Synthesis and Structure of Organotin(IV) Complexes of Maltol

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A series of organotin(IV) maltol complexes $R_{4-x}SnL_x$ (**1**–**4**, **6**; $x = 1-3$) and the dichloro-compound Cl_2SnL_2 (**5**) have been prepared and characterized on the basis of their IR-, ^1H-, ^{13}C- and ^{119}Sn-NMR data. While an X-ray crystal structure analysis of Ph_2SnL_2 (**4**) and Cl_2SnL_2 (**5**) reveals distorted *cis*-octahedral structures, the Me_2SnL_2 molecule (**2**) adopts a skew-trapezoidal bipyramidal configuration with a very significant difference in the Sn–O(keto) bond distances. The tris-maltol complex $BuSnL_3$ (**6**) exhibits a distorted pentagonal-bipyramidal geometry with the butyl carbon and a hydroxy oxygen constituting the axial orientations.

Maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one, LH) and its analogues are naturally occurring compounds and are nontoxic. Recent interest has focussed on their use as a reagent for the control of the concentrations of metal ions such as aluminium(III)[1,2] and on the introduction of some metal ions such as iron(III)[3] for therapy reasons. A recent publication of importance involves a vanadyl complex[4] $VO(L)_2$ in the treatment of diabetes. Despite extensive interest in the biological processes, earlier studies[5–7] indicated only that maltol functions as a chelating ligand via two oxgen atoms to the metal center. However, there are only a few completely characterized complexes; these are neutral tris-chelates of Al(III)[1] and Fe(III)[3] and a Re(V) complex[8], $Re(L)_2(NPh)(PPh_3)BPh_4$.

In view of the rapidly developing field of tin compounds in biological chemistry[9], we report in this paper on investigations of the coordination of maltol with organotin(IV) compounds including X-ray crystal and molecular structures of R_2SnL_2 [R = Ph (**4**), Me (**2**)], $BuSnL_3$ (**6**), and Cl_2SnL_2 (**5**). The presence of almost discrete carbonyl and hydroxy groups in the ligand allows us to distinguish a dative bond from the normal covalent bond in reference to the group-14 element tin as suggested recently by Haaland[10].

Results and Discussion

The complexes **1**, **2**, and **3** were prepared by reaction of the corresponding organotin chloride with the sodium salt of maltol, NaL, as described in eq. (1). If triphenyltin chloride was allowed to react with maltol in the presence of sodium acetate, cleavage of a tin-carbon bond occurred besides the substitution of its Cl atom furnishing only diphenyltin bis(maltolate) (**4**). Similarly, the reaction according to eq. (3) yielded Cl_2SnL_2 (**5**). $BuSnL_3$ (**6**) was obtained from butylstannoic acid and maltol as shown in eq. (4). The tetramaltolatostannane, SnL_4, could not be isolated from the reaction of $SnCl_4$ with 4 equivalents of NaL. All these complexes (Table 1) are crystalline solids except **1**, which is a liquid, and all were obtained in good yields. Compounds **2** and **4** have recently also been reported by Guo et al.[12] and compound **5** by Burgess and Parsons[13].

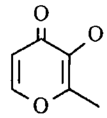
$$R_nSnCl_{4-n} + (4\text{-}n)NaL \longrightarrow (4\text{-}n)\,NaCl + R_nSnL_{4-n} \qquad (1)$$

n	3	2	2
R	Bu	Me	Bu
	1	**2**	**3**

$$Ph_3SnCl + Na(ac) + 2\,LH \longrightarrow \underset{\mathbf{4}}{Ph_2SnL_2} + C_6H_6 + NaCl \qquad (2)$$

$$PhSnCl_3 + 2\,LH \longrightarrow \underset{\mathbf{5}}{Cl_2SnL_2} + C_6H_6 + HCl \qquad (3)$$

$$BuSn(O)OH + 3\,LH \longrightarrow \underset{\mathbf{6}}{BuSnL_3} + 2\,H_2O \qquad (4)$$



