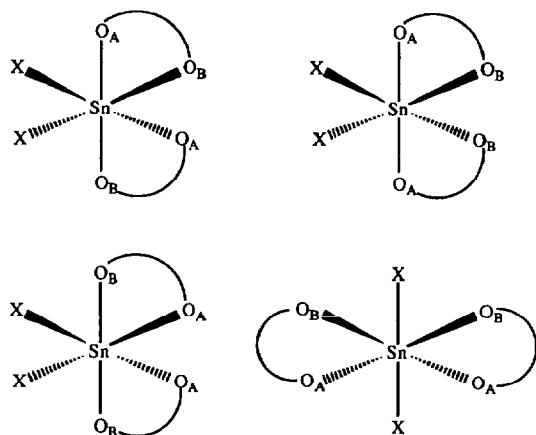


Fig. 2. The cis- and trans-isomers possible for our  $R_2SnQ_2$  complexes.

complexes  $R_2Sn(Q_A)_2$  and  $R_2Sn(Q_{Br})_2$  ( $R = Me$  and  $Ph$ ); this is consistent with the electronegativity trend and with the decreasing inductive effect of  $Ph$  in comparison with  $Me$ .

The  $Cl_2Sn(Q)_2$  complexes show a single resonance line typical of a cubic symmetry around the tin. The large value of  $F_{\perp}$  for  $Cl_2Sn(Q_A)_2$  indicates an unresolved QS due to a distortion from ideal octahedral symmetry. The QS value has been widely used to distinguish between cis or trans- $R_2$  isomers in  $R_2Sn$  complexes [30,31]. The QS values for derivatives **6**, **7**, **9**, **13**, **14**, **15**, **19** and **22** are consistent with a trans- $R_2$  configuration; instead, a cis- $R_2$  distorted arrangement can be attributed to  $Ph_2Sn(Q)_2$  complexes **2** and **20** ( $Q = Q'$  and  $Q_A$ ). Using the Parish relationship between QS and C–Sn–C bond angle [31], the latter have been calculated. An accentuated distortion from linearity has been inferred in the  $Bz_2Sn(Q)_2$  derivatives **9** and **15**.

#### 2.4. Diffraction study of $[Ph_2Sn(Q_{Br})_2]$ **14**

The crystal structure of the title compound consists of discrete molecules without any crystallographically-imposed symmetry. Atomic coordinates along with isotropic equivalent displacement parameters  $B_{eq}$  are shown in Table 5. Hydrogen atom positions are omitted and available from the Cambridge Crystallographic Data Base. Fig. 3 shows a view of the molecular structure with H atoms omitted for clarity. Bond distances and angles are given in Tables 6 and 7 respectively.

The metal is six-coordinate with two  $(Q_{Br}^-)$  ligands and two phenyl groups. Each ligand chelates the metal through two oxygen atoms asymmetrically, Sn–O(1) = 2.12(1) Å and Sn–O(2) = 2.223(8) Å for one ligand and Sn–O(51) = 2.143(7) Å and Sn–O(52) = 2.26(1) Å for the other ligand. The system is distorted octahedral whose geometry is determined by the ligand asymmetry. This distortion is characterized by a C–Sn–C axis

less than  $180^\circ$ . This folding is towards the longer Sn–O bonds. In our case C–Sn–C is  $173.0(7)^\circ$ ; the angles in the equatorial plane are O(1)–Sn–O(51) =  $91.9(3)^\circ$  (the primary oxygens bound to tin) and O(2)–Sn–O(52) =  $98.6(3)^\circ$  (the secondary oxygens bound to tin). As mentioned above, the Ph–Sn–Ph axis is projected towards the secondary oxygens. The Sn–C bonds are similar to those normally found in diorganotin compounds.

The  $(Q_{Br}^-)$  ligands show the pyrazolonate ring to be planar. An analysis, based on the Cremer and Pople [32] ring puckering coordinates, shows that the two chelate rings have different total puckering amplitudes ( $Q_T[Sn-O(1)-C(5)-C(4)-C(13)-O(2)] = 0.208(8)$  and  $Q_T[Sn-O(51)-C(55)-C(54)-C(63)-O(52)] = 0.334(8)$  Å) even if their conformation is similar, both being half-chair with a local pseudo two-fold axis running along the midpoints of the Sn–O(1) and C(4)–C(13) bonds in one ring, and the midpoints of the Sn–O(51) and C(54)–C(63) bonds in the other. These pseudo axes are therefore symmetrically situated.

The primary oxygens (O(1) and O(51)) are in close contact with the ortho hydrogens (attached to C(7) and C(57)), as found previously [9f] (in this complex O(1)  $\cdots$  H(1) = 2.24(2) Å and O(51)  $\cdots$  H(18) = 2.25(2) Å). The planarity of the corresponding phenyl groups [C(6)–C(11)] and [C(56)–C(61)] with respect to the pyrazolonate rings is responsible for this feature (the dihedral angle between the rings [N(1)–N(2)–C(3)–C(4)–C(5)] and [C(6)–C(11)] is  $11.7(4)^\circ$  and between the rings [N(51)–N(52)–C(53)–C(54)–C(55)] and [C(56)–C(61)] is  $15.9(5)^\circ$ ).

