APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 79-84 (1993)

Organometallic complexes with biological molecules. I. Diorganotin(IV)chloro protoporphyrin IX complexes: solid-state and solution-phase characterization

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Protoporphyrin IX (H_4PPIX) complexes of diorganotin(IV)chloro moieties with formula $(R_2SnCl)_2H_2PPIX$ (R = Me, Bu and Ph) have been obtained and their solid-state and solution-phase configurations have been studied through spectroscopic investigations.

Coordination of the side-chain carboxylates of H_4PPIX to $R_2Sn(IV)Cl$ moieties, with bridging carboxylate (COO^-) has been inferred by comparison of the free and coordinated H_4PPIX IR spectra, while the occurrence of a five-coordinated tin(IV) atom in a *cis*-R_2 trigonal bipyramidal structure has been deduced, for all of the synthesized complexes, by rationalization of the nuclear quadrupole splitting parameters, according to the point-charge model formalism. Finally, the solution-phase spectral features of $(R_2SnCl)_2$-H_2PPIX are in agreement with the monomeric character of the protoporphyrin IX, under the experimental conditions used.

Keywords: Organotin, protoporphyrin IX, structures, Mössbauer, infrared, UV-visible fluorescence, nuclear quadrupole splitting

INTRODUCTION

Researches on porphyrins[1,2] and on metal porphyrin derivatives have been widely developed recently.[3-25] Their use as photosensitizers in the photodynamic therapy of tumours and other diseases has been reported by Jori *et al.*[1,2] Owing to their noteworthy intercalating activity, metal porphyrins complexes have been widely studied both in the solid state and in the solution phase, through the use of numerous different techniques.[3-25]

Pasternack *et al.* claimed that several different types of complexes can exist between nucleic acids and metal porphyrins, so that by a 'judicious choice of metal derivatives, drugs showing a high degree of specificity are obtained.'[26]

On the other hand, the cytotoxicity of organotin(IV) derivatives has been well documented in several papers.[27-35] Studies on their antileukemic activity[28,29] as well as on ascidian embryonic development[30,31] and on spermatocyte chromosome alternations in *Truncatella subcilindrica (L., 1767)*[32] have been recently performed in attempts to deduce a structure–cytotoxic activity relationship for organotin(IV) complexes.

This paper deals with the synthesis and the characterization of several new diorganotin(IV)chloro protoporphyrin IX complexes, both in the solid state and in solution phase.

EXPERIMENTAL

$(R_2SnCl)_2H_2PPIX$ species were obtained as white solids by refluxing methanolic solutions of R_2SnCl_2 (gifts from Shering AG, Bergkamen, Germany) with methanolic suspensions of the disodium salt of protoporphyrin IX (a Sigma product) in the molar ratio 2:1. $SnCl_2H_2PPIX$ was synthesized according to the method described by O'Rourke and Curran.[36] The solids, recovered by filtration, were recrystallized and analysed for C, H, N, Sn and Cl contents (Table 1). C, H and N analyses were performed at Laboratorio di Chimica Organica (University of Milano). Sn and Cl contents were determined in our laboratory according to standard methods.[37,38]

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0268-2605/93/020079-06 $08.00

Received 20 May 1992
Accepted 1 September 1992

Table 1 Analytical data [Found (calcd) (%) for diorganotin(IV)chloro derivatives of protoporphyrin IX

Compound	C	H	N	Cl	Sn
$(Me_2SnCl)_2H_2PPIX$	50.83	4.78	6.45	7.29	25.84
	(50.12)	(4.73)	(6.03)	(7.63)	(25.56)
$(Bu_2SnCl)_2H_2PPIX$	54.75	6.21	5.78	9.31	21.40
	(54.72)	(6.24)	(5.10)	(9.46)	(21.64)
$(Ph_2SnCl)_2H_2PPIX$	59.83	4.46	4.68	6.48	20.06
	(59.17)	(4.45)	(4.76)	(6.02)	(20.16)
$SnCl_2H_2PPIX$	54.30	4.32	7.40	9.80	16.02
	(54.42)	(4.29)	(7.46)	(9.45)	(15.82)

IR spectra were recorded, as Nujol and hexachlorobutadiene mulls, on a Perkin–Elmer grating spectrometer model 983G, between CsI windows. The spectra were analysed in a Perkin–Elmer 3600 data station with Perkin–Elmer PE983 software (Table 2).

