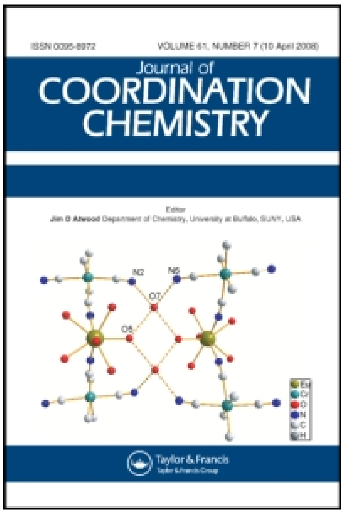

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TIN AND GERMANIUM COMPLEXES WITH MALTOL

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The reaction of tin and germanium tetrachlorides with 3-hydroxy-2-methyl-4H-pyran-4-one (HMa) in benzene yielded $M(HMa)_4Cl_4 \cdot C_6H_6$ (M = Sn or Ge) adducts, whereas in methanol the MMa_2Cl_2 complexes have been isolated. Moreover, tin complexes with the neutral donors 2,6-dimethyl-4H-pyran-4-one (DMP) and 2,6-dimethyl-4H-pyran-4-thione (DMTP), having formulae $Sn(L)_2Cl_2$ and $Sn(L)_2Cl_4$(L = DMP or DMTP) have been prepared. The compounds have been characterized by ir and proton nmr spectroscopy and by thermogravimetric (TG and DTA) analysis. The thermal behaviour of all complexes has been followed to 1200°C. The stability of the $M(HMa)_4Cl_4$ adducts in various solvents is discussed on the basis of proton nmr spectra.

KEYWORDS: Tin, germanium, maltol, 4-pyrones, nmr, thermal analysis

INTRODUCTION

As part of our studies of metal complexes with pyrone and thiopyrone derivatives,[1–4] recently we reported the interaction of organotin halides with maltol (HMa, 3-hydroxy-2-methyl-4H-pyran-4-one).[5] The complexes R_2SnMa_2 (R, Me or Ph), Me_2SnMaX (X = Cl or Br) and Ph_3SnMa were isolated, in which the maltolato ion acts as a chelate. On extending the research to inorganic tin and germanium halides, we observed that HMa could behave as either a neutral or anionic donor, the reaction trend depending essentially on solvent. For this reason we performed a detailed study of the interaction of MCl_4 (M = Sn or Ge) and $SnCl_2$ with maltol and with the neutral donors 2,6-dimethyl-4H-pyran-4-one (DMP) and 2,6-dimethyl-4H-pyran-4-thione (DMTP) bearing the carbonyl (or thiocarbonyl) group in 4 position, as for HMa.

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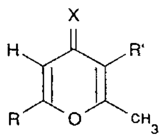

R = H; R' = OH; X = O HMa
R = CH_3; R' = H; X = O DMP
R = CH_3; R' = H; X = S DMTP

EXPERIMENTAL

Chemicals

$SnCl_4$ (Aldrich), $SnCl_2$ (Fluka) and $GeCl_4$ (Aldrich) were used as supplied. Ligands used were 3-hydroxy-2-methyl-4H-pyran-4-one (HMa, Aldrich), 2,6-dimethyl-4H-pyran-4-one (DMP, Ega Chemie), 2,6-dimethyl-4H-pyran-4-thione (DMTP)[6] and $KMA \cdot H_2O$.[5] Tin and germanium salts were handled in a dry box line under dinitrogen atmosphere. Anhydrous solvents were distilled under dinitrogen.

Preparation of the complexes

The complex $Sn(HMA)_4Cl_4 \cdot C_6H_6$ was prepared by adding a benzene solution of $SnCl_4$ (1.0 mmol in 3 cm^3) to a HMa suspension in the same solvent (4 mmol in 25 cm^3). Immediate reaction occurred, yielding a floculent white product clearly different from powdered HMa (2h with stirring). The product was filtered, washed with benzene and dried under reduced pressure (yield, 90%). Under analogous conditions germanium tetrachloride and maltol formed the $Ge(HMa)_4Cl_4 \cdot C_6H_6$ complex, complete reaction requiring 15 h. Yield, 85%.

The complex $SnMa_2Cl_2$ has been prepared by various methods, samples from different preparations showing different ir or thermal data. $SnMa_2Cl_2$ (A) was obtained by reaction of $SnCl_4$ (1 mmol) with HMa in anhydrous methanol (mol ratio 1:4; 20 cm^3). A white solid separated within a few minutes, was washed with methanol and dried under reduced pressure. Yield, 57%. $SnMa_2Cl_2$ (B) was prepared by heating solid $Sn(HMa)_4Cl_4 \cdot C_6H_6$ to 220°C in a thermobalance crucible, whereas $SnMa_2Cl_2$ (C) separated when $SnCl_4$ and HMa were allowed to react in methanol at mol ratio 1:2.