Similar compounds were recently described by our group [9a,c,f], namely,  $tBu_2Sn(Q')_2$ ,  $Me_2Sn(Q')_2$ ,

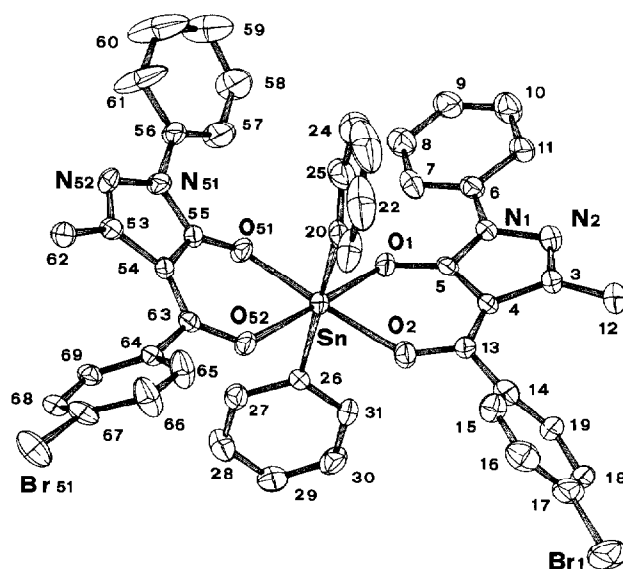


Fig. 3. A view of the molecular structure of  $Ph_2Sn(Q_{Br})_2$  **14** including anisotropic displacements parameters (H atoms are omitted).

Table 6  
Bond lengths (Å) with e.s.d.s in parentheses

<i>Coordination sphere</i>	
Sn–O(1)	2.12(1)
Sn–O(2)	2.223(8)
Sn–O(51)	2.143(7)
Sn–O(52)	2.26(1)
Sn–C(20)	2.11(2)
Sn–C(26)	2.11(1)
<i>Rest of the molecule</i>	
Br(1)–C(17)	1.89(2)
Br(51)–C(67)	1.91(2)
O(1)–C(5)	1.30(1)
O(2)–C(13)	1.28(2)
O(51)–C(55)	1.29(2)
O(52)–C(63)	1.28(1)
N(1)–N(2)	1.39(1)
N(1)–C(5)	1.34(2)
N(1)–C(6)	1.45(2)
N(2)–C(3)	1.29(2)
N(51)–N(52)	1.41(2)
N(51)–C(55)	1.38(1)
N(51)–C(56)	1.40(2)
N(52)–C(53)	1.29(2)
C(3)–C(4)	1.46(2)
C(3)–C(12)	1.47(2)
C(4)–C(5)	1.43(2)
C(4)–C(13)	1.37(2)
C(6)–C(7)	1.37(2)
C(6)–C(11)	1.37(2)
C(7)–C(8)	1.40(3)
C(8)–C(9)	1.37(2)
C(9)–C(10)	1.34(2)
C(10)–C(11)	1.40(3)
C(13)–C(14)	1.48(2)
C(14)–C(15)	1.38(3)
C(14)–C(19)	1.41(2)
C(15)–C(16)	1.38(2)
C(16)–C(17)	1.41(3)
C(17)–C(18)	1.34(3)
C(18)–C(19)	1.39(2)
C(20)–C(21)	1.40(4)
C(20)–C(25)	1.38(2)
C(21)–C(22)	1.40(5)
C(22)–C(23)	1.33(5)
C(23)–C(24)	1.40(8)
C(24)–C(25)	1.40(4)
C(26)–C(27)	1.40(2)
C(26)–C(31)	1.40(2)
C(27)–C(28)	1.37(2)
C(28)–C(29)	1.40(2)
C(29)–C(30)	1.35(2)
C(30)–C(31)	1.35(2)
C(53)–C(54)	1.46(2)
C(53)–C(62)	1.48(2)
C(54)–C(55)	1.42(2)
C(54)–C(63)	1.39(2)
C(56)–C(57)	1.38(3)
C(56)–C(61)	1.39(2)
C(57)–C(58)	1.35(3)
C(58)–C(59)	1.36(3)
C(59)–C(60)	1.35(4)
C(60)–C(61)	1.37(4)
C(63)–C(64)	1.50(2)
C(64)–C(65)	1.38(2)

Table 6 (continued)

<i>Rest of the molecule</i>	
C(64)–C(69)	1.37(2)
C(65)–C(66)	1.37(3)
C(66)–C(67)	1.39(2)
C(67)–C(68)	1.34(2)
C(68)–C(69)	1.40(2)