Mössbauer spectra (Table 3) were obtained with the apparatus described in a previous publication.[39]

The UV–visible spectra were measured with a Lambda 5 Perkin–Elmer spectrophotometer while the fluorimetric measurements were carried out using an L50 Perkin–Elmer spectrofluorimeter. In this latter case measurements were carried out with optical density lower than 0.1 in order to avoid inner-filter effects and with the ratio mode to avoid effects arising from light source fluctuations (Table 4).

RESULTS AND DISCUSSION

Solid-state investigations

Protoporphyrin IX (Fig. 1) can be regarded as a tetraprotic acid and as a potentially multidentate ligand. Coordination sites for protoporphyrin IX, as for porphyrins generally, can be the nitrogen atoms of the tetrapyrrolic ring. In such a case, deprotonation of the two imino groups takes place with metallation in the equatorial plane or with axial coordination.[4] However, there are also further coordination sites, owing to the occurrence of the two side-chain carboxylic groups.

For comparison purposes, IR spectra of the protoporphyrin IX (H_4PPIX), of the disodium salt (Na_2H_2PPIX), of the dimethyl ester [$(CH_3)_2H_2PPIX$], of $SnCl_2H_2PPIX$ and, finally, of the diorganotin(IV)chloro complexes [$(R_2SnCl)_2$-H_2PPIX], were taken. The $SnCl_2H_2PPIX$ IR spectrum was taken since it has been reported that in $SnCl_2TPP$ (H_2TPP = *meso*-tetraphenylporphyrin) the four nitrogen atoms of the porphyrin macrocycle coordinate tin(IV) atom in a distorted octahedral configuration.[4] $\Delta E = 0.91$ refers to $SnCl_2H_2PPIX$. Distortion for $SnCl_2TPP$ has been evidenced by X ray as reported in references in 4. The more relevant absorption bands, from which the protoporphyrin IX coordination mode towards the organometallic moieties can be extracted, are reported in Table 2. In fact the occurrence, in all the diorganotin(IV)chloro-protoporphyrin IX complexes (Table 2), of medium bands at 3312 cm^{-1} attributable to a

Table 2 Proposed assignment of more relevant absorption bands of the free and coordinated ligand in the 4000–250 cm^{-1} region[a]

Compound	ν (NH)	ν (COO) in COOH	ν_{as} (COO)	ν_s (COO)	ν_{as} (SnC_2)	ν_s (SnC_2)	$\nu_s + \nu_{as}$ (SnC_2I)	$\nu_s + \nu_{as}$ (SnC_2II)	Sn–Ph	ν (SnCl)	Δν
H_4PPIX	3310m	1692s									
Na_2H_2PPIX	3309m		1562s	1420s							142
$(CH_3O)_2H_2PPIX$	3314m	1731s		1405m							326
$(Me_2SnCl)_2H_2PPIX$	3312m		1590s	1410m	585m	520w				325s	180
$(Bu_2SnCl)_2H_2PPIX$	3313m		1600s	1405m			651m	515w		280s	195
$(Ph_2SnCl)_2H_2PPIX$	3312m		1602s	1409m					450s	295s	193
$SnCl_2H_2PPIX$		1711s								278m	

[a] Nujol and hexachlorobutadiene nulls: s = strong, m = medium, w = weak, v = very, bd = broad.

