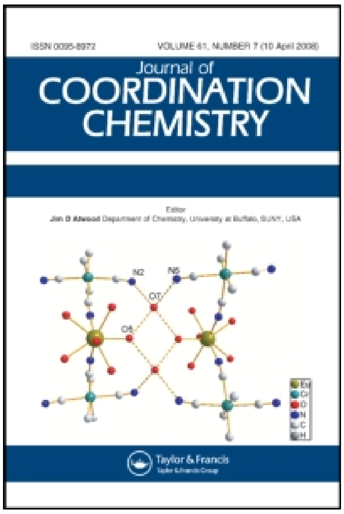

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ORGANOTIN COMPLEXES OF 4-PYRONES

Dolores Fregona[a]; Zijian Guo[ab]; Giuseppina Faraglia[a]; Sergio Sitran[c]
[a] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padova, Italy
[b] Department of Basic Courses, Agricultural University of Hebei, Baoding, P. R. C. [c] Istituto di Chimica e Tecnologia dei Radioelementi del C. N. R., Padova, Italy

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ORGANOTIN COMPLEXES OF 4-PYRONES

DOLORES FREGONA, ZIJIAN GUO,* GIUSEPPINA FARAGLIA

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, 35131 Padova, Italy

and SERGIO SITRAN§

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., corso Stati Uniti, 35020 Padova, Italy

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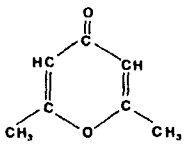
Organotin(IV) complexes with 3-hydroxy-2-methyl-4H-pyran-4-one (HMa), of formulae R_2SnMa_2 (R = Me or Ph), Me_2SnMaX (X = Cl or Br), $Ph_2SnMaCl$ and Ph_3SnMa, have been synthesized along with the 2,6-dimethyl-4H-pyran-4-one (DMP) 1:1 adducts $Me_2Sn(DMP)X_2$ (X = Cl or Br), $Ph_2Sn(DMP)Cl_2$, $Ph_3Sn(DMP)Cl$ and $PhSn(DMP)Cl_3$. Moreover, the $Me_2Sn(DMP)_2Cl_2$ complex has been obtained. The compounds have been characterized by ir and nmr (^1H and ^{13}C) spectroscopy and by thermogravimetric (TG and DTA) analysis. DMP acts as a weak donor towards organotin moieties, the complexes releasing ligand molecules in most solvents, whereas the data for the maltolato complexes support the presence of chelated ligand. DMP or HMa complexes display a more or less marked volatility, sublimation occurring after melting. At higher temperatures sample degradation replaces the sublimation process.

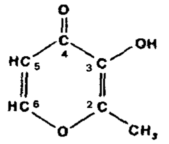
Keywords: Organotin, maltol, dimethyl-4-pyrone, nmr, thermograms

INTRODUCTION

Maltol (3-hydroxy-2-methyl-4H-pyran-4-one, HMa) is a natural product used as a food additive. The stimulatory effect of this substance on plant growth has been suggested to depend on the formation of metal chelates. Moreover, the presence of maltolato ions has been found to suppress hydrolysis of trivalent ions (of iron or aluminium group metals) at physiological pH, aqueous maltolate being employed in appropriate biological tests.$^{1-4}$ Recently we have reported the complexing behaviour of pyrone and thiopyrone derivatives towards various metal salts.$^{5-8}$ Present interest is focused on organotin complexes with either maltol or the parent neutral ligand 2,6-dimethyl-4H-pyran-4-one (DMP).



DMP



H(Ma)

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[*] On leave from the Department of Basic Courses, Agricultural University of Hebei, Baoding, P.R.C.

[§] Author for correspondence.

EXPERIMENTAL

Chemicals

Me_2SnCl_2 (Fluka), Me_2SnBr_2 (Ventron), Ph_2SnCl_2 (Janssen) and Ph_3SnCl (Ventron) were used as supplied. Ligands used were 2,6-dimethyl-4H-pyran-4-one (DMP, Ega Chemie) and 3-hydroxy-2-methyl-4H-pyran-4-one (HMa, Aldrich).