$\text{Me}_2\text{Sn}(\text{Q}_{\text{Br}})_2$ . These complexes also have STB configurations, with C–Sn–C bond angles of  $150.0(5)^\circ$ ,  $153.3(3)^\circ$  and  $154.5(3)^\circ$  respectively. Two other similar complexes which are also STB are  ${}^n\text{Bu}_2\text{Sn}(\text{Q}')_2$  [33] and  $\text{Me}_2\text{Sn}(\text{Q}'')_2$ , [34], with C–Sn–C angles of  $154.7(8)^\circ$  and  $162.1(3)^\circ$  respectively. All these complexes are compared in Table 8, together with the symmetric complexes  $\text{Me}_2\text{Sn}(\text{acac})_2$  [13a] and  ${}^n\text{Bu}_2\text{Sn}(\text{dbzm})_2$  (dbzm = 1,3-diphenylpropane-1,3-dionato) [13b] which have the same type of tin environment. These are the only non-distorted octahedral complexes in Table 8 and have the only symmetric ligands. In our complex, the two phenyl groups bound to tin are perpendicular to each other (the dihedral angle between the two planes is  $92.7(6)^\circ$ ). The plane of one ring [C(20)–C(25)] bisects the equatorial plane of the complex given by O(1)–Sn–O(51), and the other phenyl ring [C(26)–C(31)] bisects the plane O(1)–Sn–O(2). The energy associated with the rotation of these two phenyl rings through the Sn–C(20) and Sn–C(26) bonds was analysed in the following way. As the program calculating the rotational energy contribution did not contain parameters for tin, the metal was artificially substituted by silicon, since only van der Waals interactions were analysed (no atomic charge distribution was assigned or applied).

The rotation of the [C(20)–C(25)] ring showed a minimum at the position obtained from the X-ray study. This minimum corresponds to a torsion angle C(21)–C(20)–Sn–O(51) of  $49^\circ$  and is associated with 36 kcal. Another minimum was at  $136^\circ$  and showed the same energy. In addition, two maxima were obtained at  $-66^\circ$  (51 kcal) and  $115^\circ$  (58 kcal). These findings can be associated with steric hindrance between the ortho hydrogens and oxygens and carbons of the ligand. Rotation of the ring [C(26)–C(31)] shows C(27)–C(26)–Sn–O(52) torsion angles of  $47^\circ$  (this conformation was found in the crystal structure),  $130^\circ$ ,  $-50^\circ$  and  $-140^\circ$  respectively, with energy minima of 36 kcal. Four maxima are at  $87^\circ$ ,  $180^\circ$ ,  $-97^\circ$  and  $0^\circ$  corresponding to energies of 38 kcal, 39 kcal, 39 kcal and 40 kcal respectively. Therefore, this ring can rotate freely and its location is probably influenced by packing forces in the crystal.

To further understand the role of these atoms in steric hindrance, we compared the geometry of the previously described complex,  $\text{Me}_2\text{Sn}(\text{Q}_{\text{Br}})_2$ , with that

Table 7  
Bond angles (deg) with e.s.d.s in parentheses

<i>Coordination sphere</i>	
C(26)–Sn–C(20)	173.0(7)
O(51)–Sn–O(2)	176.2(3)
O(52)–Sn–O(1)	176.6(3)
O(2)–Sn–O(1)	84.5(4)
O(52)–Sn–O(51)	85.1(3)
O(51)–Sn–O(1)	91.9(3)
O(52)–Sn–O(2)	98.6(3)
C(20)–Sn–O(1)	93.2(6)
C(20)–Sn–O(2)	88.5(5)
C(20)–Sn–O(51)	90.6(5)
C(20)–Sn–O(52)	88.3(6)
C(26)–Sn–O(1)	92.8(5)
C(26)–Sn–O(2)	88.5(4)
C(26)–Sn–O(51)	92.8(4)
C(26)–Sn–O(52)	85.9(5)
<i>Rest of the molecule</i>	
C(5)–O(1)–Sn	124.0(9)
C(13)–O(2)–Sn	129.6(9)
C(55)–O(51)–Sn	119.7(9)
C(63)–O(52)–Sn	127.1(8)
C(25)–C(20)–Sn	119(1)
C(21)–C(20)–Sn	120(1)
C(31)–C(26)–Sn	121.9(9)
C(27)–C(26)–Sn	121(1)
C(5)–N(1)–N(2)	111(1)
C(6)–N(1)–N(2)	117(1)
C(6)–N(1)–C(5)	130(1)
C(3)–N(2)–N(1)	106(1)
C(55)–N(51)–N(52)	109(1)
C(56)–N(51)–N(52)	121(1)
C(56)–N(51)–C(55)	128(1)
C(53)–N(52)–N(51)	108(1)
C(4)–C(3)–N(2)	111(1)
C(12)–C(3)–N(2)	118(1)
C(12)–C(3)–C(4)	129(1)
C(5)–C(4)–C(3)	102(1)
C(13)–C(4)–C(3)	132(1)
C(13)–C(4)–C(5)	124(1)
N(1)–C(5)–O(1)	121(1)
C(4)–C(5)–O(1)	130(1)
C(4)–C(5)–N(1)	107.5(9)
C(7)–C(6)–N(1)	121(1)
C(11)–C(6)–N(1)	117(1)
C(11)–C(6)–C(7)	121(1)
C(8)–C(7)–C(6)	118(1)
C(9)–C(8)–C(7)	121(1)
C(10)–C(9)–C(8)	119(1)
C(11)–C(10)–C(9)	121(1)
C(10)–C(11)–C(6)	118(1)
C(4)–C(13)–O(2)	123(1)
C(14)–C(13)–O(2)	111(1)
C(14)–C(13)–C(4)	124(1)
C(15)–C(14)–C(13)	120(1)
C(19)–C(14)–C(13)	121(1)
C(19)–C(14)–C(15)	117(1)
C(16)–C(15)–C(14)	123(1)
C(17)–C(16)–C(15)	117(2)
C(18)–C(17)–C(16)	120(1)
Br(1)–C(17)–C(16)	116(1)
Br(1)–C(17)–C(18)	122(1)
C(19)–C(18)–C(17)	120(1)
C(18)–C(19)–C(14)	120(1)
C(25)–C(20)–C(21)	119(1)