As regard the $SnCl_2$-HMa system, no appreciable reaction was observed in benzene, whereas by mixing methanolic solutions of $SnCl_2$ and HMa (mol ratio 1:2) in air, immediate precipitation of $SnMa_2Cl_2$ (D) was observed. When the reaction was performed in anhydrous methanol under nitrogen atmosphere a colourless solution was obtained, and which by addition of *n*-pentane separated a white solid whose properties suggested the presence of $SnMa_2Cl_2$ along with $SnCl_2$-HMa adducts.

The complex $SnMa_2$ was prepared in quantitative yield by reaction of $SnCl_2$ and $KMa \cdot H_2O$ in water (mol ratio 1:2). The white solid was filtered, washed with water and *n*-exane and dried *in vacuo*.

The complex $GeMa_2Cl_2$ was prepared from $GeCl_4$ (1.2 mmol) and HMa (2.4 mmol) in anhydrous methanol (25 cm^3). The colourless solution, when evaporated to small volume (3 cm^3), gave a white solid which was filtered, washed with methanol and dried *in vacuo*. Yield 35%. The mother liquor, treated with benzene and evaporated under reduced pressure, yielded the solvated species $GeMa_2Cl_2 \cdot 0.5C_6H_6$. Yield, 40%.

The complex $Sn(DMP)_2Cl_4$ was prepared by adding a benzene solution of $SnCl_4$ (1.2 mmol) to a DMP solution in the same solvent (mol ratio from 1:2 to 1:6) with stirring (3 h). The initial oily product turned slowly into a white solid, which was filtered, washed with benzene and dried *in vacuo*. Yield, 85%. The reaction of $SnCl_2$ with DMP in anhydrous benzene (mol ratio 1:2) gave a beige solution which by addition of *n*-exane yielded the white $Sn(DMP)_2Cl_2$ adduct.

$Sn(DMTP)_2Cl_4 \cdot C_6H_6$ solvate was precipitated in quantitative yield by reacting benzene solutions of $SnCl_4$ and DMTP (mol ratio: 1:2). The orange solid was washed with benzene and dried *in vacuo* (10 min). The solvent molecule is easily removed by dichloromethane washings yielding the pink unsolvated species. Moreover, the benzene amount varied in samples from different preparations (from 0.6 to 1.0 mole) and was lower in aged samples. $Sn(DMTP)_2Cl_2$ was prepared by adding powdered $SnCl_2$ to a benzene solution of DMTP (mol ratio 1:2) with stirring overnight. The orange solid was filtered, ground in a mortar and reacted again in a benzene solution of ligand. The product was filtered, washed with benzene and *n*-pentane and dried *in vacuo*.

Germanium tetrachloride did not react with either DMP or DMTP in organic media (benzene or dichloromethane). Samples from solutions evaporated to dryness showed essentially the ir spectra of free ligands.

Measurements

Infrared spectra were recorded using Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers, in Nujol mulls between KBr and polyethylene discs. ^1H nmr spectra were obtained with a JEOL FX 90Q spectrometer. TG and DTA curves in air (flow rate 250 cm^3 min^{-1}, heating rate 5°C min^{-1}) were recorded on a Netzsch STA 429 thermoanalytical instrument (reference material Al_2O_3). Melting points (uncorrected) were determined using a Büchi apparatus.

RESULTS AND DISCUSSION

When tin and germanium tetrachlorides were reacted with excess HMa in anhydrous benzene, the adducts $M(HMa)_4 \cdot C_6H_6$ (M = Sn or Ge) were isolated whereas in methanol $M(Ma)_2Cl_2$ species were obtained (Table 1). Samples of $SnMa_2Cl_2$ prepared by different methods showed more or less marked changes in infrared and thermal data, as discussed below. The complex $SnMa_2Cl_2$ (A) was prepared in methanol by reaction of $SnCl_4$ and HMa at mol ratio 1:4, $SnMa_2Cl_2$ (B) was an intermediate of $Sn(HMa)_4Cl_4 \cdot C_6H_6$ thermal degradation and $SnMa_2Cl_2$ (D) separated when $SnCl_4$ and HMa were reacted in methanol at molar ratio 1:2. No reaction between $SnCl_2$ and HMa was observed in benzene, whereas behaviour in methanol was found to depend on the atmosphere. In fact, by operating in air, with a reagent mol ratio of 1:2, $SnMa_2Cl_2$ (C) separated, suggesting immediate oxidation of tin(II). Moreover, analytical data, which confirm the presence of two chlorine atoms, along with ir spectra, which coincide with those of $SnMa_2Cl_2$ (D), support the absence of additional oxygen, which usually forms bridges between tin atoms in polymeric tin carboxylates.[7-9] The solution obtained by reacting $SnCl_2$ and HMa in anhydrous methanol under dinitrogen yielded, when treated with *n*-pentane, solid fractions containing $SnMa_2Cl_2$ and unidentified species containing coordinated

Table 1 Analitical data[a] and selected i.r. frequencies for the complexes.