Preparation of the Complexes

Potassium maltolate ($KMa \cdot H_2O$) was prepared by adding an HMa solution in dichloromethane (35 mmol in 40 cm^3) to a KOH suspension in the same solvent (32 mmol in 10 cm^3), with stirring, overnight. The white suspension was filtered, washed with dichloromethane and *n*-pentane and dried *in vacuo*. (Yield, 88%; analysis: found: C, 39.7; H, 3.9%. Calcd. for $C_6H_7KO_4$: C, 39.6; H, 3.9%). The water molecule can be removed by prolonged heating (2 h) under reduced pressure. The infrared absorptions in the 1650–1500 cm^{-1} range (1625m, 1603m, 1578sh, 1512m) are close to those observed for hydrated sodium maltolate[9] except for the absorption at 1750 cm^{-1}, which is absent in pure samples of potassium maltolate.

The complex Me_2SnMa_2 was obtained by stirring (4 h) a suspension of anhydrous KMa (1.1 mmol) in a dichloromethane solution of Me_2SnCl_2 (0.54 mmol in 3 cm^3). The pale yellow solution was filtered from traces of either KCl or KMa and evaporated (to 1 cm^3) under nitrogen flux. By adding *n*-pentane the white yellowish complex separated, which was filtered and dried *in vacuo*. (Yield, 70%). The complexes Me_2SnMaX (X = Cl or Br), Ph_2SnMa_2, $Ph_2SnMaCl$ and Ph_3SnMa were prepared analogously at the appropriate metal to ligand molar ratios.

The DMP complexes were generally prepared by adding *n*-pentane to benzene solutions of reagents. As an example, $Me_2Sn(DMP)Cl_2$ was obtained by adding *n*-pentane until turbidity to a benzene solution containing Me_2SnCl_2 (0.52 mmol) and DMP (0.55 mmol; total volume 5 cm^3). The products obtained by operating at molar ratios 1:2 or 1:3 were mixtures of 1:1 complex and free ligand. The complex $Me_2Sn(DMP)_2Cl_2$ was obtained by evaporating a dichloromethane solution of reagents in stoichiometric ratio. The absence of free ligand was checked by infrared spectra.

Measurements

Ir spectra were recorded on Nicolet 5SXC FR-IT and Nicolet 20F Far-IR spectrometers as Nujol mulls between KBr and polyethylene discs. Nmr (^1H and ^{13}C) spectra were measured using a Bruker AC 200 spectrometer. Thermogravimetric data in air were obtained on Netzsch STA 429 thermoanalytical equipment (flux rate, 250 cm^3 min^{-1}; heating rate, 5°C min^{-1}; ref. material Al_2O_3).

RESULTS AND DISCUSSION

Organotin maltolates (Table I) have been prepared by reaction of organotin halides with anhydrous potassium maltolate in stoichiometric ratio. Despite the insolubility of potassium maltolate in dichloromethane, reactions went to completion in this