Table 7 (continued)

<i>Rest of the molecule</i>	
C(22)–C(21)–C(20)	119(2)
C(23)–C(22)–C(21)	121(4)
C(24)–C(23)–C(22)	120(4)
C(25)–C(24)–C(23)	119(2)
C(24)–C(25)–C(20)	119(2)
C(31)–C(26)–C(27)	116(1)
C(28)–C(27)–C(26)	121(1)
C(29)–C(28)–C(27)	120(1)
C(30)–C(29)–C(28)	118(1)
C(31)–C(30)–C(29)	122(1)
C(30)–C(31)–C(26)	121(1)
C(54)–C(53)–N(52)	110(1)
C(62)–C(53)–N(52)	117(1)
C(62)–C(53)–C(54)	131(1)
C(55)–C(54)–C(53)	104(1)
C(63)–C(54)–C(53)	130(1)
C(63)–C(54)–C(55)	125(1)
N(51)–C(55)–O(51)	121(1)
C(54)–C(55)–O(51)	131(1)
C(54)–C(55)–N(51)	107(1)
C(57)–C(56)–N(51)	123(1)
C(61)–C(56)–N(51)	118(1)
C(61)–C(56)–C(57)	118(1)
C(58)–C(57)–C(56)	120(1)
C(59)–C(58)–C(57)	122(2)
C(60)–C(59)–C(58)	115(2)
C(61)–C(60)–C(59)	124(2)
C(60)–C(61)–C(56)	117(2)
C(54)–C(63)–O(52)	123(1)
C(64)–C(63)–O(52)	115(1)
C(64)–C(63)–C(54)	121(1)
C(65)–C(64)–C(63)	119(1)
C(69)–C(64)–C(63)	121(1)
C(69)–C(64)–C(65)	119(1)
C(66)–C(65)–C(64)	120(1)
C(67)–C(66)–C(65)	118(1)
C(68)–C(67)–C(66)	121(1)
Br(51)–C(67)–C(66)	119(1)
Br(51)–C(67)–C(68)	119(1)
C(69)–C(68)–C(67)	118(1)
C(68)–C(69)–C(64)	120(1)

obtained by replacing the methyl groups with phenyl groups. We generated the phenyl groups by making the ipso carbon the methyl carbon in the original complex and choosing two possible orientations for the aromatic system: one ring co-planar to the Sn–L<sub>1</sub> line (L<sub>1</sub> = midpoint of O(1)–O(2)) and the other coplanar to Sn–L<sub>2</sub> (L<sub>2</sub> = midpoint of O(1)–O(51)). The longest distances between the ortho hydrogens and oxygen in the equatorial plane are 2.91 and 3.05 Å for one ring and 3.09 and 3.17 Å for the other ring. Since the sum of the van der Waals radii is 2.60 (1.20 Å for H and 1.40 Å for O), the configuration given by C–Sn–C = 153° could be achieved by a diphenyltin(IV) complex. This conformation is very stable, as shown in Table 8, where most of the complexes show a C–Sn–C bond angle close to it. Therefore, we suggest that the great change observed in

the diphenyltin(IV) complex (about 20° more in the C–Sn–C bond angle) is due to electronic effects.

As shown in Table 8, only a symmetrical ligand such as acac or dbzm stabilizes a pure octahedral geometry. This octahedral system forces the ligand to have a large bite angle and equivalent Sn–O bonds. Unsymmetrical ligands reduce the symmetry of the system, so that the bite angle becomes smaller, the two Sn–O bonds become different and the C–Sn–C angle becomes smaller. This trend is shown in Table 8. Furthermore, in Table 8 the title compound has values closer to the octahedral acac (or dbzm) complex for the three features mentioned above. Since Sn–O bond distances differ less for the phenyl species than for any other unsymmetrical complex, it appears that the phenyl group is responsible for the change. As the phenyl is an electron-withdrawing group, it may be argued that the secondary O becomes more involved in bonding to the metal, shortening the Sn–O(2) and Sn–O(52) lengths. This results in a more symmetrical system with a less distorted octahedral axis C–Sn–C.