= **LH**

The infrared spectrum of maltol[14,15] displays a characteristic four-band pattern between 1655 and 1450 cm^{-1} which essentially consists of ν(C=O) and ν(C=C) vibrations with considerable mixing. In the complexes **1**–**6** the higher frequency absorptions undergo a noticeable lowering by 50–70 cm^{-1} indicating the chelating mode of the maltolate unit. However, most of the ring modes remain unaltered. In the region 1400–600 cm^{-1} a large number of absorptions occur due to ν(C–O) besides δ(O–H) and δ(C–H) vibrations δ which are not diagnostic. In the lower frequency region the assignment of ν(Sn–O)[16] and

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Table 1. Analytical and selected IR data for compounds **1**−**6**

Compound	m.p. (°C)	Analysis (%)			IR bands (cm^{-1})			
		C	H	Sn	ν(CO + CC)[a]		ν(SnO)	ν(SnC)
Bu_3SnL **1**	red liquid	50.59	7.82[c]	-	1610	1546	448	606[b]
		52.00	7.71[d]	-	1586	1460		528
Me_2SnL_2 **2**	yellow solid	41.62	3.81	-	1612	1522	446	588
	193 - 195	42.13	4.00	-	1582	1460		526
Bu_2SnL_2**3**	yellow solid	48.70	4.90	-	1610	1528	445	610[b]
		49.00	5.61	-	1585	1465		525
Ph_2SnL_2 **4**	yellow solid	56.92	4.21	23.57	1618	1520	452	342[b]
	125 - 127	55.09	3.85	22.69	1588	1478		258
Cl_2SnL_2 **5**	colorl.solid	42.20	3.15	-	1618	1510	459	
	125 -127	41.71	3.11	-				
$BuSnL_3$ **6**	yellow solid	47.09	4.38	21.24	1612	1520	455	535
	192 - 194	47.93	4.36	21.55	1580	1465		

[a] Mixed with ring vibrations. − [b] Mixed with ligand vibrations. − [c] Calculated values. − [d] Found values.

υ(Sn−C)[17] has been possible although the latter are coupled with ligand vibrations. υ(Sn−O) is found between 445 and 456 cm^{-1}. There should of course be more bands resulting from Sn−O stretching vibrations, and there are indeed more bands in the region of 500−300 cm^{-1} which may result from υ(Sn−O) but we cannot confidently assign those. We note, however, that the bands listed in Tab. 1 differ to some extent with those reported in ref.[12,13]. The tentative assignment of the ν(Sn−C) modes precludes any comment on linear or bent CSnC orientations in R_2SnL_2 complexes **2**−**4**.

The ^{1}H-NMR spectra (Table 2) of the organotin maltol complexes indicate a pair of doublets between $\delta = 6.96$ and 7.10 as well as signals between $\delta = 7.92$ and 8.53 due to the CH ring protons. The methyl group appears as a singlet in the $\delta = 2.45-2.75$ region. The signals of two ring and the exocyclic methyl protons are shifted downfield by 0.15 to 0.56 ppm in comparison with maltol, suggesting bidentate ligation of the organotin moiety. The ^{13}C-NMR spectra (Table 2) display six characteristic resonances, five for ring carbons and one for the methyl carbon. $\delta(^{119}Sn)$ values are known to be strongly dependent on the coordination number of the tin atom in the complex. Compound **1** absorbs at $\delta = +75.9$ suggesting a fourfold or fivefold coordination for it[18]. The latter is the more likely alternative. ^{119}Sn-NMR spectra of **4** and **2** exhibit a single resonance each at $\delta = -155.8$ and -166.8, respectively, consistent with a sixfold coordination of the tin center. These data are comparable with the shielding of hexacoordinated ^{119}Sn in five-membered bischelates[19] such as dimethyltin bis(tropolonate) ($\delta^{119}Sn = -197.0$) and the corresponding bis(kojate) ($\delta^{119}Sn = -174.0$). In the ^{1}H-NMR spectrum the coupling constant $^2J_{Sn\text{-}H}$ of 86.0 Hz for **4** is also consistent with a six-coordinate environment[20] at the tin atom. The ^{119}Sn chemical shift for the tris(maltolate) **6** occurs at a much lower frequency ($\delta = -510.7$). This is within the range expected for seven-coordinated tin compounds[21]. Burgess[13] has found a ^{119}Sn-NMR signal for **5** at $\delta = -465.5$ which would be consisent with a six- or seven-coordinated tin center. This demonstrates once again that it is difficult to deduce the coordination number of tin unambiguously from NMR data due to the large range of the ^{119}Sn resonances.