Compound	Formula	C%	H%	Cl%	IR (cm^{-1})	
$Sn(HMa)_4Cl_4C_6H_6$	$C_{30}H_{30}Cl_4O_{12}Sn$	42.9	3.4	16.4	1652sh	1553s
		(42.7)	(3.6)	(16.8)	1615s	1508w
$Sn(HMa)_4Cl_4$	$C_{24}H_{24}Cl_4O_{12}Sn$	37.2	2.9		1650sh	1553s
		(37.7)	(3.2)		1615s	1508w
$SnMa_2Cl_2(A)$[b]	$C_{12}H_{10}Cl_2O_6Sn$	33.0	2.3	16.5	1608s	1545s
		(32.8)	(2.3)	(16.1)	1565s	1507w
$SnMa_2Cl_2(B)$[c]	$C_{12}H_{10}Cl_2O_6Sn$	32.8	2.3	16.5	1609m	1543s
		(32.8)	(2.3)	(16.1)	1564sh	1507w
$SnMa_2Cl_2(C)$[d]	$C_{12}H_{10}Cl_2O_6Sn$	32.9	2.3	16.0	1609m	1555m
		(32.8)	(2.3)	(16.1)	1570m	1506w
$SnMa_2Cl_2(D)$[e]	$C_{12}H_{10}Cl_2O_6Sn$	33.0	2.3	15.9	1609m	1556s
		(32.8)	(2.3)	(16.1)	1571m	1504w
$SnMa_2$	$C_{12}H_{10}O_6Sn$	38.9	2.7		1603m	1543sh
		(39.0)	(2.7)		1567s	1501s
$Ge(HMa)_4Cl_4 \cdot C_6H_6$	$C_{30}H_{30}Cl_4GeO_{12}$	40.4	3.1	17.3	1652m	1556s
		(41.6)	(3.0)	(17.9)	1621s	
$GeMa_2Cl_2$	$C_{12}H_{10}Cl_2GeO_6$	36.2	2.7	17.8	1622m	1555s
		(36.6)	(2.6)	(18.0)	1570sh	1520w
$Sn(DMP)_2Cl_2$	$C_{14}H_{16}Cl_2O_4Sn$	37.9	3.6		1662s	1570m
		(38.4)	(3.7)		1585sh	1539s
$Sn(DMP)_2Cl_4$	$C_{14}H_{16}Cl_4O_4Sn$	33.2	3.2		1674sh	1559m
		(33.1)	(3.2)		1649s	1506s
$Sn(DMTP)_2Cl_2$	$C_{14}H_{16}Cl_2O_2S_2Sn$	34.9	3.4		1641s	1555m
		(35.8)	(3.4)			
$Sn(DMTP)_2Cl_4 \cdot C_6H_6$	$C_{20}H_{22}Cl_4O_2S_2Sn$	38.4	3.7		1625vs	1535s
		(38.8)	(3.6)			1528sh
$Sn(DMTP)_2Cl_4$	$C_{14}H_{16}Cl_4O_2S_2Sn$	30.8	3.0		1625vs	1535s
		(31.1)	(3.0)			1528sh

[a]Calculated values in parentheses. [b] From $SnCl_4$ and HMa in MeOH (mol ratio 1:4). [c]By thermal degradation of $Sn(HMa)_4$ Cl_4 up to 220°C. [d]By reaction $SnCl_2$ and HMa in MeOH (mol ratio 1:2). [e]By reaction of $SnCl_4$ and HMa in MeOH (mol ratio 1:2).

HMa. By reaction of $SnCl_2$ with potassium maltolate in water, $SnMa_2$ was prepared, which has been already reported to form by electrochemical oxidation of tin in the presence of HMa in organic media.[10]

The first step in the $Sn(HMa)_4Cl_4 \cdot C_6H_6$ thermograms (Figure 1) involves benzene evolution (88°C; weight loss 9.6% against calc. 9.3%). The endotherms at 120, 152 and 179°C refer to the release of two HMa and two HCl molecules to form $SnMa_2Cl_2$ (B), with total weight loss at the beginning of the plateau (185°C) of 47.2% (calc. 47.9%). Being an intermediate stable up to 288°C, samples of $SnMa_2Cl_2$ (B) are easily prepared by heating the 1:4 adduct to 190°C. Sometimes the solid is beige, owing to the presence of small amounts of decomposition products which do not alter analytical and spectroscopic data. As shown in Figure 1, $SnMa_2Cl_2$ (B) melts with decomposition at 288°C, degration (exotherms at 338, 545 and 650°C) ending at 700°C. The weight loss for $Sn(HMa)_4 \cdot C_6H_6$ at this temperature is higher than expected for SnO_2 as final product (86.6%; calc. 82.1%), suggesting partial sublimation. The thermograms of $SnMa_2Cl_2$ (D), obtained from $SnCl_4$ and HMa in mehtanol at mol ratio 1:2, show a neat endotherm at 244°C (Figure 2). The absence of a parallel weight change supports a phase transition to form $SnMa_2Cl_2$ (B), which successively decomposes as described previously. The

