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Synthesis and spectroscopic studies on organotin(IV) complexes of some pyrazoles and pyrazol-5-ones and their antibacterial activity

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A series of organotin(IV) complexes of the general formula $R_xSnCl_{4-x}.L$ (where R = Me, n − Bu, Ph; $x = 2$ or 3; L = pyrazole or pyrazol-5-one) have been prepared and characterized by elemental analyses, IR and NMR spectroscopy. The ligands used were found to coordinate with R_3SnCl species as monodentate ligands via the more reactive nitrogen atom, to give pentacoordinate tin complexes, whilst they may coordinate with R_2SnCl_2 species as bidentate ligands through the N–N linkage to give hexacoordinate tin complexes. These were demonstrated mainly by spectroscopic data. The tautomeric behaviour of organotin complexes of pyrazol-5-one ligands in inert ($CDCl_3$) and donor (DMSO-d_6) solvents were also studied. The complexes were screened against six species of bacteria.

Keywords: Organotin, pyrazole, pyrazol-5-one, complexes, antibacterial

INTRODUCTION

Over the past several years, we have been interested in the study of the coordination behaviour of substituted pyrazolines, pyrazoles and pyrazol-5-ones with several metals, e.g. platinum(II), palladium(II),[1,2] manganese(II), nickel(II), copper(II)[3] and UO_2^{2+},[4] in which the N–N linkage of the ligand may be used in forming complexes with the metals. It was recently reported[5] that bis- and tris-pyrazolyl and analogous ligands coordinate similarly, as bidentate ligands, with diorgantin(IV) dichloride compounds to form complexes with hexacoordinate tin species. On the other hand, a wide range of biological properties were found[6–10] to be associated with some metal complexes of analogous pyrazole ligands including antibacterial and antitumour activities.

In view of this, and as a continuation of our interest in studying the interaction between nitrogenous ligands and various metals, we describe in the present work the preparation and properties of complexes derived from the organotin(IV) compounds R_xSnCl_{4-x} and some selected pyrazoles and pyrazol-5-ones, together with the tautomeric behaviour of the pyrazol-5-one complexes in both inert and donor solvents, as well as the antibacterial activity of some of these complexes.

EXPERIMENTAL

General

^1H NMR spectra were recorded on a Bruker-WH 90 DS spectrometer, using the deuterium signal of the solvent ($CDCl_3$ or DMSO-d_6) as a field signal.

IR spectra were recorded on an SP 2000 spectrometer in the range 200–4000 cm^{-1} using Nujol mull.

Analyses of the complexes were carried out using a CHN Analyser, Type 1106 (Carlo Erba).

Preparation of starting materials

The organotin compounds Ph_3SnCl, $(n\text{-}Bu)_3SnCl$ and $(n\text{-}Bu)_2SnCl_2$ are commercial products (Fluka) and were used without further purification. The compounds Me_3SnCl, Ph_2SnCl_2 and Me_2SnCl_2 were prepared by standard methods.[11,12]

The ligands (pyrazoles and pyrazol-5-ones) were prepared as described in the literature.[13–17]

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The structures of the ligands were established by NMR.

Preparation of complexes $R_xSnCl_{4-x}.L$

The complexes were prepared according to the following standard method which is outlined in general format.

The organotin(IV) compound R_xSnCl_{4-x} (R = Me, n-Bu, Ph; $x = 2$ or 3) (1 mmol) was dissolved in a minimum amount of dry chloroform, then added to a solution of the pyrazole ligand (L), prepared by dissolving the ligand (1 mmol) in a minimum amount of chloroform at ambient temperature or if necessary under moderate heating. The resulting solution was evaporated to *ca* 1/4 of its original volume. Petroleum spirit boiling range (40–60 °C) was added to the point of turbidity. The crystalline product thus formed was filtered off, washed several times with the same spirit and dried under vacuum for several hours. The yield was almost quantitative. Melting points were sharp and elemental analyses were used for characterization.