The marked difference in behavior between methyl and phenyl groups can also be observed in the complex  $[\text{Ph}_2\text{SnCl}_2(\text{Q}'\text{H})]$ , which was synthesized and described previously [9b]. The equivalent compound  $[\text{Me}_2\text{SnCl}_2(\text{Q}'\text{H})]$  could not be synthesized [9b]. A similar situation was seen for the complexes  $[\text{Ph}_2\text{SnCl}_2(\text{L}^{\text{A}})]$  and  $[\text{Me}_2\text{SnCl}_2(\text{L}^{\text{A}})]$ , ( $\text{L}^{\text{A}} = 1,2\text{-bis}(\text{pyrazol-1-yl})\text{ethane}$ ) [35]. The C–Sn–C angle calculated for  $\text{Ph}_2\text{Sn}(\text{Q}_{\text{Br}})_2$  on the basis of Mössbauer data (173°) compares well with the 173.0(7)° found from the diffraction study. It is interesting that the two other diphenyltin(IV) complexes,  $\text{Ph}_2\text{Sn}(\text{Q}')_2$  and  $\text{Ph}_2\text{Sn}(\text{Q}_{\text{A}})_2$  have C–Sn–C angles (from Mössbauer data) of 117° and 116° respectively. This can be associated with a cis arrangement, and it

shows how subtle changes in the ligand can induce dramatic changes in the diphenyltin complex geometry.

### 3. Experimental section

Solvents were dried by standard techniques. All the reagents were purchased from Aldrich (Milwaukee) except dibenzyltin dichloride, which was purchased from Alfa (Karlsruhe), and used as-received. The samples were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses (C, H, N) were carried out in-house with a Carlo Erba Strumentazione 1106 instrument. IR spectra from 4000 to 100  $\text{cm}^{-1}$  were recorded with a Perkin–Elmer 2000 FTIR instrument.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$  and 111.9 MHz for  $^{119}\text{Sn}$ ). Proton and carbon, and tin chemical shifts are reported in ppm vs.  $\text{Me}_4\text{Si}$  and  $\text{Me}_4\text{Sn}$  respectively. The tin spectra were run with a spectral width of 1000 ppm, and the chemical shifts were checked for aliasing by varying the center of the window. Each tin spectrum was acquired in ca. 4 h. Melting points were measured with an IA 8100 Electrothermal instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.  $^{119}\text{Sn}$  Mössbauer spectra were recorded at liquid nitrogen temperature by an Elscint–Laben spectrometer equipped with an AERE cryostat. The  $\text{Ca}^{119}\text{SnO}_3$  Mössbauer source, 10 mCi (from Radiochemical Centre, Amersham, UK) moved with constant acceleration and a triangular waveform was used.

The compounds Q'H, Q''H,  $\text{Q}_{\text{Br}}\text{H}$  and  $\text{Q}_{\text{A}}\text{H}$  were prepared by the published methods [10]. Compounds

Table 8  
Selected geometrical data in the coordination sphere for diorganotinbis(β-diketonate) compounds

	$[\text{Ph}_2\text{Sn}(\text{Q}_{\text{Br}})_2]$	$[\text{Me}_2\text{Sn}(\text{Q}_{\text{Br}})_2]$	$[\text{Bu}_2\text{Sn}(\text{Q}')_2]$	$[\text{Bu}_2\text{Sn}(\text{Q}'')_2]$	$[\text{Me}_2\text{Sn}(\text{Q}')_2]$	$[\text{Me}_2\text{Sn}(\text{Q}'')_2]$	$[\text{Me}_2\text{Sn}(\text{acac})_2]^{\text{a}}$	$[\text{Bu}_2\text{Sn}(\text{dbzm})_2]^{\text{b}}$
Sn–O <sub>p</sub> <sup>c</sup>	2.143(7) 2.12(1)	2.104(4) 2.099(4)	2.12(2) 2.11(1)	2.145(5) 2.135(6)	2.104(3) 2.103(4)	2.123(4) 2.105(5)	2.18(1) 2.20(2)	2.189(8) 2.199(8)
Sn–O <sub>s</sub> <sup>d</sup>	2.223(8) 2.26(1)	2.385(5) 2.436(5)	2.35(2) 2.38(2)	2.381(7) 2.461(6)	2.337(4) 2.412(4)	2.288(4) 2.321(4)		
Sn–C	2.11(1) 2.11(2)	2.097(8) 2.099(8)	2.07(2) 2.12(2)	2.20(1) 2.20(2)	2.095(8) 2.090(8)	2.101(8) 2.118(7)	2.14(2)	2.115(10)
O <sub>p</sub> –Sn–O <sub>p</sub>	91.9(3)	75.5(2)	79.2(5)	74.1(2)	77.2(1)	82.7(1)	94(1)	96.2(2)
O <sub>s</sub> –Sn–O <sub>s</sub>	98.6(3)	126.7(2)	118.7(4)	127.4(2)	121.6(1)	111.5(2)		
O <sub>p</sub> –Sn–O <sub>s</sub>	84.5(4)	78.5(2)	82.0(4)	79.3(2)	80.9(1)	82.9(2)	86(1)	83.8(2)
(bite)	85.1(3)	79.5(2)	80.3(4)	79.8(2)	80.7(1)	83.2(1)		
C–Sn–C	173.0(7)	154.5(3)	154.7(8)	150.0(5)	153.3(3)	162.1(3)	180(0)	180.0(2)
Geometry	STB	STB	STB	STB	STB	STB	octahedral	octahedral
Reference	this work	[9f]	[32]	[9a]	[9c]	[33]	[13a]	[13b]