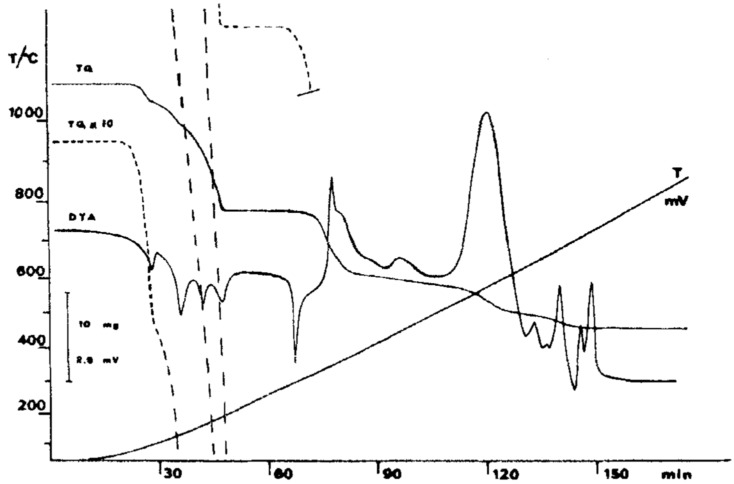

Figure 1 Thermograms of $Sn(HMa)_4Cl_4 \cdot C_6H_6$ in air (31.42 mg).

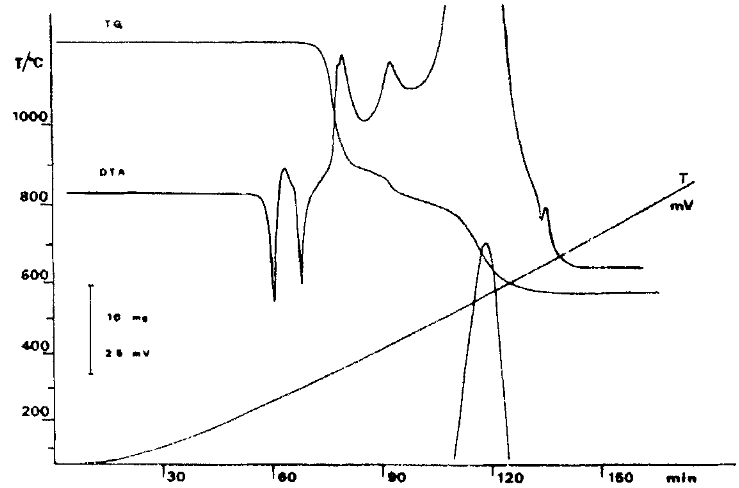

Figure 2 Thermograms of $Sn(Ma)_2Cl_2(D)$ in air (34.73 mg).

thermal behaviour of $SnMa_2Cl_2$ (A), prepared from $SnCl_4$/HMa 1:4 in methanol, is identical to that of $SnMa_2Cl_2$ (C) prepared by oxidation of $SnCl_2$ in a methanolic solution of HMa. As is shown in Figure 3 for $SnMa_2Cl_2$ (C), a nearly imperceptible peak is observed at 244°C, the melting process (286°C) being followed by pyrolysis (exotherms at 340°C, 433 and 555°C). The weight loss at 685°C is 77.0% against a calculated value for SnO_2 of 65.7%. No sublimation occurs for $SnMa_2$ (Figure 4), the initial exotherm at 164°C being probably due to sample oxidation in air. In fact a small weight increase is observed at first with contemporaneous decomposition (exotherms at 406, 515 and 570°C). Most of sample is released below 620°C. At

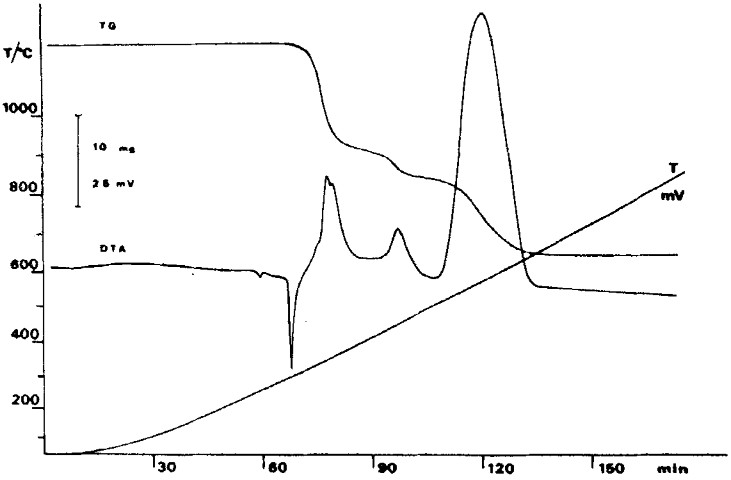

Figure 3 Thermograms of $Sn(Ma)_2Cl_2$ (C) in air (30.53 mg).