Biological tests

The six species of bacteria, *Escherichia coli*, *Salmonella agona*, *Salmonella emek*, *Salmonella Copenhagen*, *Pseudomonas aeruginosa* and *Streptococcus viridans*, used in this work were supplied from the Bacteriology Laboratories, Biology Department, College of Science, University of Mosul, Iraq. Nutrient agar and nutrient broth (Biomireux) were used for the growth of these bacteria. A solution of 100 μg cm^{-3} of the organotion(IV) complex in chloroform was used against a constant bacterial count of 10^4 cm^{-3}. For a minimum inhibitory concentration (MIC) test, various concentrations of the organotin(IV) complex(10, 20 . . . 100 μg cm^{-3}) in chloroform were used against the same bacterial count (10^4 cm^{-3}).

RESULTS AND DISCUSSION

Organotin(IV) complexes $R_xSnCl_{4-x}.L$ were prepared as described above. The physical properties of these complexes are listed in Table 1 and their ^1H NMR spectral data are listed in Table 2. The elemental composition of the complexes prepared is clearly assigned to a 1:1 ratio of organotin compound to ligand, i.e. $R_xSnCl_{4-x}.L$.

IR spectra

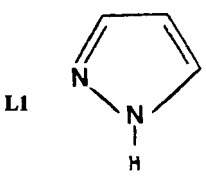
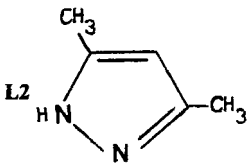
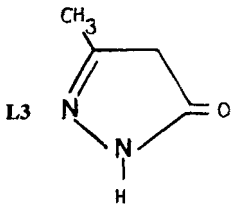
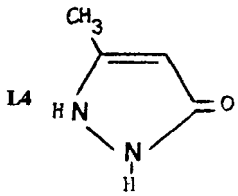
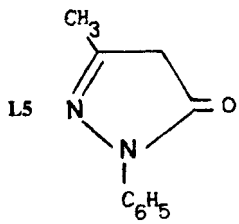
An IR spectral band which for the complexes in general appeared in the region 320–460 cm^{-1}, is tentatively assigned to ν(Sn—N) modes.[5] The band appearing in the region 250–340 cm^{-1} is attributed to ν(Sn—Cl) modes, while the ones appearing in the regions 220–270 cm^{-1} and 540–560 cm^{-1} are attributed to ν(Sn—C) modes for Sn—Ph and Sn—Me (or n-Bu), respectively.[18] Another band, which was broad, appearing in the region 1480–1615 cm^{-1} was characterized as ν(C—N), which overlapped, in most cases, with ν(C—C). The absorption band attributable to ν(C—O) for the pyrazol-5-one complexes in their solid states was observed as a weak band in the region 1650–1700 cm^{-1}. The ν(N—H) usually appeared as a very broad band but in most cases was not observed.

^1H NMR

It was reported by Visalakshi *et al.*[5] that $^2J(^{119}Sn-^1H)$ values for Me_2SnCl_2–NN complexes vary from 69–78 in $CDCl_3$ for hexacoordinate tin complexes. The reported $^2J(^{119}Sn-^1H)$ value for tetracoordinate Me_2SnCl_2 (uncomplexed) in $CDCl_3$ is ca 70 Hz[19,20] and for hexa-coordinated compounds, e.g. $Me_2SnCl_2.2DMSO$, is equal to *ca* 115 Hz.[21] In our present work, we have found that the value for $^2J(^{119}Sn-^1H)$ is equal to 83–92 Hz ($CDCl_3$) and *ca* 116 Hz (DMSO-d_6); this value is reasonable for hexacoordinate tin.[21–23] However, we could not account for the $^2J(^{119}Sn-^1H)$ values suggested by Visalakshi *et al.* (69–78 Hz) for hexacoordinate tin species.

