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SHORT COMMUNICATION

Diorganotin(IV) Complexes of Some Schiff Bases with a Potential Biological Activity

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Diorganotin dichloride compounds, R_2SnCl_2 (R=Me, nBu, Ph) react with Schiff bases (L), derived from substituted and non-substituted 2- or 3-aminopyridine with 2-hydroxy-, 2-methoxy- or 2-hydroxy-3-methoxy-benzaldehyde in a 1 : 1 molar ratio, to give complexes of general formula $R_2SnCl_2 \cdot L$. It is suggested that the Schiff bases coordinate with tin in bidentate fashion to give hexacoordinate tin species. Almost all the complexes prepared show some 1 : 1 molar conductivity in ethanol and DMF, indicating an $[R_2Sn(L)Cl]^+ Cl^-$ ionic structure type. The complexes were screened against seven species of bacteria.

Keywords: diorganotin dichloride; Schiff bases; complexes; antibacterial

INTRODUCTION AND EXPERIMENTAL

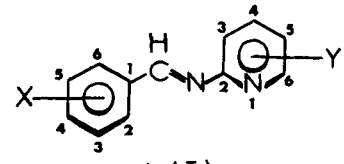
We described the preparation and properties of diorganotin(IV) complexes of some Schiff bases derived from hydroxy or methoxy aromatic aldehydes and 2- or 3-aminopyridine derivatives (Fig. 1), and examine their antibacterial activity.

Chemical and physical methods

The starting material Bu_2SnCl_2 is a commercial product, Me_2SnCl_2 and Ph_2SnCl_2 were prepared by standard methods. The Schiff bases (I_{1-5}–IV) were prepared in our laboratories[1] by refluxing equimolar quantities of 2- or 3-aminopyridine and the appropriate aldehyde for *ca* 1 h. The Schiff base thus formed was filtered off from cold solution and recrystallized from hot methanol.

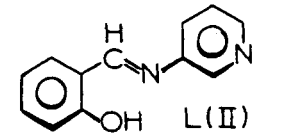
The complexes $R_2SnCl_2 \cdot L$ were prepared according to the following general procedure.

The diorganotin(IV) compound R_2SnCl_2 (R=Me, nBu, Ph; 1 mmol) was dissolved in the minimum amount of dry diethyl ether. To this solution was

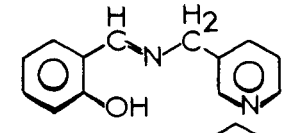


L(I)

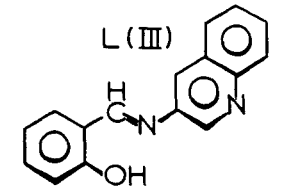
I1, X=2-OH, Y=H
I2, X=2-OCH_3, Y=H
I3, X=2-OH,3-OCH_3, Y=H
I4, X=2-OH, Y=3-CH_3
I5, X=2-OH, Y=4-CH_3



L(II)



L(III)



L(IV)

Figure 1 The Schiff bases used in the coordination with R_2SnCl_2 (R=Me, nBu, Ph).

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added a filtered solution of the ligands $\mathbf{I}_{1,3-5}$–**IV** (Fig. 1) (1.1 mmol) in the minimum amount of dry diethyl ether. The reaction mixture was stirred at room temperature for *ca* 30 min or under reflux for few minutes. The resulting solid thus formed was filtered off, recrystallized from ether and dried *in vacuo* for several hours. Yields were almost quantitative.

With the ligand $\mathbf{I}_2$ (Fig. 1), chloroform was used as a solvent instead of dimethyl ether because of the insolubility of this ligand in the ether. In the case of Bu_2SnCl_2 complexes of the ligands $\mathbf{I}_2$, $\mathbf{I}_4$ and **IV**, the products were oils and although numerous attempts were carried out to solidify them, they were unsuccessful.

The physical properties of the new complexes are summarized in Table 1. IR spectra were recorded on a Unicam SP2000 spectrometer in a range between 200 and 4000 cm^{-1}, using Nujol mulls and CsI discs. Conductivity measurements were done on 10^{-3} M solutions of the complexes at room temperature using a conductivity meter, model 4070 (Jenway). Elemental analyses of the complexes were carried out on a CHN analyser, type 1106 (Carlo Erba). They were satisfactory.