It is evident that the spectroscopic features are consistent with a bidentate monoanionic ligation of maltolate containing an organotin moiety. In order to obtain reliable structural details, single-crystal X-ray analyses of **2**, **4**, **5**, and **6** were performed. The molecular geometry and atomic labelling scheme of **2** and **4** are depicted in Figures 2 and 1, respectively. Selected bond distances and angles are given in Table 3. Compound **4** crystallizes in discrete molecular units with no unusual intermolecular contacts. It exhibits a distorted octahedral geometry around the tin atom with the two phenyl group in *cis* position (Figure 1) and with a bond angle C−Sn−C of 106.8(1)°. The small bite angle (aver. 76.1°) could be one of the prime factors for this distortion as is evident from the "octahedral" angles (Table 3). On the other hand, four oxygen atoms of **2** are almost all located in a plane forming a trapezoid (Figure 2). The two methyl groups are skewed at an angle C13−Sn−C14 of 148.4(3)° to the edge formed by the ketonic oxygens of the trapezoid, and the C13−Sn−C14 plane is almost perpendicular to the trapezoid. The bond angles at the tin atom involving the methyl carbons and O1 and O2 range from 83.1 to 84.7° demonstrating that the tin-carbon bonds are symmetrically bent towards the longer Sn−O(keto) bonds. Thus, the coordination polyhedron around the tin center of **2** can be described to be approximately skew-trapezoidal bipyramidal. There seems to be an *intermolecular* interaction between the tin atom and the carbonyl oxygen atom of the ligand having a Sn−O distance of 3.435 Å (sum of the van der Waals radii 3.57 Å[22]); this is indicated by the dashed lines in Figure 2. Any such interaction is perhaps a consequence of coordinative unsaturation arising from an asymmetry between the two bound donor atoms of a bidentate ligand as observed earlier also for dimethyltin bis(pyrrolethiocarbamate)[23], bis(pyrroledithiocarbamate)[24], and bis(thio-β-diketonates)[25].

The asymmetric unit of the dichloro complex **5** contains also one benzene molecule. As depicted in Figure 4 the molecule exhibits a distorted octahedral coordination sphere with two chlorine atoms in *cis*-position. The Cl−Sn−Cl bond angle is 97.8(1)°. This angle is closer to the ideal octahedral angle as compared with **4**, and the bite angle (79.4°) is larger than in **4**. Compound **5** possesses a crystallographically imposed C_2 axis bisecting the Cl−Sn−Cl angle. **5** also exhibits fairly short Sn−Cl bonds [2.370(1)Å] which are slightly shorter than the sum of the covalent radii (2.39 Å)[22].

The considerable distortion and deviation of the molecular structures of **2**, **4**, and **5** from an octahedral environment is due to the geometry resulting from the chelating function of the maltol ligand and the difference in the Sn−O bond strengths (Table 3). In **2**, the Sn−O(hydroxy) average distance of 2.10 Å is close to the sum of the covalent radii (2.11 Å). In contrast, the Sn−O(keto) distance with an average value of 2.438 Å is much longer. With the much weaker delocalization of the π electrons in the maltol ring

Table 2. NMR data of compounds **1**–**6** recorded in $CHCl_3$ solution

	δ^1H				$\delta^{13}C$						$\delta^{119}Sn$
Compound	-CH	-CH	$-CH_3$	R	C=O	-C-O-	-CH	-CH	CMe_3	CH_3	Sn
1	8.48	6.96	2.54	0.86-2.01	175.5	153.6	151.6	146.8	111.8	14.4	75.9
2	8.49	7.08	2.73	0.69	175.6	153.2	152.2	148.9	111.1	15.1	-166.8
3	8.53	7.20	2.75	0.74-1.75	176.2	152.9	151.9	148.9	111.2	15.1	-
4	[a]	7.10	2.65	7.92-8.68	174.7	153.5	151.9	144.4	110.7	14.9	-155.8
5	7.92	6.69	2.54								
6	8.52	7.08	2.56	0.62	174.5	152.7	151.5	148.5	109.8	15.1	-510.7

Additional ^{13}C resonances for group R: **1**: 28.0, 27.0, 19.0, 13.6; **4**: 136.9, 130.4, 128.9, 128.1; **2**: 6.5; **3**: 27.2, 27.0, 26.6, 13.7; **6**: 29.6, 27.2, 25.2, 13.2.