It is well known that R_3SnCl compounds can coordinate with various donor ligands to give penta-coordinate tin species and this may well be correlated with $^2J(^{119}Sn-^1H)$ values or $^1J(^{119}Sn-^{13}C)$ in ^{13}C NMR.[19] Our reactions of Me_3SnCl and $(n\text{-}Bu)_3SnCl$ with the ligands used were unsuccessful; even $(n\text{-}Bu)_2SnCl_2$ did not react with all the ligands used, apart from the simple pyrazole, i.e. **L1** (Table 1), and this may be explained on the basis of electronegativity considerations and/or steric factors of the bulky butyl group. Therefore, we were unable to examine the coordination number of tin in Me_3SnCl complexes by measuring $^2J(^{119}Sn-^1H)$ values.

Table 1 Physical properties and analyses for some organotin complexes $R_xSnCl_{4-x}.L$

Ligand, L	Complex	Colour	M.p. (°C)	Analysis (%): Found (Calc.) C	H	N	IR data[a] (cm^{-1}) ν(Sn—Cl)	ν(Sn—N)	ν(Sn—C)	ν(C=N) + ν(C=C)
 L1	$Ph_3SnCl.L1$	Off-white	74–75	54.9 (55.6)	4.2 (4.2)	6.15 (6.2)	280s	450s	250s	1580w,b
	$Ph_2SnCl_2.L1$	White	116–118	44.0 (43.7)	3.5 (3.4)	7.0 (6.8)	330s	430m	220m	1578m,b
	$Bu_2SnCl_2.L1$	Off-white	70–72	35.1 (35.5)	6.0 (5.9)	7.8 (7.5)	315m	410w	510m	1570m,b
	$Me_2SnCl_2.L1$	Yellow	130	21.0 (20.9)	3.45 (3.5)	10.0 (9.7)	285m	390w	650m	1510m
 L2	$Ph_2SnCl.L2$	Pale yellow	84–88	56.9 (57.4)	4.55 (4.8)	5.7 (5.8)	310s	420s	250s	1540w,b
	$Ph_2SnCl_2.L2$	Off-white	118–122	45.9 (46.4)	4.3 (4.1)	6.3 (6.4)	280m	420m	220m	1550, 1600m,b
	$Me_2SnCl_2.L2$	White	96	26.4 (26.6)	4.4 (4.4)	8.8 (8.9)	270m	420m	550m	1570m,b
 L3	$Ph_3SnCl.L3$	Yellow	162–166	54.3 (54.6)	4.4 (4.35)	5.9 (5.8)	320s	450s	270s	1615w,b
	$Ph_2SnCl_2.L3$	Pale orange	134–136	43.0 (43.5)	3.8 (3.6)	6.8 (6.35)	320m	440m	225m	1570s,b
	$Me_2SnCl_2.L3$	Pale orange	166–168	23.0 (22.7)	3.7 (3.8)	9.0 (8.8)	280s	330m	520m	1570m,b
 L4	$Ph_3SnCl.L4$	White	120	54.35 (54.6)	4.55 (4.35)	6.0 (5.8)	333s	455m	245s	1590m,sh
	$Ph_2SnCl_2.L4$	Pale orange	110–112	43.3 (43.5)	3.8 (3.6)	6.6 (6.3)	320s	415m	260m	1605s,b
	$Me_2SnCl_2.L4$	Pale pink	188–190	23.0 (22.7)	3.5 (3.8)	9.1 (8.8)	320s	390w	510m	1570s,b
 L5	$Ph_3SnCl.L5$	Pale pink	120	54.35 (54.65)	4.6 (4.35)	6.0 (5.8)	295m	465s	233w	1560, 1585s,b
	$Ph_2SnCl_2.L5$	Orange	92–93	50.9 (51.0)	3.9 (3.9)	5.35 (5.4)	340m	460s	250w	1560, 1590m,b
	$Me_2SnCl_2.L5$	Dirty white	120–122	36.5 (36.6)	4.1 (4.05)	7.1 (7.1)	300m	330w	450w	1530, 1585m

[a] IR spectra recorded with Nujol mull: s, strong; m, medium; w, weak; b, broad; sh, shoulder.