Biological methods

The bacterial species used are listed in Table 2. All strains were obtained from the Pasteur Institute (Paris). They were grown to the stationary phase in a nutrient broth at 37°C and a sample of 0.5 cm^3 of each bacterium was spread over a surface of a nutrient agar plate.[2]

For the antibacterial assay, discs of filter paper, 6 mm in diameter, were sterilized at 140 °C for 1 h and impregnated with 1 cm^3 of stock solution of 10 $\mu g/cm^{-3}$ of each tin complex and then dried. Dimethyl sulphoxide (DMSO) was used as a solvent for these complexes. Three separate sets of controls containing the tin complex, the solvent and the antibiotics (amoxicillin and chloramphenicol) were used.

The inoculated plates were incubated at 37 °C for 18 h and the inhibition zones were measured. In each experiment, the mean of each triplicate was measured.

Table 1 The new diorganotin(IV) complexes of Schiff bases

Complex	Colour	M.p. (°C)
$Me_2SnCl_2 \cdot \mathbf{I}_1$	Yellow	132–135
$Bu_2SnCl_2 \cdot \mathbf{I}_1$	Pale yellow	107–108
$Ph_2SnCl_2 \cdot \mathbf{I}_1$	Yellow–orange	148–149
$Me_2SnCl_2 \cdot \mathbf{I}_2$	Yellow	122–123
$Ph_2SnCl_2 \cdot \mathbf{I}_2$	Yellow–brown	118–120
$Me_2SnCl_2 \cdot \mathbf{I}_3$	Yellow	152–153
$Bu_2SnCl_2 \cdot \mathbf{I}_3$	Orange	117–118
$Ph_2SnCl_2 \cdot \mathbf{I}_3$	Orange	130–132
$Me_2SnCl_2 \cdot \mathbf{I}_4$	Yellow	146–148
$Ph_2SnCl_2 \cdot \mathbf{I}_4$	Pale yellow	152–153
$Me_2SnCl_2 \cdot \mathbf{I}_5$	Yellow	146–147
$Bu_2SnCl_2 \cdot \mathbf{I}_5$	Yellow	121–122
$Ph_2SnCl_2 \cdot \mathbf{I}_5$	Yellow	143–144
$Me_2SnCl_2 \cdot$ **II**	Yellow	143–145
$Bu_2SnCl_2 \cdot$ **II**	White	134–135
$Ph_2SnCl_2 \cdot$ **II**	Pale yellow	135–136
$Me_2SnCl_2 \cdot$ **III**	Yellow	146–147
$Bu_2SnCl_2 \cdot$ **III**	Yellow	85–86
$Ph_2SnCl_2 \cdot$ **III**	Yellow	187–188
$Me_2SnCl_2 \cdot$ **IV**	Yellow–orange	180–181
$Ph_2SnCl_2 \cdot$ **IV**	Yellow	137–139

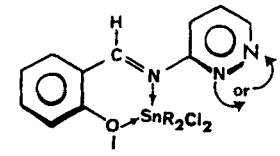

Figure 2 The structure suggested for R_2SnCl_2 complexes with the Schiff bases $\mathbf{I}_{1-5}$-**IV**.

RESULTS AND DISCUSSION

The complexes have a 1 : 1 molar ratio of organotin to ligand, i.e. $R_2SnCl_2 \cdot L$, where R=Me, nBu, Ph and L=Schiff bases $\mathbf{I}_{1-5}$–**IV** (Fig. 1) (elemental analyses).

The IR measurements showed that coordination of tin to the ligands had taken place. The IR bands in the regions 380–430 cm^{-1} and 315–375 cm^{-1} are tentatively assigned to $\nu(Sn-(N)_{im})$ and $\nu(Sn-O)$ respectively.[3–5] This is supported by the large decrease ($\Delta\nu = 20 - 60\,cm^{-1}$) of $\nu(C{=}N)_{im}$ on going from the free Schiff base to the complex.[6,7] The $\nu(Sn-(N)_{py})$ absorption appeared in the region 245–300 cm^{-1}, usually, as a very weak band. The $(C{=}N)_{py}$ stretching frequency of the free Schiff base is little affected upon coordination. These results suggest the structure shown in Fig. 2.