[a] Mixed with the multiplet of the phenyl group.

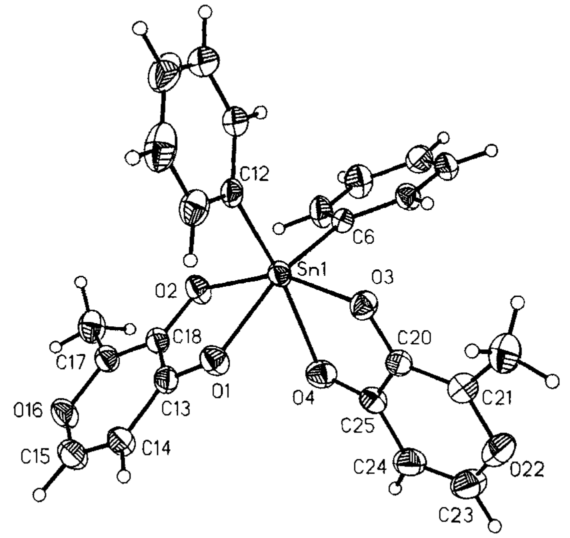

Figure 1. ORTEP-type representation of the molecular structure of **4**. Thermal ellipsoids are drawn on a 25% probability level

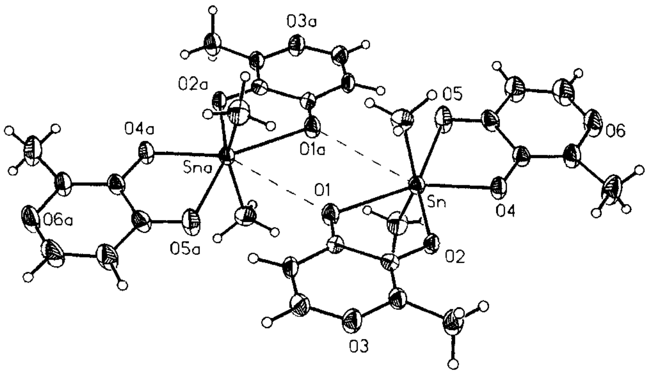

Figure 2. ORTEP-type representation of the molecular structure of **2** in the crystal. The two molecules are related to one another by a two-fold axis. Thermal ellipsoids are represented on a 25% probability level

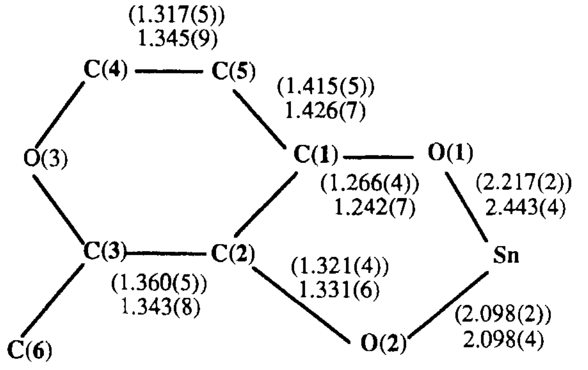

Figure 3. Selected bond distances [Å] within a maltol ring for **2**. The corresponding dimensions of one of the rings for **4** are given in parentheses