Tautomeric behaviour of complexes

The ^1H NMR spectral data for the complexes were recorded in $CDCl_3$ as inert solvent and in DMSO-d_6 as donor solvent in an attempt to study the solvent effects and tautomeric behaviour, particularly of pyrazol-5-one complexes of organotin(IV) compounds.

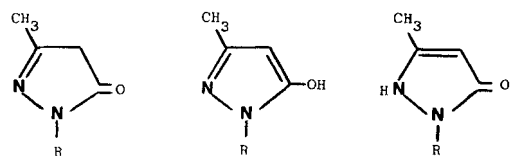
It is known that free pyrazol-5-ones can exist in solution in the three tautomeric forms **I**, **II** and **III**[24] shown in Fig. 1.

We found that the change of solvent on going from $CDCl_3$ to DMSO-d_6 had no significant effect on the ^1H NMR spectral data of the complexes of the ligands **L1** and **L2** (Table 2). The complexes of the ligands **L3** and **L4** (Table 2) were found to be insoluble in $CDCl_3$, so DMSO-d_6 was used in this case; the ^1H NMR spectrum of the **L3** and **L4**

Table 2 Proton NMR data[a] for the organotin complexes $R_xSnCl_{4-x}.L$

Ligand/Complex	Solvent	δ(Sn–R) (ppm) [$^2J(^{119}Sn-^1H)$ (Hz)]	Ligand protons and assignments[b]
L1	$CDCl_3$		7.5 (2CH), 7.7 (CH)
$Ph_3SnCl.L1$	$CDCl_3$	7.23–8.3m (Ph)	Y (2CH), 6.57 (CH)
$Ph_2SnCl_2.L1$	$CDCl_3$	7.0–8.0m (Ph)	Y (2CH), 6.53 (CH)
$Bu_2SnCl_2.L1$	$CDCl_3$	0.72–2.37m (Bu)	7.85 (2CH), 5.64 (CH), 10.0 (NH)
	DMSO-d_6	0.77–2.0m (Bu)	7.63 (2CH), 6.33 (CH), 10.36 (NH)
$Me_2SnCl_2.L1$	$CDCl_3$	1.28 (Me) [92]	7.86 (2CH), 6.60 (CH), 10.3b (NH)
L2	$CDCl_3$		2.60 (CH_3), 6.15 (CH), 13.0 (NH)
	DMSO-d_6		2.35 (CH_3), 6.25 (CH), Z
$Ph_3SnCl.L2$	DMSO-d_6	7.3–8.0m (Ph)	2.13 (CH_3), 5.78 (CH), Z
$Ph_2SnCl_2.L2$	DMSO-d_6	7.4–8.0m (Ph)	2.10 (CH_3), 5.80 (CH), Z
$Me_2SnCl_2.L2$	$CDCl_3$	1.20 (Me) [82.8]	2.3 (CH_3), 6.0 (CH), 11.5 (NH)
	DMSO-d_6	1.04 (Me) [115.5]	2.13 (CH_3), 5.74 (CH), Z
L3[c]	DMSO-d_6		2.18 (CH_3), 5.45 (CH), 9.0 (NH)
$Ph_3SnCl.L3$[c]	DMSO-d_6	7.3–8.0m (Ph)	2.07 (CH_3), 5.26 (CH), Z
$Ph_2SnCl_2.L3$[c]	DMSO-d_6	7.2–8.0m (Ph)	2.11 (CH_3), 5.22 (CH), Z
$Me_2SnCl_2.L3$[c]	DMSO-d_6	1.07 (Me) [116.5]	2.13 (CH_3), 5.24 (CH), 3.4b (OH)
L4	DMSO-d_6		2.13 (CH_3), 5.36 (CH), 9.0 (2NH)
$Ph_3SnCl.L4$	DMSO-d_6	7.33–8.0m (Ph)	2.07 (CH_3), 5.28 (CH), Z
$Ph_2SnCl_2.L4$	DMSO-d_6	7.32–8.0m (Ph)	2.09 (CH_3), 5.32 (CH), Z
$Me_2SnCl_2.L4$	DMSO-d_6	1.0 (Me) [114.5]	2.07 (CH_3), 5.27 (CH), 10.2vb (NH)
L5	DMSO-d_6		2.27 (CH_3), 5.82 (CH), 7.5–8.0m (Ph)
	$CDCl_3$		2.35 (CH_3), 3.45 (CH_2), 7.2–7.8m (Ph)
$Ph_3SnCl.L5$	$CDCl_3$	7.18–8.0m (Ph)	2.23 (CH_3), 3.5 (CH_2), 7.18–8.0m (Ph)
	DMSO-d_6	7.1–8.2m (Ph)	2.14 (CH_3), 3.68 (CH_2), 5.41 (CH), 7.1–8.2m (Ph), 11.5b (NH), 3.4 (OH)
$Ph_2SnCl_2.L5$	$CDCl_3$	7.25–8.0m (Ph)	2.23 (CH_3), 3.50 (CH_2), 7.25–8.0m (Ph)
	DMSO-d_6	7.20–8.0m (Ph)	2.13 (CH_3), 3.65 (CH_2), 5.43 (CH), 7.2–8.0 (Ph)
$Me_2SnCl_2.L5$	$CDCl_3$	1.23 (Me) [92]	2.23 (CH_3), 3.48 (CH_2), 7.14–8.0m (Ph)
	DMSO-d_6	1.07 (Me) [115]	2.14 (CH_3), 3.63 (CH_2), 5.41 (CH), 7.23–8.0m(Ph)