Table 3 Experimental Mössbauer parameters, isomer shift, δ mm s^{-1}, and nuclear quadrupole splittings $|\Delta E|_{exp}$ mm s^{-1}, measured at liquid-N_2 temperature, and Nuclear Quadrupole Splittings calculated according to the point-charge formalism applied to the idealized structures of Fig. 3

Compound[a]	δ	$\lvert\Delta E_{exp}\rvert$	Γ_1	Γ_2	ΔE_{calcd}	η_{calcd}	ϕ
$(Me_2SnCl)_2H_2PPIX$	1.34	3.18	0.93	0.94	3.25	0.33	125
$(Bu_2SnCl)_2H_2PPIX$	1.42	3.29	0.94	1.02	3.25	0.33	128
$(Ph_2SnCl)_2H_2PPIX$	1.07	2.53	0.96	0.98	2.86	0.30	118
$SnCl_2H_2PPIX$	0.23	0.91	0.83	0.86	1.18	0.53	—

[a] Sample thickness ranged between 0.50 and 0.60 mg ^{119}Sn cm^{-2}; isomer shift, $\delta \pm 0.03$ mm s^{-1} with respect to $BaSnO_3$ RT; Γ_1 and Γ_2 values are the full width at half-height of the resonant peaks at greater and lower velocity, respectively, with respect to the centre of the Mössbauer spectra; nuclear quadrupole splittings, $\Delta E \pm 0.02$ mm s^{-1}; the partial quadrupole splittings (pqs mm s^{-1}) values used for theoretical ΔE are discussed in the text; $\eta = (|V_{XX}| - |V_{YY}|)/V_{ZZ}$ is the asymmetry parameter;[50] ϕ is the C–Sn–C angle evaluated according to Parish.[49]

Table 4 Experimental spectroscopic parameters of the free protoporphyrin IX and of diorganotin(IV)chloro protoporphyrin IX complexes

Compound	Solvent	$\varepsilon_M \times 10^3$ of the Soret band (M^{-1} cm^{-1})	Fluorescence[a] emission bands λ_{max} (nm)	Quantum yield[b]
H_4PPIX	DMSO	145	633, 673	0.047
$(Me_2SnCl)_2H_2PPIX$	DMSO	127	633, 673	0.053
$(Bu_2SnCl)_2H_2PPIX$	$CHCl_3$	127	633, 673	0.035
$(Ph_2SnCl)_2H_2PPIX$	DMSO	134	633, 673	0.042
$SnCl_2H_2PPIX$	DMSO	196	590, 643	0.011

[a] Excitation wavelength 440 nm. [b] With respect to standard Cresyl Violet (=0.53).

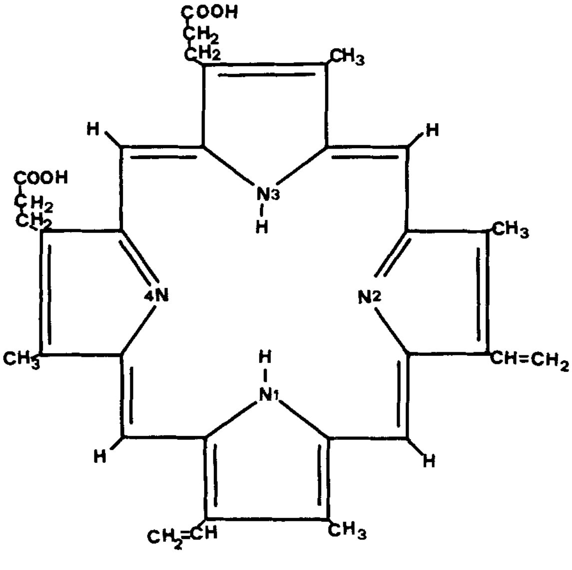

Figure 1 Protoporphyrin IX.

