Inorg. Chem. **1990**, *29*, 4126–4130

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Tin(II) Porphyrins: Synthesis and Spectroscopic Properties of a Series of Divalent Tin Porphyrins. X-ray Crystal Structure of (2,3,7,8,12,13,17,18-Octaethylporphinato)tin(II)

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Received January 2, 1990

A series of tin(II) porphyrins (P)Sn, where P is the dianion of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), tetra-*p*-tolylporphyrin (TpTP), tetra-*m*-tolylporphyrin (TmTP), and tetramesitylporphyrin (TMP), were synthesized and characterized by IR, UV–visible, ^{1}H NMR, and ^{119}Sn Mössbauer spectroscopy. The crystal structure of (OEP)Sn(II), monomeric in the solid state (orthorhombic, *Pnma*; $a = 9.489$ (1), $b = 15.171$ (2), $c = 22.373$ (2) Å; $Z = 4$; $R(F) = 0.031$, $R_w(F) = 0.036$), shows that the central metal lies 1.018 Å from the mean nitrogen plane. Comparison of Mössbauer and X-ray data of compounds of this type with those of (P)SnFe(CO)$_4$ derivatives shows a formal +II oxidation state for the porphyrin metal.

Introduction

Tin porphyrins and phthalocyanins have been known since a long time, and the first representatives of phthalocyanins, (Pc)Sn, (Pc)SnCl$_2$, and (Pc)$_2$Sn, were described by Linstead et al.[2] Since then numerous papers have appeared relative to the porphyrin analogues and especially to the tin(IV) derivatives.[3-10] The first tin(II) porphyrin complex, (OEP)Sn, was characterized by Whitten et al.[10] on the basis of ^{1}H NMR data. More recently Landrum et al. have published the synthesis and spectroscopic characterization of (TPP)Sn.[11]

At the same time parallel studies have been published in biology describing tin porphyrins as inhibitors of bilirubin synthesis,[12-14] since tin protoporphyrin can replace modified heme before lysis by heme oxygenase. This decreases the rate of bilirubin and moderates postnatal jaundice in human newborns. Moreover, antitumor activity of group 14 metalloporphyrins, i.e., bis(alkyl)germanium(IV) porphyrins,[15] has been shown and implication of the alkyl groups attached to the germanium atom has been postulated to explain this property. Low oxidation state metalloporphyrins resulting from the cleavage of the metal–carbon bond could occur.

Other pseudo tin(II)[16-18] and germanium(II)[19] derivatives were also described in metal–metal porphyrin series. Indeed, carbene type complexes, (Por)MFe(CO)$_4$ (M = Sn, Ge), have been prepared,[17-19] and on the basis of UV–visible and ^{57}Fe Mössbauer data, a +II oxidation state was assigned to the M atom. Curiously, in a recent ^{57}Fe and ^{119}Sn Mössbauer study, a +IV oxidation state has been postulated for phthalocyanin analogues (Pc)SnFe(CO)$_4$ but no comparison with tin(II) porphyrins was done.[20] Moreover for (P)Sn$^{\text{II}}$ complexes a monomeric or dimeric structure can be invoked in the solid state.

We report here the synthesis and the spectroscopic characterization of a series of (P)Sn$^{\text{II}}$ porphyrins (where P is the dianion of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), tetra-*p*-tolylporphyrin (TpTP), tetra-*m*-tolylporphyrin (TmTP), or tetramesitylporphyrin (TMP)).

Experimental Section

Chemicals. Synthesis and handling of metalloporphyrins were carried out under an argon atmosphere. All common solvents were thoroughly dried in an appropriate manner and were distilled under argon prior to use. All operations were achieved according the Schlenk technique by using dry oxygen-free solvents. The glassware was heated under vacuum for 2 h at 250 °C before use.

The tin(II) porphyrins were synthesized by the reaction of anhydrous tin dichloride with the porphyrin free base according to Landrum et al.[11] The detailed procedure is given below.