<sup>a</sup> acac = pentane-2,4-dionato; <sup>b</sup> dbzm = 1,3-diphenylpropane-1,3-dionato; <sup>c,d</sup> Sn–O<sub>p</sub> and Sn–O<sub>s</sub> stand for primary and secondary bonds respectively.

1–3, 5–9, 11–15, 17–20 and 23 were prepared according to procedures previously reported [9].

### 3.1. Syntheses of the complexes

#### 3.1.1. Dicyclohexylbis[1-phenyl-3-methyl-4-benzoylpyrazolon-5-ato]tin(IV), $[(C_6H_{11})_2Sn(Q')_2]$ , (4)

(a) To a methanolic solution (50 ml) of the ligand Q'H (2 mmol, 556 mg) were added potassium hydroxide (2 mmol, 112 mg) and  $Cy_2SnBr_2$  (1 mmol, 445 mg). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), recrystallized from chloroform–methanol and shown to be compound 4. Yield 60%; m.p. 219–220°C. Found: C, 65.5; H, 5.6; N, 6.4.  $C_{46}H_{48}N_4O_4Sn$ . Calc.: C, 65.8; H, 5.8; N, 6.7%.  $^1H$  NMR data ( $CDCl_3$ ): 1.80s (6 H, 3- $CH_3$ ); 1.05–1.40m, 1.50–1.77m, 2.00–2.22m (22 H, Sn- $C_6H_{11}$ ); 7.15–7.30m, 7.40–7.60m, 8.00d (20 H, aromatics).  $^{13}C$  NMR data ( $CDCl_3$ ): 26.8, 28.8, 29.6, 47.9 (Sn- $C_6H_{11}$ ); 16.6 (3- $CH_3$ ); 149.3 (C(3)); 105.1 (C(4)); 163.1 (C(5)); 192.0 (C=O); 120.5, 125.2, 127.4, 128.3, 128.9, 130.8, 138.6, 140.0 (aromatics).

(b) Q'H (2 mmol, 556 mg) and  $Cy_2SnBr_2$  (1 mmol, 445 mg) were reacted in chloroform in the presence of triethylamine (2.2 mmol, 222 mg); upon addition, to a clear filtered solution (30 ml) of diethyl ether (10 ml), a precipitate was formed which was filtered, washed with diethyl ether and recrystallized from chloroform–light petroleum.

(c) Q'Na (2 mmol, 600 mg) was reacted with  $Cy_2SnBr_2$  (1 mmol, 445 mg) in benzene (50 ml): the volume of the clear filtered solution was reduced in a rotary evaporator (0.1 atm) and upon addition of 15 ml of petroleum ether, a pale-yellow precipitate was formed, filtered and washed with diethyl ether (10 ml).

#### 3.1.2. Dicyclohexylbis[1-phenyl-3-methyl-4-acetylpyrazolon-5-ato]tin(IV), $[(C_6H_{11})_2Sn(Q'')_2]$ , (10)

To a methanolic solution (50 ml) of the ligand Q''H (2 mmol, 432 mg) were added potassium hydroxide (2 mmol, 112 mg) and  $Cy_2SnBr_2$  (1 mmol, 445 mg). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), recrystallized from chloroform–methanol and shown to be compound 10. Yield 70%; m.p. 245–248°C. Found: C, 60.5; H, 6.0; N, 7.7.  $C_{36}H_{44}N_4O_4Sn$ . Calc.: C, 60.4; H, 6.2; N, 7.8%.  $^1H$  NMR data ( $CDCl_3$ ): 2.45s (6 H, 3- $CH_3$ ); 2.48s (6 H,  $CH_3C=O$ ); 1.07–1.23m, 1.40–1.70m, 1.86m–2.04m (22 H, Sn- $C_6H_{11}$ ); 7.15–7.35m, 7.90–7.98m (10 H, aromatics).  $^{13}C$  NMR data ( $CDCl_3$ ): 27.3, 29.3, 30.3, 47.6 (Sn- $C_6H_{11}$ ); 18.0 (3- $CH_3$ ); 149.2 (C(3)); 105.6 (C(4)); 162.7 (C(5)); 27.3 ( $CH_3-C=O$ ); 193.7 (C=O); 121.2, 125.6, 129.4, 139.1 (aromatics).