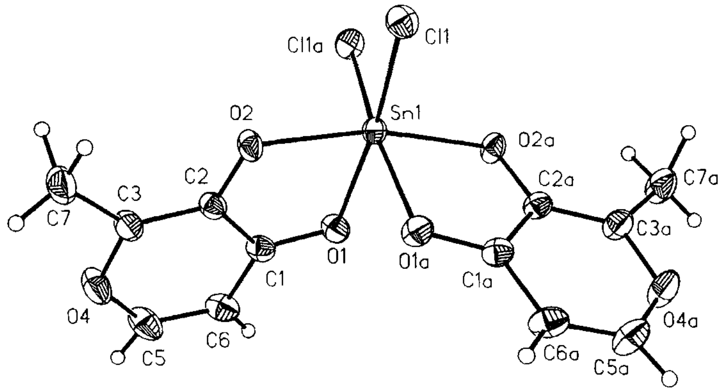

Figure 4. ORTEP-type representation of the molecular structure of **5**. Thermal ellipsoides are drawn on a 25% probability level

as evidenced by the significant double bond character [e. g. C4–C5 1.345(9) and C3–C2 1.343(8) Å, Figure 3], the two tin-oxygen bonds within a chelate ring provide a useful distinction of covalent versus dative bond lengths in reference to tin chemistry as suggested recently by Haaland[10]. He has argued that the strength of a dative or donor-acceptor

Table 3. Selected bonding parameters of complexes **2**, **4**, **5**, and **6**[29]

Selected Bond lengths in Å							
4		**2**		**6**		**5**	
Sn-O2	2.098(2)	Sn-O2	2.098(4)	Sn-O1	2.120(2)	Sn-O1	2.129(3)
Sn-O3	2.086(2)	Sn-O4	2.104(4)	Sn-O8	2.124(3)	Sn-O2	2.056(2)
Sn-O1	2.217(3)	Sn-O1	2.443(4)	Sn-O4	2.052(2)	Sn-Cl1	2.370(1)
Sn-O4	2.280(3)	Sn-O5	2.433(5)	Sn-O2	2.333(3)	O1-C1	1.295(5)
Sn-C12	2.142(3)	Sn-C13	2.091(7)	Sn-O5	2.316(2)	O2-C2	1.336(5)
Sn-C6	2.147(3)	Sn-C14	2.097(7)	Sn-O7	2.363(3)	C1-C2	1.423(4)
O2-C18	1.321(4)	O2-C2	1.331(6)	Sn-C19	2.145(4)	C2-C3	1.365(5)
O3-C20	1.322(4)	O4-C7	1.325(7)	O1-C1	1.329(4)	C3-O4	1.354(6)
O1-C13	1.266(4)	O1-C1	1.242(7)	O8-C18	1.318(4)	O4-C5	1.342(5)
O4-C25	1.272(4)	O5-C8	1.246(7)	O4-C12	1.338(4)	C5-C6	1.329(7)
C13-C18	1.431(5)	C1-C2	1.456(8)	O2-C6	1.262(5)		
C20-C25	1.420(5)	C7-C8	1.433(9)	O5-C7	1.256(4)		
C17-C18	1.360(5)	C2-C3	1.343(8)	O7-C13	1.258(4)		
C20-C21	1.360(5)	C7-C11	1.349(8)	C1-C6	1.438(5)		
C13-C14	1.415(5)	C1-C5	1.426(7)	C7-C12	1.448(5)		
C24-C25	1.418(5)	C8-C9	1.423(9)	C13-C18	1.448(5)		
C14-C25	1.317(5)	C4-C5	1.345(9)	C1-C2	1.366(5)		
C23-C24	1.332(6)	C9-C1	1.336(10)	C11-C12	1.344(5)		
Selected Bond Angles in °							
C12-Sn-C6	106.8(1)	C13-Sn-C14	148.4(3)	O1-Sn-O2	73.9(1)	Cl-Sn-Cla	97.8(1)
O1-Sn-O2	76.6(1)	O1-Sn-O2	72.7(1)	O2-Sn-O5	71.0(1)	Cl-Sn-O1	168.0(1)
O3-Sn-O2	75.6(1)	O4-Sn-O5	72.4(19	O5-Sn-O7	69.7(1)	O1-Sn-O2	79.4(1)
C6-Sn-O1	161.6(1)	O2-Sn-O4	80.7(1)	O7-Sn-O8	72.6(1)	Cl-Sn-O2	90.3(1)
C12-Sn-O4	164.1(1)	O1-Sn-O5	134.4(1)	O1-Sn-O8	75.6(1)	O1-Sn-O1a	83.6(1)
O3-Sn-O2	155.7(1)	O1-Sn-C14	84.7(2)	C19-Sn-O4	163.2(1)	O1-Sn-O2a	89.3(1)
C12-Sn-O2	100.0(1)	O5-Sn-C14	84.3(1)	O4-Sn-O5	75.5(1)	O1-Sn-Cla	90.2(1)
C12-Sn-O1	91.0(1)	O1-Sn-O4	153.1(1)	O4-Sn-O7	82.4(1)	Cl-Sn-O2a	99.2(1)
C12-Sn-O3	96.5(1)	O2-Sn-O5	152.9(1)	O4-Sn-O2	83.0(1)		
C6-Sn-O2	94.8(1)	O2-Sn-C13	100.4(2)	C19-Sn-O1	112.5(1)		
C6-Sn-O4	88.2(1)	O1-Sn-C13	83.1(2)	C19-Sn-O2	87.3(1)		
C6-Sn-O3	97.5(1)	O4-Sn-C13	104.0(2)	C19-Sn-O5	88.1(1)		
		O5-Sn-C13	83.1(2)	C19-Sn-O7	87.9(1)		
		O4-Sn-C14	99.6(2)	C19-Sn-O8	94.6(1)		
		O2-Sn-C14	103.9(2)				

