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SYNTHESIS AND SPECTROSCOPIC STUDIES OF ORGANOTIN DERIVATIVES OF 3-HYDROXYFLAVONE

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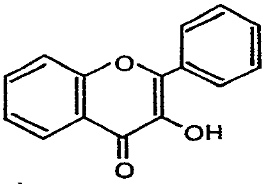
Summary

A series of air stable organotin derivatives of 3-hydroxyflavone (Hof), of general formula, R_3Snof, where R = Bu, Ph, cyclo-C_6H_{11} (Cy) or $PhMe_2CCH_2$ (Np), and $R_2Sn(of)_2$, where R = Me, Bu or Ph, has been synthesised by the reaction of the free ligand with the appropriate organotin hydroxide or oxide in boiling toluene. Two novel mixed ligand complexes, $Ph_2SnCl(of)$ and $MeSnCl(of)_2$, were also prepared.

The ^{119m}Sn Mössbauer, ^{119}Sn NMR and infrared spectra indicate that, in the solid state and in solution, these complexes contain penta- or hexa-coordinate tin atoms, with an intramolecularly coordinated carbonyl group from the 3-hydroxyflavone ligand. The fluorescence properties of the new complexes have also been investigated.

Introduction

The analytical reagent 3-hydroxyflavone (Hof; I) has been shown to form fluorescent complexes with both inorganic [1] and organic [2—6] tin compounds and these have been utilised for the spectrofluorimetric determination of sub-microgram quantities of these species. Although most organotins appear to form complexes with this reagent in solution, not all are fluorescent, e.g. in the R_3SnX series, only the trimethyl- and triphenyl-tin complexes exhibit flu-



(I)

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orescent properties [2,5], and none have been isolated in the solid state.

In order to investigate the factors influencing structure/fluorescence relationships in the organotin/3-hydroxyflavone system, a series of complexes of this reagent has been prepared and their structures studied by ^{119m}Sn Mössbauer, ^{119}Sn NMR and IR spectroscopy.

Experimental

Preparation of complexes

3-Hydroxyflavone was obtained from Eastman Kodak Ltd., and was used without further purification.

With the exception of $Ph_2SnCl(of)$ and $MeSnCl(of)_2$, the complexes were prepared by an azeotropic dehydration reaction between stoichiometric amounts of the appropriate organotin hydroxide or oxide and 3-hydroxyflavone in refluxing toluene, using a Dean and Stark trap. Reflux times were typically 1—2 h. After removal of the toluene, the crude products were recrystallised from the solvents shown in Table 1. $Me_2Sn(of)_2$ and $Ph_2Sn(of)_2$ crystallised out of the toluene solution on cooling and required no further purification. The triphenylstannyl derivative of dibenzoylmethane, $Ph_3Sn(bzbz)$, was prepared similarly, m.p. 137—140°C (lit. [7] 135—136°C).

$Ph_2SnCl(of)$ crystallised on mixing equimolar quantities of Ph_2SnCl_2 and 3-hydroxyflavone at room temperature in methanol and $MeSnCl(of)_2$ was precipitated when methanolic solutions of Bu_3Snof (2 moles) and $MeSnCl_3$ (1 mole) were mixed and then cooled.

The melting points and analytical data for the new complexes are shown in Table 1.

TABLE 1

ANALYTICAL DATA FOR THE ORGANOTIN COMPLEXES OF 3-HYDROXYFLAVONE

Complex	Analysis (Found (Calcd.) (%))			M.p. (°C)	Recrystallisation solvent
	C	H	Cl		
Ph_3Snof	57.46	4.25		202—205	[a]
	(67.46)	(4.09)			
Bu_3Snof	61.51	6.96		54— 55	[a]
	(61.51)	(6.83)			
Cy_3Snof	65.38	7.10		157—160	[a]
	(65.48)	(6.94)			
Np_3Snof	70.90	6.57		110—112	Isopropanol
	(71.52)	(6.36)			
$Ph_2Sn(of)_2$	67.68	4.05		204(dec.)	Toluene
	(67.45)	(3.90)			
$Bu_2Sn(of)_2$	64.61	5.19		178—180	Petroleum ether (B.p. 60—80°C)
	(64.49)	(5.09)			
$Me_2Sn(of)_2$	61.48	3.96		250(dec.)	Toluene
	(61.64)	(3.85)			
$Ph_2SnCl(of)$	59.64	3.54	6.41	192—195	Methanol
	(59.39)	(3.48)	(6.51)		
$MeSnCl(of)_2$	57.29	3.40	5.14	269(dec.)	Methanol
	(57.81)	(3.26)	(5.52)		

[a] Product obtained pure after removal of toluene.