#### 3.1.3. Dicyclohexylbis[1-phenyl-3-methyl-4-p-bromobenzoylpyrazolon-5-ato]tin(IV), $[(C_6H_{11})_2Sn(Q_{Br})_2]$ , (16)

To a methanolic solution (50 ml) of the ligand  $Q_{Br}H$  (2 mmol, 704 mg) were added potassium hydroxide (2 mmol, 112 mg) and  $Cy_2SnBr_2$  (1 mmol, 445 mg). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), recrystallized from chloroform–methanol and shown to be compound 16. Yield 70%; m.p. 221–222°C. Found: C, 55.6; H, 4.8; N, 6.0.  $C_{46}H_{46}Br_2N_4O_4Sn$ . Calc.: C, 55.4; H, 4.7; N, 5.6%.  $^1H$  NMR data ( $CDCl_3$ ): 1.80s (6 H, 3- $CH_3$ ); 1.05–1.45m, 1.50–1.77m, 1.90–2.15m (22 H, Sn- $C_6H_{11}$ ); 7.15–7.25m, 7.40d, 7.65d, 7.98d (18 H, aromatics).  $^{13}C$  NMR data ( $CDCl_3$ ): 26.7, 28.8, 29.9, 47.9 (Sn- $C_6H_{11}$ ); 16.8 (3- $CH_3$ ); 148.9 (C(3)); 105.1 (C(4)); 162.9 (C(5)); 190.4 (C=O); 120.6, 125.4, 125.9, 129.0, 129.2, 131.7, 138.4, 138.7.

#### 3.1.4. Dibenzylbis[1-phenyl-3-methyl-4-p-methoxybenzoylpyrazolon-5-ato]tin(IV), $[(C_7H_7)_2Sn(Q_A)_2]$ , (21)

To a methanolic solution (50 ml) of the ligand  $Q_AH$  (2 mmol, 616 mg) were added potassium hydroxide (2 mmol, 112 mg) and  $Bz_2SnCl_2$  (1 mmol, 372 mg). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), recrystallized from chloroform–methanol and shown to be compound 21. Yield 73%; m.p. 160–162°C. Found: C, 65.6; H, 4.8; N, 6.1.  $C_{50}H_{44}N_4O_6Sn$ . Calc.: C, 65.6; H, 4.8; N, 6.1%.  $^1H$  NMR data ( $CDCl_3$ ): 1.78s (6 H, 3- $CH_3$ ); 2.98s (4 H, Sn- $CH_2$ ); 3.90s (6 H, O- $CH_3$ ); 6.80–7.00m, 7.25–7.48m, 7.65d, 7.92d (28 H, aromatics).  $^{13}C$  NMR data ( $CDCl_3$ ): 36.7, 124.3, 127.5, 129.0, 138.7 (Sn- $CH_2C_6H_5$ ); 55.5 (O- $CH_3$ ); 16.5 (3- $CH_3$ ); 149.0 (C(3)); 102.3 (C(4)); 162.4 (C(5)); n.o. (C=O); 113.4, 120.8, 125.4, 128.0, 130.6, 131.5, 138.3, 163.8 (aromatics).

#### 3.1.5. Dicyclohexylbis[1-phenyl-3-methyl-4-p-methoxybenzoylpyrazolon-5-ato]tin(IV) $[(C_6H_{11})_2Sn(Q_A)_2]$ , (22)

To a methanolic solution (50 ml) of the ligand  $Q_AH$  (2 mmol, 616 mg) were added potassium hydroxide (2 mmol, 112 mg) and  $Cy_2SnBr_2$  (1 mmol, 889 mg). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), recrystallized from chloroform–methanol and shown to be compound 22. Yield 85%; m.p. 248–250°C. Found: C, 64.3; H, 5.8; N, 6.1.  $C_{48}H_{52}N_4O_6Sn$ . Calc.: C, 64.1; H, 5.8; N, 6.2%.  $^1H$  NMR data ( $CDCl_3$ ): 1.94s (6 H, 3- $CH_3$ ); 0.97–1.18m, 1.40–1.70m, 1.98–2.15m (22 H, Sn- $C_6H_{11}$ ); 3.91s (6 H, O- $CH_3$ ); 7.00d, 7.15–7.30m,

7.58d, 8.03d (18 H, aromatics).  $^{13}\text{C}$  NMR data ( $\text{CDCl}_3$ ): 26.8, 28.8, 29.8, 47.8 (Sn– $\text{C}_6\text{H}_{11}$ ); 55.4 (O– $\text{CH}_3$ ); 16.8 (3– $\text{CH}_3$ ); 149.0 (C(3)); 105.0 (C(4)); 162.2 (C(5)); 191.2 (C=O); 113.5, 120.5, 125.1, 128.9, 130.3, 132.3, 138.7, 162.8 (aromatics).