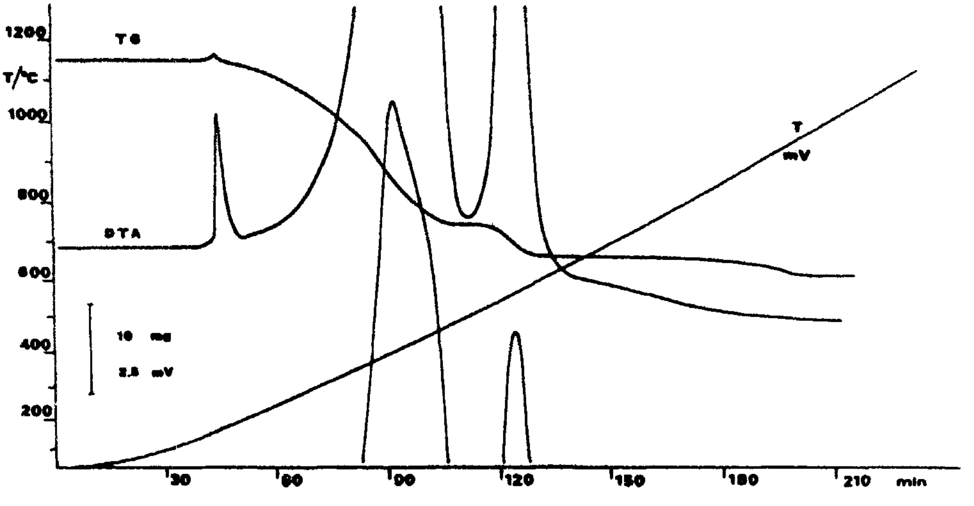

Figure 4 Thermograms of $SnMa_2$ in air (37.74 mg).

higher temperature slow degradation takes place, ending at 1050°C (62.0% against calc. 59.1%). After benzene evolution (97°C; 9.5% against calc. 9.8%), the $Ge(HMa)_4Cl_4 \cdot C_6H_6$ thermograms display a shapeless trend with a progressive weight decrease to 840°C, as for $GeMa_2Cl_2$ (Figure 5). In this case the endotherm at 1100°C is due to melting of the GeO_2 residue, which is formed in low yield owing to partial sublimation of the sample (total weight loss, *ca* 90% against calc. 83.5%).

The formation of the 1:4 MCl_4-HMa adducts in benzene should depend mainly on the presence of hydrogen bridges among ligand molecules and chlorine atoms, which could favour carbonyl coordination. In fact, by reaction of $SnCl_4$ with large

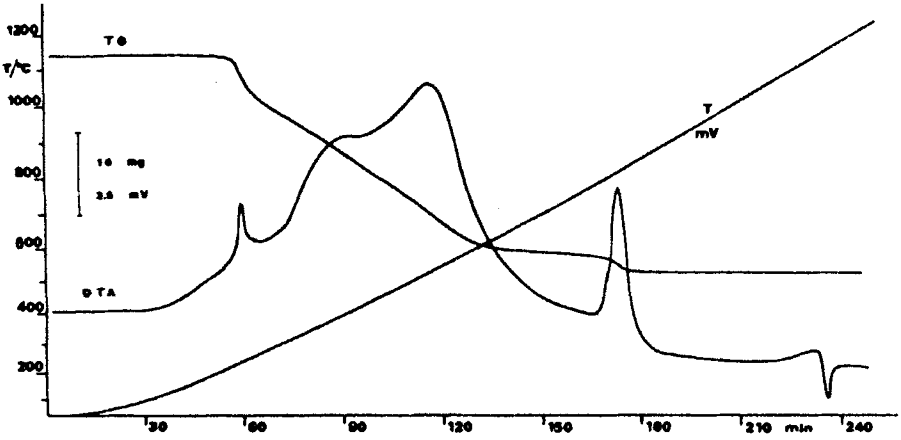

Figure 5 Thermograms of $Ge(Ma)_2Cl_2$ in air (33.91 mg).

excess of the parent DMP, which does not contain the OH group, $Sn(DMP)_2Cl_4$ is obtained, whereas $GeCl_4$ does not react within ten days. Similar behaviour is observed in the presence of the thio-analogue DMTP, which forms with $SnCl_4$ the $Sn(DMTP)_2Cl_4 \cdot C_6H_6$ solvate. Both neutral ligands reacts with $SnCl_2$ in benzene to give $Sn(L)_2Cl_2$ (L = DMP or DMTP). Thermograms of $Sn(DMTP)_2Cl_4 \cdot C_6H_6$ (Figure 6) show benzene evolution at 90°C. The unsolvated sample is stable to 190°C, then melts (213°C) with decomposition (exotherms at 322, 389 and 489°C) to SnO_2 (565°C; total weight loss, 86.5%; calc. 75.6%). The $Sn(DMP)_2Cl_4$ adduct melts with decomposition at 235°C, contemporaneous degradation and sublimation being observed at higher temperatures, as for $Sn(DMP)_2Cl_2$ (m.p., 89°C; decom-