Other IR absorptions include a band in the region 265–300 cm^{-1} which is attributed to $\nu(Sn-Cl)$ modes, and others in the regions, 240–270 cm^{-1} and 510–550 cm^{-1} (usually as very weak bands)

Table 2 The antibacterial activity of (R_2SnCl_2· Schiffbase) complexes

Bacterium tested	Complexes/Concentrations (μg cm^{-3})																				Antibiotics/Concentrations (μg cm^{-3})								Control
	Me_2SnCl_2·I_1				Ph_2SnCl_2·I_2				Ph_2SnCl_2·I_3				Bu_2SnCl_2·II				Ph_2SnCl_2·IV				Amoxicillin				Chloramphenicol				(DMSO)
	10	1.0	0.1	0.01	10	1.0	0.1	0.01	10	1.0	0.1	0.01	10	1.0	0.1	0.01	10	1.0	0.1	0.01	10	1.0	0.1	0.01	10	1.0	0.1	0.01	All concns
	Diameter of inhibition zone (mm)																												
Staphylococcus aureus	10	8	7	—	20	15	15	10	20	17	14	11	12	11	9	—	23	18	15	12	30	25	13	—	20	14	6	2	—
Bacillus subtilis	12	9	6	—	14	11	10	7	14	10	8	—	18	13	9	—	14	10	8	—	18	14	9	—	19	12	2	—	—
Pseudomonas vulgaris	12	10	8	—	9	6	—	—	11	9	8	—	13	12	10	7	10	8	7	—	14	9	—	—	3	—	—	—	—
Klebsiella pneumonia	—	—	—	—	—	—	—	—	10	8	7	—	14	11	—	—	8	7	—	—	—	—	—	—	25	15	—	—	—
Pseudomonas aeruginosa	27	23	15	—	—	—	—	—	21	16	12	—	13	11	10	—	23	16	13	—	—	—	—	—	7	3	2	—	—
Salmonella typhimurium	—	—	—	—	10	10	7	—	13	10	8	—	15	12	8	—	13	11	8	—	—	—	—	—	—	—	—	—	—
Streptococcos flexneri	10	8	7	—	nt[a]	nt[a]	nt[a]	nt[a]	12	10	7	—	15	11	—	—	13	10	8	—	20	14	5	—	20	14	5	—	—

[a] nt, Not tested.

which are attributed to ν(Sn–C) modes for Sn–Ph and Sn–Me (or nBu) respectively.[8]

The molar conductivities of selected complexes measured in ethanol and dimethylformamide (DMF) for 10^{-3} M solutions at room temperature (e.g. 45 and 85 ohm^{-1} mol^{-1} cm^2 respectively) revealed in almost all cases that ionic structures with a 1 : 1 ratio of cation to anion are present in solution.[9] The suggested structure for such ionic cases is $[R_2SnLCl]^+Cl^-$, where L is the Schiff base, behaving as a bidentate ligand.

Antibacterial tests

From Table 2 it appears that the most promising compounds are Ph_2SnCl_2**·I₃**, Bu_2SnCl_2**·II** and Ph_2SnCl_2**·IV**, which showed quite similar activity to amoxicillin and chloramphenicol against *Staphylococcus aureus*, *Bacillus subtilis* and *Pseudomonas vulgaris* and significant activity against *Pseudomonas aeruginosa* and *Salmonella typhimurium* (inhibition zones 10–23 mm and 8–15 mm respectively) compared with amoxicillin and chloramphenicol, where no activity were obtained. Furthermore, the complex Ph_2SnCl_2**·I₂** displayed a significant role at concentrations of 0.01–10 μg cm^{-3} (inhibition zones 10–20 mm and 7–14 mm) in comparison with amoxicillin at concentrations of 0.1–10 μg cm^{-3} (inhibition zones 13–30 mm and 9–18 mm respectively) and chloramphenicol at concentrations of 0.1–10 μg cm^{-3} (inhibition zones 6–20 mm and 2–19 mm respectively) (no activity against *S. typhimurium*). Finally, the complex Me_2SnCl_2**·I₁** demonstrated good activity against *Staph. aureus*, *B. subtilis* and *P. vulgaris* at concentrations of 0.1–10 μg cm^{-3} (7–10 mm, 6–12 mm and 8–12 mm respectively) in comparison with the antibiotics and a remarkable activity against *P. aeruginosa* at concentrations of 0.1–10 μg cm^{-3} (inhibition zone 15–27 mm) whereas chloramphenicol showed weak activity against the same bacteria (inhibition zone 2–7 mm) and amoxicillin, and the control showed no inhibition zone.

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