Spectroscopic measurements

Infrared spectra were obtained as Nujol mulls or as solutions in toluene (using KBr discs or 0.1 mm NaCl windows) on a Grubb—Parsons Spectromaster Mark I instrument.

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A Ba^{119m}SnO$_3$ source was used at room temperature and samples were packed in perspex discs and cooled to 80 K, using a liquid nitrogen cryostat. The experimental error in the isomer shift, δ, and quadrupole splitting, ΔE_Q, parameters is ± 0.05 mm s^{-1} and the isomer shifts are quoted relative to SnO$_2$.

^{119}Sn NMR spectra were recorded at 298 K with a JEOL FX90Q instrument, using 10 mm tubes and an internal deuterium lock on approximately 10% internal deuteriotoluene or deuteriochloroform. Spectra were recorded under nuclear Overhauser suppressed conditions [8,9]. ^{119}Sn chemical shifts, $\delta(^{119}\mathrm{Sn})$, are quoted relative to Me$_4$Sn with an experimental error of ± 0.2 ppm.

Fluorescence emission spectra were recorded with a Perkin—Elmer Model 1000 fluorescence spectrophotometer, with suitable filters for the isolation of excitation wavelengths.

Results and discussion

The ^{119m}Sn Mössbauer parameters and the solid state antisymmetric carbonyl stretching frequencies, ν_{as}(CO), for the complexes are shown in Table 2, and the ^{119}Sn NMR chemical shifts and solution ν_{as}(CO) IR bands in Table 3.

The ΔE_Q values for the tributyl- and triphenyl-tin derivatives are consistent [17] with a tetrahedral tin atom geometry (IIa) or a pentacoordinate trigonal bipyramidal structure (IIb), with an intramolecularly coordinated carbonyl moiety. However, the reduced ν_{as}(CO) frequencies observed for these com-

TABLE 2

^{119m}Sn MÖSSBAUER PARAMETERS AND ANTISYMMETRIC CARBONYL STRETCHING FREQUENCIES FOR THE COMPLEXES

Complex	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	ν_{as}(CO) (cm^{-1})
Bu$_3$Snof	1.30	2.46	1574
Ph$_3$Snof	1.08	1.90	1550
Ph$_3$SnONPhCOPh	1.26 [a]	1.94 [a]	1540 [a]
Np$_3$Snof	1.34	2.59	1587
Cy$_3$Snof	1.36	2.81	1574
Ph$_2$SnCl(of)	1.10	2.61	1530
(Et$_4$N)$^+$(Ph$_2$SnCl$_3$)$^-$	1.25 [b]	2.62 [b]	—
Me$_2$Sn(of)$_2$	1.09	3.09	1548
Me$_2$Sn(ONMeCOMe)$_2$	1.16 [c]	3.06 [c]	1609 [c]
Bu$_2$Sn(of)$_2$	1.25	3.27	1550
Ph$_2$Sn(of)$_2$	0.77	1.75	1548
MeSnCl(of)$_2$	0.71	1.77	1550
BuSnCl(ox)$_2$	0.78 [d]	1.65 [d]	—

[a] Ref. 10. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13.