ν(NH) stretching in the complexes, present, *inter alia*, in the free protoporphyrin IX, in its disodium salt and in the dimethyl ester but absent in $SnCl_2H_2PPIX$, strongly supports the idea that in our complexes the imino acidic hydrogens are not replaced by the tin(IV) atoms.[40]

The occurrence of two absorption bands attributable, respectively, at $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ and the values of $\Delta\nu$ $[\nu_{as}(COO^-) - \nu_s(COO^-)]$ (Table 2), suggests bidentate bridging behaviour of the carboxylate groups upon coordination to the tin(IV) atoms.[41]

In the 600–250 cm^{-1} region peaks are present that are attributable to $\nu_{as}(SnC_2)$, $\nu_s(SnC_2)$ and ν(SnCl), characteristic of dialkyltin(IV)chloro moieties in a bent C–Sn–C configuration[42–44] and of a SnCl bond (Table 2).[45] As far as $(Ph_2SnCl)_2H_2PPIX$ is concerned, the bands at 450 cm^{-1} (s) and 295 cm^{-1} (m) are attributable, respectively, to $Sn–C_6H_5$[46] and to SnCl stretching modes.[45]

The Mössbauer spectra (Fig. 2), and in particular the full-width values calculated at half-height of the resonant peaks (Table 3), show the presence, in each complex, of only one absorbing species, indicating that the same environment is present around the two tin(IV) atoms.[47]

The isomer shift, δ mm s^{-1}, of all the $(R_2SnCl)_2H_2PPIX$ complexes was characteristic of diorganotin(IV) derivatives.[47] According to the properties of this parameter, it increases with the charge density on tin(IV) atom on going from the diphenyl to the dibutyltin(IV) derivative.[47]

The nuclear quadrupole splitting data (Table 3), ΔE mm s^{-1}, are fully consistent with trigonal bipyramidal R_2SnClO_2 coordination, O being the oxygen atom of the carboxylate side chain of protoporphyrin IX.[48,49]

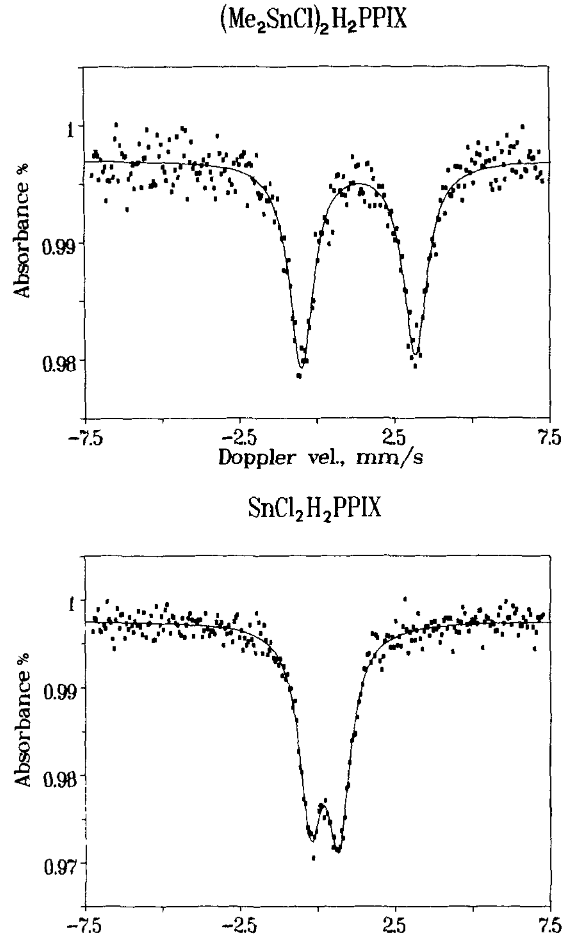

Figure 2 Mössbauer spectra, at 77.3 K, of (a) $(Me_2SnCl)_2H_2PPIX$ and (b) $SnCl_2H_2PPIX$. Full lines are the computer fittings of experimental points.