bond of group-13 and -14 elements may exceed half of the strength of the isoelectronic normal bond of the same atom pair. The Sn−O bond lengths in the only known five-membered chelate ring (−Sn−O−C−C−O) of tris(tropolonate)-tin(IV) complexes[26] with its highly delocalized ring system are rather similar. Furthermore, the dative bond is expected to be sensitive to the inductive effect of the organic ligand at the tin atom. In fact, in **4**, while the Sn−O(hydroxy) distance (aver. 2.092 Å) is very close to the corresponding value of **2**, its Sn−O(keto) bond length becomes distinctly shorter with an average of 2.248 Å. The corresponding parameters of **5** demonstrate an even shorter Sn−O(keto) bond length (2.129 Å) which comes closer to the Sn−O(hydroxy) distance (2.056 Å). There is, obviously, a correlation between the strengths of the Lewis acidity at the tin center and the Sn−O bond lengths in the tin maltol compounds: the stronger the acid the smaller the differences between the two types of Sn−O bonds. Even when the two Sn−O bond lengths approach each other these changes do not have any significant effect on the bonding within the maltol ring. Expectedly, the C−O(hydroxy) single bond distances in **5** (1.336 Å), **4** (aver. 1.321 Å), and **2** (aver. 1.328 Å) are also similar. In contrast, the C=O bond length happens to be significantly longer in **5** (1.295 Å) and **4** (aver. 1.269 Å) in comparison with **2** (aver. 1.244 Å). This is consistent with the change in the strength of the Sn−O dative bond.

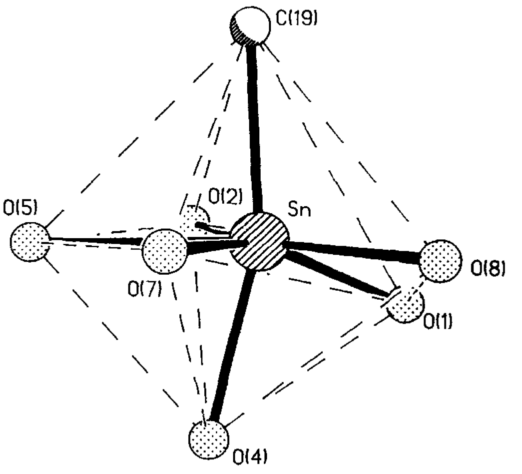

Figure 5. ORTEP-type representation of the molecular structure of **6** in the crystal. Thermal ellipsoids are drawn on a 25% probability level

The molecular structure and the numbering scheme of **6** are presented in Figure 5. The crystal structure exhibits four discrete monomeric molecules in the unit cell. The coordination polyhedron around the tin atom closely resembles a pentagonal bipyramid with five maltol oxygens, O1, O2, O5, O7, and O8, constituting the pentagon while the atom O4 and a butyl carbon atom occupy the axial positions. The interplanar angle of 160.9° between the Sn−O1−O2 and Sn−O7−O8 planes reflects the distortion of the pentagon. The angles subtended at the tin center, however, lie within a