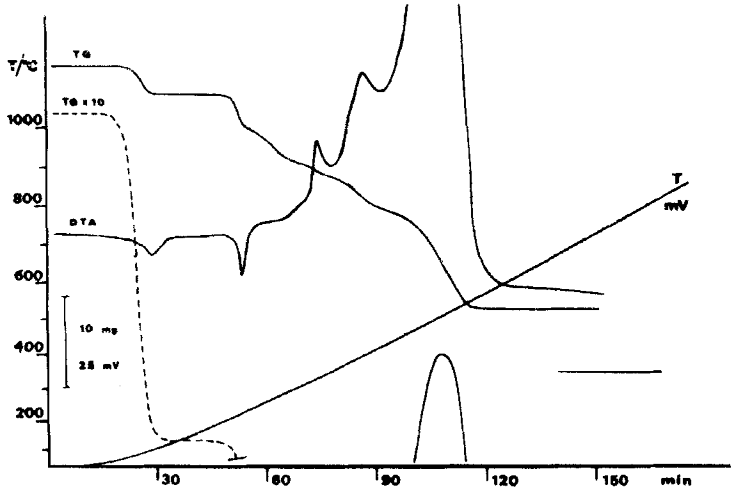

Figure 6 Thermograms of $Sn(DMTP)_2Cl_4 \cdot C_6H_6$ in air (31.25 mg).

position in the 150–700°C range). Sn(DMTP)$_2$Cl$_2$ melts at 119°C, then decomposes to SnO$_2$ in the 140–585°C interval (71.8% against calc. 67.9%).

The infrared spectrum of maltol shows a strong band at 1652 cm^{-1}, assigned as mainly υ(C=O). The bands at 1616 cm^{-1} (strong) and 1559 cm^{-1} (medium) belong to strongly mixed υ(C=C) and υ(C=O) modes.[10–12] The position of these bands is nearly unchanged in the M(HMa)$_4$Cl$_4$·C$_6$H$_6$ (M = Sn or Ge) complexes, whereas their intensity is reversed (Table 1). In fact the absorption at 1652 cm^{-1} is weaker than in free HMa, a parallel intensity increase being observed for the band at *ca* 1555 cm^{-1}. As expected, the high energy band is absent in the maltolato complexes, owing to the low energy shift of υ(C=O) on coordination. Such an absorption, found in the 1585–1570 cm^{-1} range in organotin maltolates,[5] is observed at 1567 cm^{-1} for SnMa$_2$ and in the 1540–1555 cm^{-1} region for MMa$_2$Cl$_2$ (M = Sn or Ge; Table 1) complexes. The carbonyl group stretch in DMP gives rise to a strong band at 1611 cm^{-1}, whereas ring vibrations cause absorptions at 1669 and 1599 cm^{-1}, as for DMTP (1641 and 1559 cm^{-1}).[13,14] Carbonyl coordination causes a low energy shift of υ(C=O), which is observed at 1539 cm^{-1} in Sn(DMP)$_2$Cl$_2$ and at 1506 cm^{-1} in Sn(DMP)$_2$Cl$_4$. As regards ring vibrations, they are slightly shifted in the DMP or DMTP complexes, the effect being larger for the Sn(L)$_2$Cl$_4$ (L = DMP or DMTP) adducts (Table 1). For example the high energy υ(C=C) mode is observed at 1641 cm^{-1} in Sn(DMTP)$_2$Cl$_2$, but at 1625 cm^{-1} in Sn(DMTP)$_2$Cl$_4$. The free DMTP υ(C=S) absorption (1095 cm^{-1}) shifts slightly to low energy in the adducts (of the order of 5 cm^{-1})

The spectrum of maltol below 400 cm^{-1} is very simple with a medium intensity band at 321 cm^{-1} and a weak one at 215 cm^{-1} (Table 2). Anhydrous potassium maltolate has a medium intensity absorption at 314 cm^{-1}, as for SnMa$_2$ (339 cm^{-1}). Metal-chlorine vibrations give rise to a strong band (328 cm^{-1}) in Sn(HMa)$_4$Cl$_4$·C$_6$H$_6$, present at 342 cm^{-1} in the germanium analogue. The spectra of SnMa$_2$Cl$_2$ samples from different preparations fall in two groups. SnMa$_2$Cl$_2$ (C) and SnMa$_2$Cl$_2$ (D) present a strong Sn-Cl band at 331 cm^{-1} whereas SnMa$_2$Cl$_2$ (A) shows three bands of medium intensity at 324, 308 and 270 cm^{-1}. The spectrum of SnMa$_2$Cl$_2$ (B) has the same shape as SnMa$_2$Cl$_2$ (A), the bands around 300 cm^{-1} being slightly shifted (328, 308 and 265 cm^{-1}). The presence of two strong Sn-Cl absorptions (336 and 324 cm^{-1}) supports an octahedral configuration for Sn(DMP)$_2$Cl$_4$. In fact, these bands are very close to those of Sn(Me$_2$SO)$_2$Cl$_4$ (339 and 321 cm^{-1}), which has a distorted *cis*-octahedral coordination geometry as established by crystal structure data.[15] The Sn(DMTP)$_2$Cl$_2$ spectrum shows a low energy shift of the Sn-Cl absorptions (308 and 291 cm^{-1}), being probably caused by sulphur *trans* influence. The Sn-Cl bands in Sn(DMP)$_2$Cl$_2$ (287 and 253 cm^{-1}) resemble those of Sn(Ph$_3$PO)$_2$Cl$_2$ (282 and 252 cm^{-1}),[16] a low energy shift being again observed for Sn(DMTP)$_2$Cl$_2$ (266 and 230 cm^{-1}).