[a] Downfield from internal TMS at room temperature: m, multiplet; b, broad; vb, very broad signals. [b] Abbreviations: Y, signals not observed (overlapped with Ph signals); Z, signals obscured. [c] **L3** present as **L4** in DMSO-d_6.



(I) (II) (III)

Figure 1 Tautomers of free pyrazol-5-ones (R = H, Ph).

complexes revealed the presence of signals attributed to the resonance of CH_3 and CH protons only and no signals for CH_2 protons. Therefore the stable form for the **L3** and **L4** complexes in DMSO-d_6 is that of the latter (**L4**) complex (Table 2), i.e. the **L3** complex is not stable in DMSO (**L3** in $CDCl_3$ has signals at $\delta = 3.5$ ppm for CH_2 protons while **L4** does not have such signals):

$$R_xSnCl_{4-x}.L3 \xrightarrow{DMSO} R_xSnCl_{4-x}.L4 \qquad [1]$$

The $R_xSnCl_{4-x}.L4$ formula may be present in either of the two tautomeric forms (**II**) and (**III**), or both may be present in solution. In DMSO – d_6 only $R_xSnCl_{4-x}.L4$ is present.

In order to study this point in more detail, the soluble complexes of pyrazol-5-ones (**L5**) in $CDCl_3$ were chosen. In $CDCl_3$, the ^1H NMR spectrum for these complexes revealed the presence of only one tautomeric from (**I**, in 100% proportion), and this is clear from the observed resonance of the CH_2 protons of the ring ($\delta = 3.5$ ppm) with no sign of any CH protons. On using DMSO-d_6, the case is different from that for the **L3** and **L4** complexes. The spectrum of the complex $Me_2SnCl_2.L5$ revealed the presence of probably both tautomeric forms (**I** and **III**) with resonance of CH_2 protons (form **I**) ($\delta = 3.63$ ppm, in 25% proportion) and CH proton resonance (form **II** or/and form **III**) ($\delta = 5.41$ ppm, in 75% proportion) also observed. Similarly for the phe-