Table 4. Compilation of crystallographic data of compounds **2**, **4**, **5**, and **6** and information on the data collection and structure solution

Crystal Data	**4**[a]	**2**[b]	**6**[b]	**5**[c]
Formula	$C_{24}H_{20}O_6Sn$	$C_{14}H_{16}O_6Sn$	$C_{22}H_{24}O_9Sn$	$C_{18}H_{16}Cl_2O_6Sn$
M	523.1	399.0	551.1	258.9
a [Å]	14.653(6)	9.281(3)	12.640(1)	13.929(3)
b [Å]	9.032(3)	15.345(4)	11.890(1)	11.493(3)
c [Å	16.396(7)	11.158(3)	14.890(1)	13.628(4)
β [°]	91.47(2)	102.43(2)	95.23(6)	111.30(1)
V [Å^3]	2156.0(21)	1551.8(8)	2233.6(4)	2032.4(13)
$d_{(calc)}$ (g/cm^3)	1.612	1.708	1.639	1.692
Z	4	4	4	4
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	C2/c
μ (Mo-K_a) (cm^{-1})	12.23	16.72	11.94	15.5
F(000)	1048	792	1112	1024
Crystal size (mm)	.35x.30x.7	.2x.30x.71	.3x.42x.52	.3x.32x.33
Data Collection and Structure Solution				
2Θ-range (°C)	4 - 46	3 - 49	5 - 50	3 - 50
h, k, l	-15≤h≤15 0≤k≤9 0≤l≤18	0≤h≤10 0≤k≤17 -13≤l≤12	0≤h≤5 0≤k≤14 -17≤l≤17	-1≤ h≤15 -1≤k≤13 -16≤l≤15
Scan speed(°/min)	2.5 - 23	2.4 - 29	2.0 - 29.3	3 - 60
No. measd. refl.	2845	2348	4334	2215
No. unique refl.	2845	2077	3926	1757
No. observ. refl.	2505	1721	3672	1584
F > σ (F), σ:	3	3	3	4
Max./min. Transm.	0.328/0.309	0.906/0.839	0.659/0.511	0.999/0.825
Structure Solution	Direct Meth.	Direct Meth.	Patterson	Patterson
No. of Variables	280	190	295	147
R (%)	2.39	3.14	3.70	2.54
R_w (%)	5.37	3.98	4.59	2.66
GOOF	1.022	1.15	2.24	1.84
Δ_{max} [e/Å^3]	0.71	0.57	0.61	0.43

[a] Crystals from CH_2Cl_2/MeOH. – [b] Crystals from CH_2Cl_2/*n*-hexane. – [c] Crystals from benzene.

narrow range of 69.7–75.6°. The axial angle O4–Sn–C19 [163.2(1)°] is also responsible for this distortion.

Amongst the Sn–O(hydroxy) bond lengths, the axial Sn–O4 bond is remarkably short. Nevertheless, their average (2.098 Å) turns out to be no more different than the corresponding dimensions in **2** and **4**. In consonance with the earlier argument, the Sn–O(keto) distances (aver. 2.337 Å) are definitely longer. The magnitude of the difference between the two types of the tin-oxygen distances is on an average 0.239 Å which happens to be between the corresponding values for the bis(malolate) complexes of **4**, (0.156 Å) and **2** (0.337 Å). Seemingly, the overall inductive effect extending over the tin atom is of greater importance than the increase of the coordination from six to seven in the determination of the strength of the dative bond.

The Sn–C distances in **4** (aver. 2.144 Å) and **2** (aver. 2.094 Å) are comparably similar to the reported values for six-coordinate diorganotin bis(chelate) complexes[27]. The difference may be related to the electron-donating ability of the methyl group. However, small differences in the Sn–C bond lengths may also arise due to the extension of the covalent character of the bonds to the donor centers of the ligand. In **6**, the Sn–C bond length of 2.145(4) Å does not exhibit the expected increase due to the higher coordination number.