TABLE I
Analytical data[a] and selected i.r. frequencies for the complexes

Compound	Formula	C%	H%	IR (cm^{-1})	
Me_2SnMa_2	$C_{14}H_{16}O_6Sn$	42.3	4.0	1608sh	1542sh
		(42.1)	(4.0)	1581s	1517m
$Me_2SnMaCl$	$C_8H_{11}ClO_3Sn$	31.0	3.6	1614m	1548sh
		(31.1)	(3.6)	1570s	1507m
$Me_2SnMaBr$	$C_8H_{11}BrO_3Sn$	27.3	3.1	1616m	1548sh
		(27.2)	(3.1)	1575s	1515m
Ph_2SnMa_2	$C_{24}H_{20}O_6Sn$	54.5	3.8	1604m	1547sh
		(55.1)	(3.8)	1572s	1505m
$Ph_2SnMaCl$	$C_{18}H_{15}ClO_3Sn$	48.7	3.5	1616m	1548sh
		(49.9)	(3.5)	1575s	1509m
Ph_3SnMa	$C_{24}H_{20}O_3Sn$	60.3	4.2	1614m	1545sh
		(60.7)	(4.2)	1584s	1515m
$Me_2Sn(DMP)Cl_2$	$C_9H_{14}Cl_2O_2Sn$	31.3	4.0	1663s	1567s
		(31.4)	(4.1)		1555sh
$Me_2Sn(DMP)_2Cl_2$	$C_{16}H_{22}Cl_2O_4Sn$	41.6	4.8	1652s	1570sh
		(41.1)	(4.7)		1540s
$Me_2Sn(DMP)Br_2$	$C_9H_{14}Br_2O_2Sn$	24.9	3.1	1652s	1581sh, 1564sh
		(25.0)	(3.3)		1545s
$PhSn(DMP)Cl_3$	$C_{13}H_{13}Cl_3O_2Sn$	37.2	3.1	1652s	1567sh
		(36.6)	(3.1)		1542s
$Ph_2Sn(DMP)Cl_2$	$C_{19}H_{18}Cl_2O_2Sn$	48.9	3.9	1646s	1573w
		(48.8)	(3.9)		1534s
$Ph_3Sn(DMP)Cl$	$C_{25}H_{23}ClO_2Sn$	58.8	4.3	1655s	1586sh
		(58.9)	(4.5)		1559s

[a] Calculated values in parentheses.

solvent, in which all organotin maltolates are fairly soluble. Along with the fully substituted species R_2SnMa_2 (R = Me or Ph) and Ph_3SnMa, the mixed complexes Me_2SnMaX (X = Cl or Br) and $Ph_2SnMaCl$ were isolated in nearly quantitative yields. As regards DMP complexes, the examined organotin halides formed 1:1 adducts in benzene/*n*-pentane and also in the presence of excess ligand (Table I). For only dimethyltin dichloride was there some evidence of 1:2 adduct formation in different solvent media, but the pure $Me_2Sn(DMP)_2Cl_2$ adduct could be obtained by evaporating to dryness a dichloromethane solution containing the reagents in stoichiometric ratio.

The infrared spectra of the DMP complexes in the 1650–1500 cm^{-1} range (Table I) are consistent with coordinated ligand. In this region free DMP gives rise to two strong absorptions at 1669 cm^{-1} and 1611 cm^{-1} which have been assigned as ν(C=C) and ν(C=O), respectively, whereas the shoulder at 1599 cm^{-1} is due to ring vibrations.[10] On coordination the ring absorptions shift downfield by some 20 cm^{-1}. The ν(C=O) position depends on the metal-oxygen bond strength, being generally observed in the 1570–1520 cm^{-1} range.[8,11,12] In the present series of organotin complexes (Table I), the low energy shift of both ν(C=C) and ν(C=O) absorptions is at a maximum for $Ph_2Sn(DMP)Cl_2$ (with $\Delta\nu$ of 23 cm^{-1} and 77 cm^{-1}, respectively), smaller parallel changes in the $Me_2Sn(DMP)Cl_2$ spectrum (6 cm^{-1} and 44 cm^{-1}, respectively) suggesting that phenyl groups enhance the acceptor properties of the organotin moiety.

TABLE II
Infrared bands in the 500–100 cm^{-1} region for the maltol complexes[a]

Compound	Wavenumber (cm^{-1})											
HMa	504w				321m					215w		
KMa	492m			382vvw	314m						195s	140s
Me_2SnMa_2	468w	446m		341m	316m			222sh	206s	194sh	176sh	135s
$Me_2SnMaCl$	486m			353m	321w	*281s*		227w	210m	208sh	170w	156m
$Me_2SnMaBr$	486w			354m	325vvw				226w	213m	*194m*	161mw
Ph_2SnMa_2	475m	452s		347m	321m		265ms	246m	236m	219w	189w	
$Ph_2SnMaCl$	488w	450s	441m	352w	329w	290sh	*278s*	240sh	230s	204m		
Ph_3SnMa	477w	454m	445m	347w	322w		264m	258sh	243m	215w		

[a] ν(Sn–halide) in italics.