The proton nmr of maltol in deuterated acetone (Table 3) gives CH$_3$ and OH singlets at 2.29 and 7.4 ppm, respectively, along with ring CH doublets at 6.32 ppm (CH bound to carbonyl) and 7.95 ppm (CH bound to ring oxygen). The trend is similar in deuterated dimethyl sulphoxide except for the OH resonance, whose position depends on solvent and concentration. In deuterated chloroform the CH resonances undergo opposite shifts, *i.e.*, slightly downfield for the CH group bound to the carbonyl against *ca* 0.25 ppm upfield for the CH group bound to oxygen. The SnMa$_2$ spectrum in deuterated acetone (CH$_3$, 2.39 ppm; CH, 6.63 and 7.76 ppm) resembles that in deuterated chloroform,[10] whereas in dimethyl sulphoxide the CH

Table 2 Infrared bands in the 400–150 cm^{-1} region for the complexes.[a]

Compound	Wavenumber (cm^{-1})											
HMa					321m				215w			
KMa	382vvw				314m						195s	140s
$SnMa_2$			339m						221m	207w	194m	169wbr
$SnMa_2Cl_2$(A)	367s		343w	*324m*	308m	270m		241sh	228m	201w	192vw	155mbr
$SnMa_2Cl_2$(B)	367s		343w	*328m*	308m	265m			228m	200w	193sh	153mbr
$SnMa_2Cl_2$(C)	375m	361vw	341sh	*331vs*			244m	236sh	226sh	203w	182sh	173m
$SnMa_2Cl_2$(D)	375m	361vw	341sh	*331vs*			244m	236sh	226sh	203w	182sh	173m
$Sn(HMa)_4Cl_4 \cdot C_6H_6$	373m	350vw		*328vs*		258sh	244m	238m		205w	172m	166sh
$Ge(HMa)_4Cl_4 \cdot C_6H_6$	391m	351sh		*342vs*		285vw	271w	262sh	251sh	221m	206w	
$GeMa_2Cl_2$	398m	353sh		*341vs*	333sh	282vw	275vw	261vw	245vw	223m		
$Sn(DMP)_2Cl_2$			340m			*287s*	277sh		*253s*		201w	192sh
$Sn(DMP)_2Cl_4$	381w			*336s*	*324s*	288w		246m			203m	197sh
$Sn(DMTP)_2Cl_2$								*266m*	*230vs*			197w
$Sn(DMTP)_2Cl_4$			330m		*308s*	291s					206w	

[a] υ(M-halide) in italics.

Table 3 ^{1}H NMR data for ligands and complexes (ppm; *ca* 25°C).

Compound	Solvent	CH[a]	CH_3	other
HMa	$(CD_3)_2CO$	7.95, 6.32	2.29	7.40(OH)[b]
HMa	$CDCl_3$	7.69, 6.41	2.36	6.95(OH)[b]
HMa	$(CD_3)_2SO$	7.99, 6.31	2.22	8.80 (OH)[b]
$Sn(HMa)_4Cl_4$[c]	$(CD_3)_2CO$	8.34, 6.84	2.47	d
$Sn(HMa)_4Cl_4$[c]	CD_3OD	8.24, 6.74	2.48	d
$Sn(HMa)_4Cl_4$[e]	$(CD_3)_2SO$	8.01, 6.31	2.21	8.67(OH)[b]
$Ge(HMa)_4Cl_4 \cdot C_6H_6$	$(CD_3)_2CO$	8.54, 6.95	2.62	7.35(C_6H_6)[d]
		w 8.19, 6.68	2.45	
		vvw 8.80, 7.20	2.65	
$Ge(HMa)_4Cl_4 \cdot C_6H_6$[f]	$(CD_3)_2SO$	8.00, 6.31	2.22	9.70(OH)[b]
		w 8.65, 7.16	2.56	9.90(OH)[b]
$SnMa_2Cl_2$	$(CD_3)_2CO$	8.48, 6.94	2.60	
$SnMa_2Cl_2$	$(CD_3)_2SO$	8.65, 7.25	2.57	
$SnMa_2Cl_2$	$CDCl_3$	8.03, 6.79	2.65	
$GeMa_2Cl_2$	$(CD_3)_2CO$	8.55, 6.95	2.62	
$SnMa_2$	$(CD_3)_2CO$	7.76, 6.63	2.39	
$SnMa_2$	$(CD_3)_2SO$	8.21, 6.68	2.26	
DMP	$CDCl_3$	6.01	2.21	
$Sn(DMP)_2Cl_2$	$CDCl_3$	6.55	2.39	
$Sn(DMP)_2Cl_4$	$CDCl_3$	6.84	2.42	