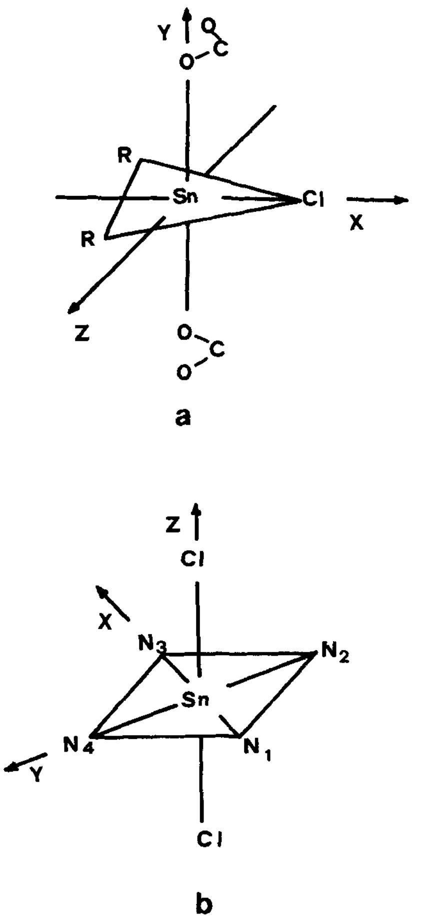

Figure 3 Idealized structures of: (a) R_2SnClO_2 group in $(R_2SnCl)_2H_2PPIX$; (b) $SnCl_2N_4$ group in $SnCl_2H_2PPIX$. *X*, *Y*, and *Z* are the directions of the principal components of the electric field gradient, **efg** ($|V_{ZZ}| \gg |V_{YY}| \gg |V_{ZZ}|$); off-diagonal components of **efg** are diagonalized.

In order to verify the correctness of the interpretation, the experimental nuclear quadrupole splitting parameters have been rationalized according to the point-charge model formalism,[48,49] applied to the idealized trigonal bipyramidal structure of Fig. 3a.

The partial quadrupole splittings (mm s^{-1}) [$\{Alk\}^{tbe} = -1.13$, $\{Ph\}^{tbe} = -0.98$, $\{COO\}^{tba}_{bridg} = +0.075$, $\{Cl\}^{tbe} = 0.20$], employed for the calculation of the theoretical ΔE and of the asymmetry parameter $\eta = (|V_{XX}| - |V_{YY}|)/V_{ZZ}$[48] (Table 3) were literature values.[48,49,51,52] Since the discrepancy between calculated and experimental ΔE did not exceed ±0.4 mm s^{-1} in any of the diorganotin(IV)chloro protoporphyrin IX complexes, the point-charge model formalism strongly supported the hypothesized trigonal bipyramidal structure around the tin(IV) atom.

A further confirmation arises from the evaluation of the C–Sn–C angle (see Refs 49, 50), ϕ, which in all cases, resulted in a value close to 120°, characteristic of the *cis*-$\mathrm{R_2Sn}$ configuration in a trigonal bipyramidal environment.

The smaller Ph–Sn–Ph angle ($\phi \approx 118°$) in $\mathrm{(Ph_2SnCl)_2H_2PPIX}$ compared with the Bu–Sn–Bu value ($\phi \approx 128°$) for $\mathrm{(Bu_2SnCl)_2H_2PPIX}$, was expected on the basis of the larger steric hindrance of the organic residue in the latter case.

Finally the Mössbauer parameters, isomer shift (δ mm s^{-1}) and nuclear quadrupole splitting (ΔE mm s^{-1}), for $\mathrm{SnCl_2H_2PPIX}$ were in good agreement with previous findings for $\mathrm{Hal_2SnL_4}$ complexes where the tin(IV) atom is coordinated by $\mathrm{Hal_2L_4}$ basic atoms.[36, 53]

Solution-phase investigations

The solution-phase characterization of diorganotin(IV)chloro protoporphyrin IX derivatives has been performed both by electronic absorption and fluorescence emission spectroscopy. All derivatives are soluble in organic solvents and stable in solution as demonstrated by the constancy of intensity and lineshape of spectra. The main spectroscopic parameters are reported in Table 4.