As regards maltol, the strong bands at 1652 cm^{-1} and 1616 cm^{-1}, along with the medium one at 1559 cm^{-1}, should be caused by strongly mixed $\nu(C{=}C)$ and $\nu(C{=}O)$ modes, the high energy band being mainly involved with carbonyl group vibrations.[2,13–16] Maltolato complexes, such as MMa_3 (M = Al or Ga, [2]), give three bands in the 1650–1500 cm^{-1} region, the stronger one at 1570 cm^{-1} being assigned as mainly $\nu(C{=}O)$. Ring vibrations should cause the medium intensity absorptions at 1610 cm^{-1} and *ca* 1510 cm^{-1}. The organotin maltolate spectra (Table I) show a similar trend, with the strong absorption of the coordinated carbonyl in the 1585–1570 cm^{-1} interval and two ring absorptions in the 1616–1604 cm^{-1} and 1517–1505 cm^{-1} ranges.

Below 500 cm^{-1} the infrared spectrum of maltol contains only one significant band at 321 cm^{-1} (Table II), shifted to 314 cm^{-1} in anhydrous potassium maltolate. The Me_2SnMa_2 spectrum shows in the $\nu(Sn{-}O)$ region medium intensity bands at 446, 341 and 316 cm^{-1}, slightly shifted in Ph_2SnMa_2 and superimposed in part on phenyl group absorptions. The position of the Sn-halide absorption in $Me_2SnMaCl$ (281 cm^{-1}), $Ph_2SnMaCl$ (278 cm^{-1}) and $Me_2SnMaBr$ (194 cm^{-1}) does not exclude the presence of halide bridges. The Sn–Cl absorptions in $Me_2Sn(DMP)Cl_2$ (316 and 262 cm^{-1}, Table III) and $Ph_2Sn(DMP)Cl_2$ (331 and 268 cm^{-1}) are close to those observed for similar adducts with monodentate O-donors, for which a trigonal bipyramidal structure was suggested. The $Me_2Sn(DMP)_2Cl_2$ bands resemble those of octahedral analogues probably containing a *cis* chlorine arrangement.[17]

The proton nmr spectrum of DMP in deuterated chloroform (Table IV) contains singlets due to methyl and ring CH protons at 2.21 and 6.01 ppm, respectively, which shift upfield in deuterated benzene owing to solvent interaction with the ligand aromatic ring.[7,18,19] A general downfield shift of the DMP signals is observed on coordination, which is particularly evident for the CH singlet in $Zn(DMP)_2X_2$ (X = halide; *ca* 6.7 ppm) and $UO_2(DMP)_2(NO_3)_2$ (Refs. 11, 12). The small shifts observed in Table IV for dimethyltin adducts support complex dissociation in either benzene or chloroform with partial ligand release. The proton nmr spectrum of maltol contains the OH (6.95 ppm) and methyl (2.36 ppm) proton singlets along with two doublets (6.41 and 7.69 ppm), the downfield one belonging to the CH group bonded to the ring oxygen atom. As expected, the phenolic proton signal is absent in the complex spectra (Table IV), whereas the ligand methyl singlet shifts downfield by

TABLE III

Infrared bands in the 500–200 cm^{-1} for the pyrone complexes[a]

Compound	Wavenumber (cm^{-1})								
$Me_2Sn(DMP)Cl_2$	513m		454w	*316s*	285sh	*262s*			190m
$Me_2Sn(DMP)_2Cl_2$	516m		359m		283w		*243m*	*211m*	190w
$Me_2Sn(DMP)Br_2$	513m		356w		277w		*221s*	207sh	201sh
$PhSn(DMP)Cl_3$	523w 516w	443m	*350s*		290m		248w	227m	204w
$Ph_2Sn(DMP)Cl_2$	523w 518w	452m	365w	*331s*	281sh	*268s*	243m	235m	201w
$Ph_3Sn(DMP)Cl$	514w	457m 450m 444m	355w		*275s*		230w	222sh	201w

[a] ν(Sn–halide) in italics.