Table 3 The growth of bacteria at constant concentration (100 μg cm^{-3}) of organotin(IV) complexes[a]

Complex	*E. coli*	*S. agona*	*S. emek*	*S. Copenhagen*	*P. aeruginosa*	*Strept. viridans*
Ph_3SnCl.**L1** –	–	–	–	–	+	–
Ph_2SnCl_2.**L1**	+	+	±	+	+	–
Me_2SnCl_2.**L1**	+	+	+	+	+	±
Me_2SnCl_2.**L2**	–	–	–	–	–	–
Ph_3SnCl.**L3**	+	–	–	+	+	±
Ph_2SnCl_2.**L3**	+	+	+	+	+	–
Ph_3SnCl.**L4**	–	–	–	–	+	–
Me_2SnCl_2.**L4**	+	+	+	+	+	+
Ph_3SnCl.**L5**	±	–	–	–	–	–

[a] Symbols: +, growth; –, decline; ±, no change.

nyltin complex, Ph_3SnCl.**L5** in DMSO-d_6, the spectrum again showed signals for CH_2 protons (form **I**) ($\delta = 3.68$ ppm, in 35% proportion) and for CH proton (form **II** or/and **III**) ($\delta = 5.41$ ppm, in 65% proportion). Some broad signals attributed to NH and OH protons were also observed, but in some cases these were obscured by the noise.

In order to check whether the tautomerisms are time-dependent, an *in situ* experiment was carried out by recording the ^{1}H NMR spectra of Ph_3SnCl.**L5** in DMSO-d_6 soon after dissolving the solid and then after 10-minute intervals. However, the spectrum recorded after *ca* 3 h showed that there is no significant difference from that recorded immediately, and again this means that the three tautomeric forms (**I–III**) may present in equilibrium. Moreover, it is rather difficulty to distinguish precisely between the two tautomeric forms **II** and **III** using ^{1}H NMR, since their signals are very close to each other.

Contrary to the spectra of the **L5** complexes in DMSO-d_6, the spectrum of the free ligand (**L5**) in DMSO-d_6 revealed the presence of the **II** or/and **III** signals only, with no signal for form **I** (Table 2).

Antibacterial tests

The antibacterial activities of some selected organotin(IV) complexes against the six species of bacteria, *E. coli, S. agona, S. emek, S. Copenhagen, P. aeruginosa* and *Strept. viridans* are summarized in Table 3. These species of bacteria were chosen since they are known as pathogens for human beings. From the data obtained, it is evident that some of these complexes exhibited a good activity against the tested species of bacteria with the concentration used (100 μg cm^{-3}), but especially significant is the complex Me_2SnCl_2.**L2**, which showed the highest activity among the complexes.

A Minimum Inhibitory Concentration (MIC) test for this complex was therefore carried out using concentrations of 10–100 μg cm^{-3} and the collected data are listed in Table 4. As a conclusion, the preliminary *in vitro* studies of the complex Me_2SnCl_2.**L2** are promising since it exhibited activity against all species of bacteria tested in the applied concentrations, especially *P. aeruginosa*. The latter is the most resistant of the bacteria used in this study and exhibited resistance to different antimicrobial drugs.[25] Further studies

Table 4 The growth of bacteria at different concentrations of the complex Me_2SnCl_2.**L2**

Bacteria tested (10^4 cm^{-3})	Concentration (μg cm^{-3})									
	10	20	30	40	50	60	70	80	90	100
E. coli	+	+	+	–	–	–	–	–	–	–
S. agona	+	+	+	–	–	–	–	–	–	–
S. emek	+	–	–	–	–	–	–	–	–	–
S. Copenhagen	+	+	–	–	–	–	–	–	–	–
P. aeruginosa	+	–	–	–	–	–	–	–	–	–
Strept. viridans	–	–	–	–	–	–	–	–	–	–

concerning other tests for these complexes are in progress.

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