The high values of the molar extinction coefficients of the Soret band around 450 nm are a clear indication of the monomeric state of $\mathrm{H_4PPIX}$ itself and of its diorganotin(IV)chloro derivatives. This conclusion can be drawn also from the relatively high quantum yield values and the position of emission wavelength maxima.[54]

$\mathrm{(Me_2SnCl)_2H_2PPIX}$, $\mathrm{(Bu_2SnCl)_2H_2PPIX}$ and $\mathrm{(Ph_2SnCl)_2H_2PPIX}$ exhibit molar extinction coefficients and emission properties very similar to those of $\mathrm{H_4PPIX}$, indicating that organotin coordination involves the side groups of the porphyrin macrocycle, in agreement with the proposed model. Such a coordination mode is expected to leave the electronic characteristics of the porphyrin macrocycle π-molecular orbitals almost unaffected. In contrast with the other derivatives, $\mathrm{SnCl_2H_2PPIX}$ exhibits a relatively strong hyperchromic effect on the Soret band together with a blue shift in the fluorescence emission maximum and a lower quantum yield. This result is a clear indication that the coordination of tin metal here occurs in the porphyrin macrocycle, since these changes are typical of metal porphyrins in which the metal orbitals interact with the π-orbitals of the macrocycle.[55]

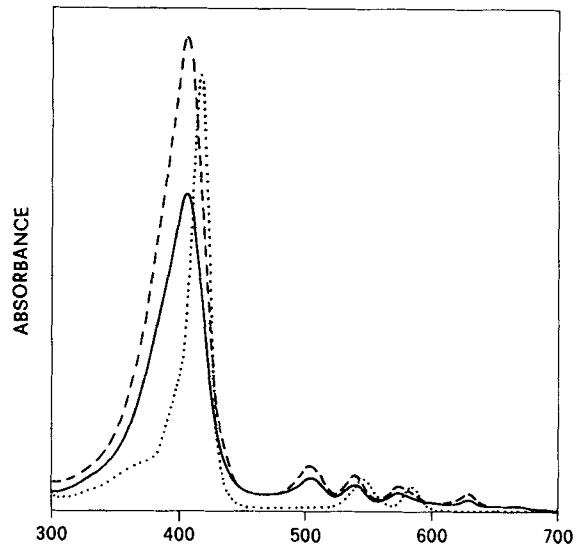

Figure 4 Absorption spectra of: $\mathrm{H_4PPIX}$ (2.2×10^{-6} M, solid line; absorbance maximum = 0.319); $\mathrm{(Me_2SnCl)_2H_2PPIX}$ (3.7×10^{-6} M, broken line; absorbance maximum = 0.470); and $\mathrm{SnCl_2H_2PPIX}$ (6.6×10^{-6} M, dotted line; absorbance maximum = 1.290). Solvent: DMSO.

This conclusion is further supported by the absorption spectrum lineshapes exhibited by the different metal-coordinated protoporphyrins and by the free base $\mathrm{H_4PPIX}$. As an example, the visible spectra of $\mathrm{H_4PPIX}$, $\mathrm{(Me_2SnCl)_2H_2PPIX}$ and $\mathrm{SnCl_2H_2PPIX}$ are reported in Fig. 4. In addition to the Soret band, $\mathrm{(Me_2SnCl)_2H_2PPIX}$, $\mathrm{(Bu_2SnCl)_2H_2PPIX}$ and $\mathrm{(Ph_2SnCl)_2H_2PPIX}$ show four Q-bands in the lower energy side of the spectrum, typical of free base porphyrins (see the spectrum of $\mathrm{H_4PPIX}$). In contrast, $\mathrm{SnCl_2H_2PPIX}$ shows only two Q-bands as found for metalporphyrins and attributable to the different symmetry of their tetrapyrrole macrocycles.

Acknowledgements Financial support by the Ministero per l'Università e la Ricerca Scientifica e Tecnologica, Roma, is gratefully acknowledged.

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