TABLE IV
^{1}H nmr data for ligands and complexes ($CDCl_3$; ppm; *ca* 25°C)

Compound	C*H*	C*H*$_3$	Sn(C*H*$_3$)$_2$
DMP	6.01	2.21	
DMP[a]	5.85	1.41	
$Me_2Sn(DMP)Cl_2$	6.20	2.28	1.18
$Me_2Sn(DMP)Cl_2$[a]	5.88	1.36	0.92
$Me_2Sn(DMP)_2Cl_2$[a]	5.89	1.39	1.17
$Me_2Sn(DMP)Br$	6.13	2.25	1.37
HMa	7.69[b], 6.41	2.36	6.95[c]
Me_2SnMa_2	7.72[b], 6.43	2.50	0.62[d]
$Me_2SnMaCl$	7.87[b], 6.56	2.50	0.90[e]
$Me_2SnMaBr$	7.90[b], 6.60	2.55	1.06[f]
Ph_2SnMa_2	7.64[b,g], 6.53	2.52	

[a] In C_6D_6.
[b] Ring CH near to the ring oxygen.
[c] OH proton.
[d] $J(H\text{-}^{119}Sn) = 87$ Hz.
[e] $J(H\text{-}^{119}Sn) = 78$ Hz.
[f] $J(H\text{-}^{119}Sn) = 77$ Hz.
[g] Superimposed on phenyl proton signals.

about 0.15 ppm. The position of the CH resonances is close to that observed for various maltolates such as $RhMa_3$, $PdMa_2$ or $SnMa_2$,[15,16] whereas the Me_2Sn signal shifts downfield in the partly substituted Me_2SnMaX species (X = Cl, 0.90 ppm; X = Br, 1.06 ppm) with respect to Me_2SnMa_2 (0.62 ppm). For octahedral dialkyltin complexes of the type R_2SnCh_2, in which Ch is a bidentate ligand, a relationship has been found between the C–Sn–C angle in the Me_2Sn moiety and the related $^{1}H-^{119}Sn$ coupling constant in proton nmr spectra.[20] In particular, coupling constant values of the order of 100 Hz suggest a *trans* octahedral configuration whereas values close to 70 Hz are consistent with a *cis* arrangement of the methyl groups. Intermediate values could suggest irregular trapezoidal bipyramidal frameworks, as for tropolonato (*ca* 80 Hz), picolinato (*ca* 75 Hz) of dialkyldithiocarbamato (84 Hz) complexes. Me_2SnMa_2 should belong to the last group, the appropriate coupling constant being 87 Hz. Assignment of the ^{13}C nmr signals for maltol and dimethyltin maltolates has been made on the basis of previous works.[15,16,21] As is shown in Table V, the organotin maltolate spectra are very similar and show small shifts with respect to the free ligand. In particular, the carbonyl signal at 173.1 ppm in free HMa, is observed at 175.5 ppm in the complexes, whereas larger downfield shifts have been reported for the analogous resonance in the MMa_2 (M = Zn or Sn, *ca* 177 ppm), $PdMa_2$

TABLE V
^{13}C nmr data for maltol and complexes ($CDCl_3$; ppm; *ca* 25°C)

Compound	C_4	C_6	C_2, C_3	C_5	CH_3	$Sn(CH_3)_2$
HMa	173.1	154.0	149.4, 143.2	113.2	14.2	
Me_2SnMa_2	175.6	153.0	157.9, 148.9	111.1	15.0	6.4
$Me_2SnMaCl$	175.5	154.7	155.1, 147.6	110.6	15.2	6.9
$Me_2SnMaBr$	175.5	154.8	154.8, 147.3	110.5	15.1	8.9