[a] The downfield signal in maltol and complexes belongs to ring CH near the ring oxygen. [b] The signal position varies with concentration. [c] The spectrum is unchanged during one week. [d] The OH signal is not observed. [e] Within 2 min. from dissolution; after one day two further sets of signal are observed at 8.49, 7.08 and 2.44 ppm and 8.64, 7.23 and 2.51 ppm. [f] The weaker signal set is present at *ca* 40% within 3 min. from dissolution. After one day the intensity of this set decreases with parallel increase of a new set (8.90, 7.40 and 2.55 ppm).

(bound to oxygen) signal undergoes a noticeable downfield shift (*ca* 0.4 ppm). The nmr spectra of $SnMa_2Cl_2$ samples prepared by different methods are identical in solution. The related resonances, at 6.94 and 8.48 ppm (CH) and 2.60 ppm (CH_3) in deuterated acetone, appear downfield in dimethyl sulphoxide and upfield in chloroform, whereas the $GeMa_2Cl_2$ spectrum in acetone is analogous to that of the parent tin complex in the same solvent (6.95, 8.55 and 2.62 ppm). The main feature in the $Sn(HMa)_4Cl_4$ spectra in deuterated acetone or methanol is the absence of the OH proton signal in the 0–20 ppm range. The resonances of the other proton groups undergo a downfield shift with respect to the corresponding values for free HMa, more evidently for the CH protons (*ca* 0.4 ppm). No reaction seems to occur in solution, the spectra being unchanged during one week. Conversely, fast decomposition is observed in deuterated dimethyl sulphoxide. The $Sn(HMa)_4Cl_4$ spectrum in this solvent, recorded immediately after dissolution, is like that of free HMa, the OH proton resonance being evident at 8.67 ppm. The spectrum changes within a few minutes, two further sets of signal being observed at 8.49, 7.08 and 2.44 ppm (unknown species) and 8.64, 7.23 and 2.51 ppm (probably $SnMa_2Cl_2$). In this case the strongly coordinating solvent replaces HMa in the metal coordination sphere. The $Ge(HMa)_4Cl_4 \cdot C_6H_6$ adduct shows analogous behaviour, incipient decomposition being observed in deuterated acetone as well (Table 3). In order to identify the reaction products, $Sn(HMa)_4Cl_4$ samples were heated under reflux in benzene (2h). Under these conditions colourless solutions were obtained, and which were evaporated under nitrogen to small volume. No precipitation was observed at room temperature. Addition of *n*-pentane caused a white solid to separate and whose analytical, thermal and spectroscopic data are in accordance with the formula $SnMa_2Cl_2 \cdot 0.7HMa \cdot C_6H_6$ (Found: C, 44.1; H, 3.4; Cl, 11.7%. Calcd. for $C_{22.2}H_{20.2}Cl_2O_{8.1}Sn$: C, 44.0; H, 3.4; Cl, 11.7%). Thermograms of this compound show benzene evolution (103°C; weight loss 13% against calcd. 14.6%) followed by HMa released (13.9% against calcd. 14.6%) to form $SnMa_2Cl_2$ which melts at 284°C and then decomposes. The degradation trend above 290°C is similar to that shown in Figure 1. Accordingly, the nmr spectrum in deuterated acetone contains $SnMa_2Cl_2$ signals at 8.49, 6.94 and 2.60 ppm along with HMa signals at 7.92, 6.30 and 2.28 ppm and the benzene resonance at 7.35 ppm. The behaviour of $Sn(HMa)_4Cl_4$ on heating either in benzene or in the solid phase confirms $SnMa_2Cl_2$ as the degradation intermediate, other species such as $SnMaCl_3$ or $SnMa_3Cl$ being unfavoured. The stability of $Sn(HMa)_4Cl_4$ in methanol, in which $SnCl_4$ and HMa react easily to yield $SnMa_2Cl_2$, supports the presence of strong bonds in the 1:4 adduct, owing to cooperative carbonyl and hydrogen coordination.

DMTP complexes are insoluble in non coordinating solvents, whereas the DMP analogues dissolve easily in deuterated chloroform. The proton nmr spectrum of DMP in this solvent shows the methyl and ring CH proton resonances at 2.21 and 6.01 ppm, respectively. Both signals are observed downfield in the complexes, as expected for ligand coordination through the carbonyl group.

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