Free-base (P)H$_2$ (1.63 mmol) and anhydrous tin dichloride (4.9 mmol) were dissolved in 200 mL of THF in the presence of 10 g of molecular sieves (size 4 Å, dried during 2 hours at 250 °C under vacuum). Pyridine (5 mL) was added with a syringe, and the reaction mixture was then refluxed for 6 h with stirring. The metalation reaction was monitored by UV–visible spectroscopy, and after completion of the reaction, the green solution was filtered out and then evaporated under reduced pressure. The crude material was redissolved in toluene and chromatographed over an alumina-packed column previously dried for 2 h at 250 °C under vacuum. Toluene was used as eluent in an argon atmosphere. The solid obtained after solvent removal was recrystallized from toluene or toluene/heptane mixture yielding (40–76%) green crystals of the corresponding tin(II) porphyrin. The purity of the complexes was checked on the basis of spectroscopic data (^{1}H NMR, UV–visible, IR). Yields and recrystallization solvents are detailed in Table I.

Due to the low solubility of the (TMP)H$_2$ free base in tetrahydrofuran, benzonitrile was used as solvent. The (TMP)Sn compound was obtained with a low yield (27%) (Table I).

Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker WM 400 spectrometer of the Cerema (Centre de Résonance Magnétique de l'Université de Bourgogne). Spectra were obtained from solutions in 0.5 mL of C$_6$D$_6$ with tetramethylsilane as internal reference. Infrared spectra were performed on a Perkin–Elmer 580 B apparatus, and samples were prepared as 1% dispersions in CsI. Electronic absorption spectra were recorded on a Perkin-Elmer 559 spectrophotometer.

X-ray Structure Determination. Crystals of (OEP)Sn were obtained by recrystallization in toluene. Preliminary Weissenberg photographs

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Table I. Recrystallization Solvents, Yields, and UV-Visible Data for (P)Sn^{II} Complexes (Toluene Solvent)

compd	recrystn solvent^a	yield, %	λ_{max}, nm^b B(1,0)(I)	B(0,0)(II)	Q(0,0)(III)	ϵ(I)/ϵ(II)
(TPP)Sn	A	50	397 (133.2)	489 (62.5)	693 (7.3)	2.13
(TmTP)Sn	A/B (1/2)	76	397 (128.0)	490 (61.0)	695 (7.1)	2.09
(TpTP)Sn	A/B (1/2)	54	398 (141.4)	489 (69.6)	695 (8.5)	2.03
(TMP)Sn	A/B (1/2)	27	394 (119.9)	491 (63.5)	695 (6.8)	1.88
(OEP)Sn	A	40	386 (123.0)	495 (38.7)	595 (5.1)	3.17

^{a}A, toluene; B, heptane. $^b\epsilon = 10^{-3}$ M^{-1}·cm^{-1} (given in parentheses).

Table II. Crystallographic Data for (OEP)Sn

molecular formula	$C_{36}H_{44}N_4Sn$
fw	651.47
cryst system, space group	orthorhombic, *Pnma*
cell dimens of *a–c*, Å	9.489 (1), 15.171 (2), 22.373 (2)
V; calcd density, g·cm^{-3}; *Z*	3221; 1.344; 4
λ, Å; μ, cm^{-1}	0.71073 (Mo Kα); 7.41
R(*F*), *R*$_w$(*F*), GOF	0.0313, 0.0357, 1.629

revealed an orthorhombic unit cell; systematic extinctions ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) led to the *Pnma* (centric) or $Pn2_1a$ (acentric) possible space groups. The calculated density (d_{cal} = 1.344 g cm^{-3}) imposes 4 molecules per unit cell. In the centric space group the tin atom must be in the 4c position, assuming a crystallographic *m* symmetry for the (OEP)Sn molecule.

X-ray data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer of the Ceredi (Centre régional de diffractomêtrie, Université de Bourgogne). The crystal data are given in Table II. Each reflection was corrected for Lorentz, polarization, and decay effects with the SDP program.[21] Of 3500 unique reflections measured with (sin θ)/λ < 0.6 Å^{-1}, 2192 with $I \geq 3\sigma(I)$ were used to solve and refine the structure. The crystal structure was solved in the *Pnma* centric space group by Patterson and Fourier methods. The Sn, N_1, and N_3 atoms belong to the mirror plane of the *Pnma* space group. Full-matrix least-squares methods[22] were used to refine the positional and anisotropic thermal parameters of the non-hydrogen atoms. Hydrogen atoms were included as fixed contributors to structure factor calculations. The final cycle of refinement (N_o/N_v = 11.5) led to $R(F)$ = 3.13%, $R_w(F)$ = 3.57%, and GOF = 1.63. The excellent agreement indices and inspection of the thermal motion ellipsoids confirm the choice of the space group. Table III gives the fractional coordinates, equivalent temperature factors, and esd's of the atoms of the asymmetric unit. Hydrogen atom coordinates, anisotropic temperature factors, least-squares planes, details of experimental data, and a list of structure factors are given in the supplementary material.