The maltol chelate rings are almost planar which, in turn, are coplanar with the SnO2C2 heterocyclic ring. Evidently the bond lengths (Figure 3) within the ring suggest only a small degree of delocalization. It may be concluded from the present data that an asymmetric SnO_2C_2 ring will cause a significant effect on the bonding at the chelate center. In addition, intermolecular interactions play obviously a role. More such structural information on comparable systems would be helpful for a generalization.

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Experimental

All experimental manipulations were carried out under dry nitrogen. Solvents were purified and dried by standard methods. $BuSnCl_3$ (b.p. 93°C/10 Torr), Bu_2SnCl_2 (b.p. 135°C/10 Torr), Bu_3SnCl (b.p. 105°C/1 Torr) and $SnCl_4$ (b.p. 114°C) were distilled before use. Me_2SnCl_2 (Alfa) was used as commercialy available and Ph_3SnCl (M & T chemicals) was crystallized before us. Butylstannoic acid[11] and triphenyltin chloride[28] were prepared by literature procedures. Maltol (Aldrich) was crystallized before use and converted into its sodium salt by treatment with NaH. – IR: Perkin-Elmer 783 spectrometer, 4000–200 cm^{-1}, CsI plates. – NMR (^1H, ^{13}C, and ^{119}Sn): Jeol FX 90Q, 25°C, in $CDCl_3$, TMS internal reference for ^1H and ^{13}C and Me_4Sn in a sealed capillary as an external reference for ^{119}Sn. – MS: Kratosconcept 321S Model (70 eV), accelerating voltage 8 KV, source temp. 25°C.

General Procedure for the Preparation of **1–3** (Table 1): To a suspension of the sodium salt of maltol in dichloromethane was added a solution of the organotin chloride in dichloromethane with continuous stirring at room temp. (30°C). The reaction mixture was stirred for an additional 4 h. The white insoluble solid was filtered and the filtrate concentrated to afford the products which were crystallized from CH_2Cl_2/*n*-hexane or CH_2Cl_2/MeOH mixtures. Results are summarized in Table 1. Amounts of starting materials used and yields are as follows: 1.27 g of Bu_3SnCl, 0.57 g of NaL, yield: 1.43 g of **1**. – 0.50 g of Me_2SnCl_2, 0.67 g of NaL, yield: 0.85 g of **2**. – 0.73 g of Bu_2SnCl_2, 0.75 g of NaL, yield: 1.46 g of **3**.

Diphenyltin Bis(maltolate) (**4**): To a suspension of sodium acetate (0.22 g) in dichloromethane (10 ml) was added a solution of maltol (0.34 g) in the same solvent (20 ml) followed by addition of triphenyltin chloride (1.07 g) in 20 ml of dichloromethane. The mixture was stirred for 4 h and the insoluble material removed by filtration. The solvent was then evaporated from the filtrate and the remaining solid crystallized from dichloromethane/hexane. Yield: 0.69 g of **4**.

Dichlorotin Bis(maltolate) (**5**): To a solution of maltol (0.37 g) in hot benzene (10 ml) was added a solution of $PhSnCl_3$ (0.45 g) in benzene (10 ml). The reaction mixture was refluxed for 3 h until evolution of HCl ceased. Cooling to ambient temperature yielded 0.48 g of **5** (74%).

Butyltin Tris(maltolate) (**6**): To a suspension of BuSn(O)OH (0.76 g) in benzene (20 ml) was added a solution of maltol (1.37 g) in hot benzene (45 ml) with continuous stirring at 35°C. After stirring for 6 h all the butylstannoic acid hat dissolved. The solvent was then removed and the crude product crystallized from CH_2Cl_2/*n*-hexane (1:1) (Table 1). Yield: 1.68 g of **6**.

X-ray Structure Determinations were performed by using a Siemens P4 or R3m four-circle diffractometer with a graphite monochromator and Mo-K_α radiation (λ = 0.71069 Å) for data collection at 20°C. The SHEXTL-PLUS program package was used for structure solution and refinement. Crystallographic data and details of the data collection, structure solution and refinement are compiled in Table 4[29].

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