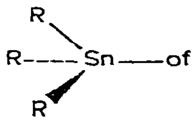
TABLE 3

^{119}Sn NMR CHEMICAL SHIFTS

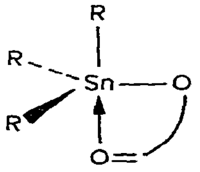
Complex	Solvent	Concentration (M)	$\delta(^{119}Sn)$ (ppm)
Ph_3Snof	Toluene	0.035 [a]	—149.8
$Ph_3Sn(bzbz)$	Toluene	0.025	—82.2
Np_3Snof	Toluene	0.06 [b]	51.4
Np_3SnOH	$CDCl_3$	<0.5	161 [c]
Cy_3Snof	Toluene	0.06	—27.4
Bu_3Snof	Toluene	0.09 [d]	70.6
Bu_3Snox	—	Neat liquid	29 [e]
$Ph_2SnCl(of)$	$CHCl_3$	0.06	—196.0
Ph_2SnCl_2	CH_2Cl_2	[f]	—32 [g]
$Ph_2Sn(of)_2$	$CHCl_3$	0.06	—340.7

[a] $\nu_{as}(CO)$ 1560 cm^{-1}. [b] $\nu_{as}(CO)$ 1587 cm^{-1}. [c] Ref. 14. [d] $\nu_{as}(CO)$ 1587 cm^{-1}. [e] Ref. 15. [f] Not quoted. [g] Ref. 16.

plexes (Table 2) are indicative of coordination to tin by the carbonyl group,



(IIa)

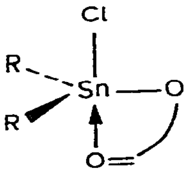


(IIb)

favouring structure IIb, cf. $Ph_3SnONPhCOPh$, which is known [18] by X-ray crystallography to adopt this stereochemistry and shows similar ΔE_Q and $\nu_{as}(CO)$ values to Ph_3Snof. Cy_3Snof and Np_3Snof show rather larger quadrupole splittings than are usually associated [17] with structure IIb, but their $\nu_{as}(CO)$ values are seen to be similar, both in the solid state and in solution (Tables 2 and 3), and therefore structure IIb is again favoured.

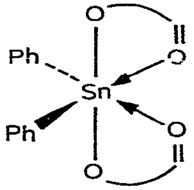
^{119}Sn NMR chemical shifts are also indicative of coordination number, pentacoordinate organotin compounds generally having a $\delta(^{119}Sn)$ value upfield of tetrahedral species [15]. $Ph_3Sn(bzbz)$ is known [7] to have the *cis*-R_3SnX_2 trigonal bipyramidal structure IIb and has a $\delta(^{119}Sn)$ value of —82 ppm and so the value of —149.8 recorded for Ph_3Snof in toluene is indicative of a similar geometry. The $\delta(^{119}Sn)$ value recorded for Np_3Snof (51.4 ppm) is approximately 110 ppm to high field of that for the 4 coordinate Np_3SnOH (161 ppm) and also implies a coordination number of 5. Unfortunately, however, data is not at present available for similar comparison for Cy_3Snof. The value of $\delta(^{119}Sn)$ of 70.5 ppm for Bu_3Snof is at an unusually low field for 5 coordinate organotin species, cf. Bu_3Snox, but other examples of low field ^{119}Sn chemical shifts for pentacoordinate organotin compounds with the geometry IIb are known, e.g. $Me_3SnOCH_2CH_2NMe_2$, $\delta(^{119}Sn)$ 92.1 ppm [19].

The ΔE_Q value observed for $Ph_2SnCl(of)$ is indicative [17] of a *cis*-R_2SnX_3 trigonal bipyramidal tin atom geometry (III, R = Ph), cf. $Ph_2SnCl_3^-$ (Table 2), with a chelating 3-hydroxyflavone ligand and, in solution, this compound

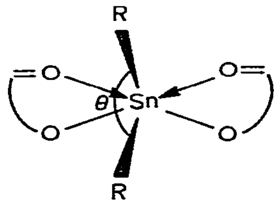


(III)

shows a $\delta(^{119}Sn)$ value which is ca. 160 ppm upfield from that of tetrahedral Ph_2SnCl_2, indicating that structure III is maintained. $Ph_2Sn(of)_2$ shows an even higher field tin chemical shift, indicative of 6-coordination (IV), the Mössbauer parameters revealing a *cis*-configuration of the aromatic groups [17]. In contrast, however, the two dialkyltin complexes of 3-hydroxyflavone contain distorted *trans*-octahedral tin atoms (V), as found [20] in $Me_2Sn(ONMeCOMe)_2$,



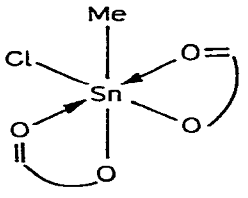
(IV)



(V)

and the approximate CSnC bond angle, θ, may be predicted [21] to be ~135° for $Me_2Sn(of)_2$.