### 3.1.6. Di-*t*-butylbis[1-phenyl-3-methyl-4-*p*-methoxybenzoylpyrazolon-5-ato]tin(IV), $[(t\text{-C}_4\text{H}_9)_2\text{Sn}(\text{Q}_A)_2]$ , (22)

To a methanolic solution (50 ml) of the ligand  $\text{Q}_A\text{H}$  (2 mmol, 616 mg) were added potassium hydroxide (2 mmol, 112 mg) and  $^1\text{Bu}_2\text{SnCl}_2$  (1 mmol, 304 mg). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), recrystallized from chloroform–methanol and shown to be compound **24**. Yield 75%; m.p. 223–225°C. Found: C, 62.2; H, 5.5; N, 6.4.  $\text{C}_{44}\text{H}_{48}\text{N}_4\text{O}_6\text{Sn}$ . Calc.: C, 62.4; H, 5.7; N, 6.6%.  $^1\text{H}$  NMR data ( $\text{CDCl}_3$ ): 1.27s (9 H, Sn– $\text{C}(\text{CH}_3)_3$ ); 1.98s (3 H, 3– $\text{CH}_3$ ); 3.90s (3 H, O– $\text{CH}_3$ ); 7.00d, 7.20–7.45m, 7.63d, 8.05d (9H, aromatics).  $^{13}\text{C}$  NMR data ( $\text{CDCl}_3$ ): 29.3, 51.0 (Sn– $\text{C}(\text{CH}_3)_3$ ); 16.4 (3– $\text{CH}_3$ ); 55.4 (O– $\text{CH}_3$ ); 148.7 (C(3)); n.o. (C(4)); 162.3 (C(5)); n.o. (C=O); 113.5, 120.4, 125.0, 128.4, 128.5, 128.9, 129.7, 130.4, 131.9, 132.0, 133.9, 134.1, 163.8 (aromatics).

### 3.2. Crystallographic study

A preliminary study of  $[\text{Ph}_2\text{Sn}(\text{Q}_{\text{Br}})_2]$  **14** was performed using a Weissenberg Camera to determine cell parameters and space group. A Rigaku rotating anode diffractometer was used for the measurements of the cell constants and for the data collection. A summary of crystal data together with details of data collection and computer resolution are given in Table 9.

Monitoring of the reflections  $[-2, 4, 0]$ ,  $[-2, -2, 0]$  and  $[-1, -5, -2]$ , taken every 150 reflections, indicated no decay. A  $\psi$ -scan for the reflections  $[0, 0, 1]$ ,  $[0, 0, 2]$  and  $[0, -1, -2]$  showed absorption anisotropy (with minimum transmission of 32%) and the corresponding correction was applied. Data were also corrected for Lorentz and polarization effects.

The molecular structure was solved with direct methods running SHELX-86 [36]. Subsequent calculations were performed with the CAOS program [37] as follows: refinement based on the minimization of the function  $\sum w(|F_o| - |F_c|)^2$  with the weighting scheme  $w = 1/(a + F_o + cF_o^2)$ , where  $a$  and  $c$  are  $2F_o(\text{min})$  and  $2/F_o(\text{max})$  [38] respectively; H atoms were introduced at fixed positions according to a C–H distance of 0.96 Å. Anisotropic displacement parameters were allowed for non-H atoms and H isotropic displacement parameters were kept fixed. Calculations were performed on a Vax 3300 computer. Atomic scattering factors and anomalous dispersion terms were taken from Ref. [39]. Conformation of chelating rings were analyzed with the

Table 9  
Summary of crystal data

Formula	$\text{C}_{46}\text{H}_{34}\text{N}_4\text{O}_4\text{Br}_2\text{Sn}$
Formula weight	981.31
$a$ (Å)	10.882(1)
$b$ (Å)	36.515(3)
$c$ (Å)	11.513(1)
$\alpha$ (deg)	90
$\beta$ (deg)	116.193(8)
$\gamma$ (deg)	90
Volume (Å <sup>3</sup> )	4105.2(8)
Space group	$P2_1/a$
$Z$	4
Crystal dimensions (mm <sup>3</sup> )	0.35 × 0.20 × 0.20
Density calcd. (g cm <sup>-3</sup> )	1.595
Temperature (K)	298
$F(000)$	1960
$\mu$ (cm <sup>-1</sup> )	80.956
Radiation	Cu rotating anode
Data collection mode	$2\theta - \theta$
Scan speed (deg min <sup>-1</sup> )	32
Scan range (deg)	0.8
Background counts	1/4 of scan time at the end of scan range
$2\theta$ range (deg)	5–125
Reflections collected	7125
Reflections used	4421
Final no. variables	514
$R_f, R_w$	0.084, 0.104

PARST program [40] and rotation of phenyl rings were done with the CHEMX program [41].

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