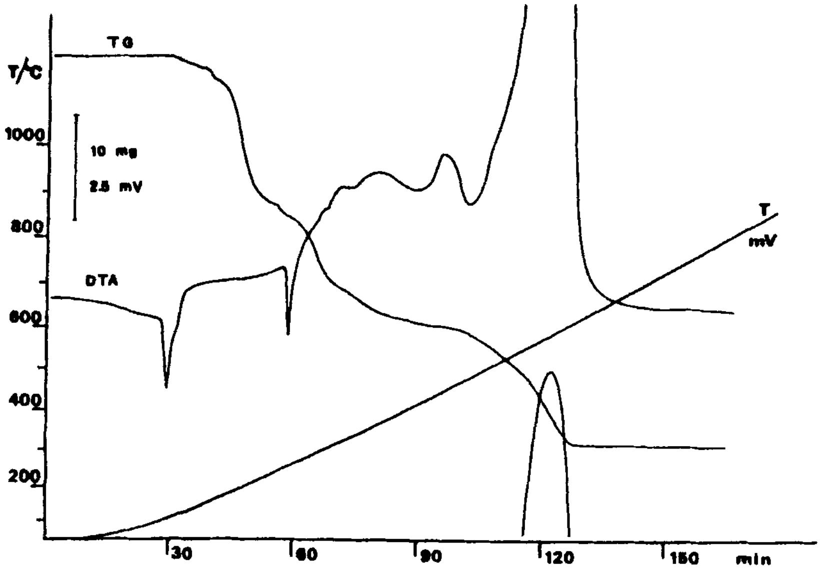

FIGURE 1 Thermograms of Me_2SnMa_2 in air (25.89 mg).

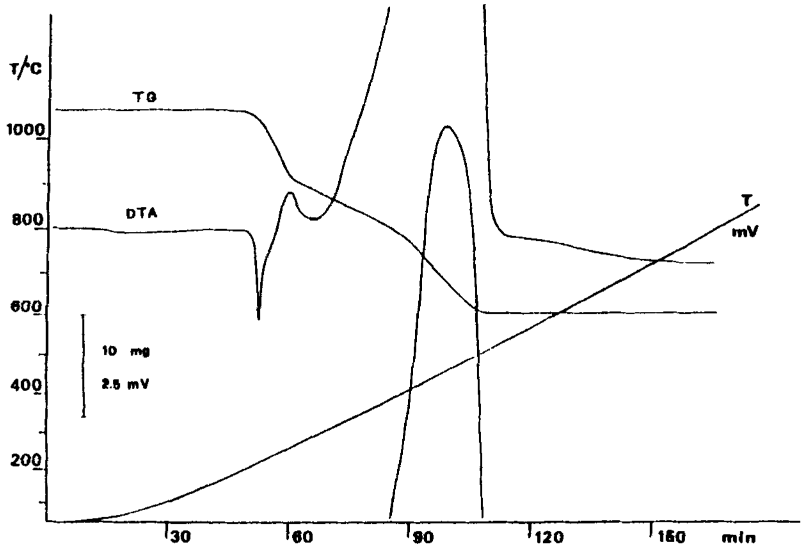

FIGURE 2 Thermograms of $Me_2SnMaBr$ in air (42.61 mg).

(185 ppm) and $RhMa_3$ (187 ppm) complexes. The resonance of the CH group bound to the ring oxygen is nearly unchanged, whereas that of the other CH group undergoes an upfield shift of the order of 2 ppm. The ring carbons bearing the CH_3 and OH substituents give weak signals for which mutual assignment has not been attempted.

Thermograms of the DMP complexes indicate sample sublimation immediately after melting. For example, $Me_2Sn(DMP)Cl_2$ melts at 100°C, all sample being evolved below 300°C. As shown in Figure 1, Me_2SnMa_2 melts with decomposition at 229°C, sublimation being replaced by sample degradation giving rise to the broad exotherm at 440°C. Pyrolysis ends at 500°C with a total weight loss of 77%, larger than that calculated for SnO as final product (66%) and in accordance with simultaneous sublimation. Thermograms of the partially substituted maltolates Me_2SnMaX ($X = Cl$ or Br) are very similar, the sublimation effect being more marked than for Me_2SnMa_2. As shown in Figure 2 for $Me_2SnMaBr$, sample melting (86°C) is followed by substantial weight loss (32%) in the 100–200°C interval, whereas the DTA curve is nearly flat, suggesting a thermal balance between sublimation and degradation processes. The residue melts at 235°C, sample pyrolysis ending at 600°C with a total weight loss of 86%. $Me_2SnMaCl$ shows an identical trend, the sample melting at 74°C. Constant weight is attained at 580°C with a weight loss of 84%.

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