The ΔE_Q and δ values for $MeSnCl(of)_2$ are very similar to those of $BuSnCl(ox)_2$, which has [22] an octahedral $RSnX_5$ configuration, and therefore structure VI is proposed.



(VI)

Of the organotin derivatives of 3-hydroxyflavone prepared, the only compounds found to be strongly fluorescent in toluene solution were Ph_3Snof (excitation wavelength 397 nm; emission wavelength 495 nm) and $Ph_2SnCl(of)$ (excitation wavelength 397 nm; emission wavelength 450 nm). Aldridge and Street [5] investigated the fluorescent properties of a number of triorganotins with 3-hydroxyflavone (in solution) and concluded that fluorescent complexes were produced only with the triphenyl- and trimethyl-tin derivatives. Our attempts to prepare the trimethyltin derivative of 3-hydroxyflavone were unsuccessful, although a 1/1 mixture of trimethyltin hydroxide and 3-hydroxyflavone in toluene, produced a yellow solution with a strong fluorescence emission at 510 nm. It was believed that the failure to isolate this complex was due to a disproportionation reaction, as has been noted for other trimethyltin complexes [7]:

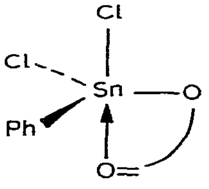
$2\ Me_3Snof \rightarrow Me_2Sn(of)_2 + Me_4Sn$

Evidence for this reaction was obtained from the chromatographic detection [23] of a dimethyltin species in the solid residue obtained from the preparative procedure.

The 6-coordinate diorganotin derivatives of 3-hydroxyflavone, along with $MeSnCl(of)_2$, were all found to display a weak fluorescence emission at 465 nm, (using a 397 nm excitation wavelength), the intensity of the emission being approximately 100 times less than that of Ph_3Snof or $Ph_2SnCl(of)$. Further evidence for the disproportion of the trimethyltin complex was therefore obtained, since, upon standing in solution for a few days, the 510 nm emission was no longer present, but, instead, a weak emission remained with a 465 nm maximum. Similar disproportionation reactions in solution were observed for the other triorganotin derivatives of 3-hydroxyflavone, by chromatographic detection [24] of the R_2SnX_2 species. The relative rates of these disproportionation reactions were found to be: $Me_3Sn > Bu_3Sn > Cy_3Sn \approx Np_3Sn > Ph_3Sn$.

In our earlier work on the fluorescent determination of triphenyltin compounds in water [2], it was noted that the fluorescence emission of a toluene solution of diphenyltin dichloride and 3-hydroxyflavone was quenched by shaking with saturated aqueous sodium acetate. It has been shown that the 6-coordinate $Ph_2Sn(of)_2$ exhibits only a very weak fluorescence and so the quenching of the diphenyltin species emission by sodium acetate might have been due to the formation of a similar 6-coordinate complex, e.g. $Ph_2SnOAc(of)$.

It was observed that a strongly fluorescent complex (maximum excitation wavelength 395 nm, maximum emission wavelength 450 nm), in solution, was produced by 1/1 mixtures of Bu_2SnCl_2, Me_2SnCl_2 or $PhSnCl_3$ with 3-hydroxyflavone in toluene. This effect has been reported previously for Me_2SnCl_2 [6] and $PhSnCl_3$ [2]. Although these complexes were not isolated in the solid state, it is likely that, since $Ph_2SnCl(of)$ has similar excitation and emission wavelengths, the strongly fluorescent di- and mono-organotin species are the pentacoordinate compounds, $R_2SnCl(of)$ (III, R = Me or Bu) and $PhSnCl_2(of)$ (VII).



(VII)

It therefore appears that strong fluorescence in the organotin complexes of 3-hydroxyflavone is associated with (a) pentacoordination at tin and (b) increasing Lewis acidity of the tin atom within a series of pentacoordinate complexes, R_3Snof.

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