^{119}Sn and ^{57}Fe Mössbauer Spectroscopy. The Mössbauer spectra have been recorded at 80 and 95 K on a Halder constant-acceleration spectrometer in conjunction with a multichannel analyzer. The masses of the studied samples (OEP)Sn, (OEP)SnFe(CO)$_4$, and (TpNEt$_2$PP)SnFe(CO)$_4$ were calculated to contain 10 mg·cm^{-2} of tin or iron. The sources consisted in 10 mCi of Ca^{119}SnO$_3$ and 25 mCi of ^{57}Co diffused into metallic palladium. The velocity scale and isomer shifts were measured relative to Ba^{119}SnO$_3$ and α-Fe at 295 K. The spectra were computer-fitted to Lorentzian line shapes. Mössbauer parameters appear in Table IV.

Results and Discussion

Reaction of anhydrous SnCl$_2$ with (P)H$_2$ porphyrins in tetrahydrofuran or benzonitrile affords the corresponding (P)Sn complexes. Yields range from 27 to 76% (see Table I). With respect to the synthesis described by Landrum et al.[11] molecular sieves were added to the reaction mixture. Tin(II) complexes are quite unstable in solution, and a strictly oxygen-free medium is required to avoid the formation of dichloro derivatives (P)SnCl$_2$. (P)Sn also decomposes with trace moisture, giving the corresponding (P)Sn(OH)$_2$ complexes. In the solid state, the tin(II) porphyrins are more stable and it was possible to achieve an X-ray structure determination of (OEP)Sn.

Table III. Positional Parameters and Equivalent Isotropic Thermal Temperature Factors for (OEP)Sn

atom	*x*	*y*	*z*	*B*$_{eq}$, Å^2
Sn	0.35730 (4)	0.750	0.56557 (1)	3.054 (6)
N1	0.1645 (4)	0.750	0.6261 (2)	3.28 (9)
N2	0.2624 (3)	0.6155 (2)	0.5450 (1)	3.26 (6)
N3	0.3578 (4)	0.750	0.4634 (2)	3.31 (8)
C3	0.0307 (5)	0.7053 (3)	0.7066 (2)	4.82 (9)
C4	0.1163 (4)	0.6780 (3)	0.6566 (2)	3.69 (8)
C5	0.1414 (4)	0.5907 (3)	0.6396 (2)	4.09 (8)
C6	0.2056 (4)	0.5613 (2)	0.5878 (2)	3.56 (7)
C7	0.2150 (4)	0.4700 (3)	0.5688 (2)	3.98 (8)
C8	0.2784 (4)	0.4707 (2)	0.5144 (2)	3.91 (8)
C9	0.3082 (4)	0.5615 (2)	0.4995 (2)	3.45 (7)
C10	0.3699 (4)	0.5909 (3)	0.4474 (2)	3.87 (8)
C11	0.3887 (4)	0.6773 (3)	0.4290 (2)	3.68 (8)
C12	0.4410 (5)	0.7052 (3)	0.3719 (2)	4.74 (9)
C27	−0.0484 (6)	0.6429 (3)	0.7485 (2)	6.5 (1)
C28	0.0420 (8)	0.6165 (4)	0.7997 (3)	8.5 (2)
C29	0.1583 (5)	0.3924 (3)	0.6024 (2)	5.6 (1)
C30	−0.0004 (6)	0.3789 (4)	0.5932 (3)	9.3 (2)
C31	0.3066 (5)	0.3930 (3)	0.4740 (2)	4.81 (9)
C32	0.1905 (7)	0.3788 (4)	0.4288 (2)	7.6 (1)
C33	0.4784 (6)	0.6439 (4)	0.3222 (2)	7.0 (1)
C34	0.3532 (8)	0.6179 (5)	0.2858 (3)	10.7 (2)

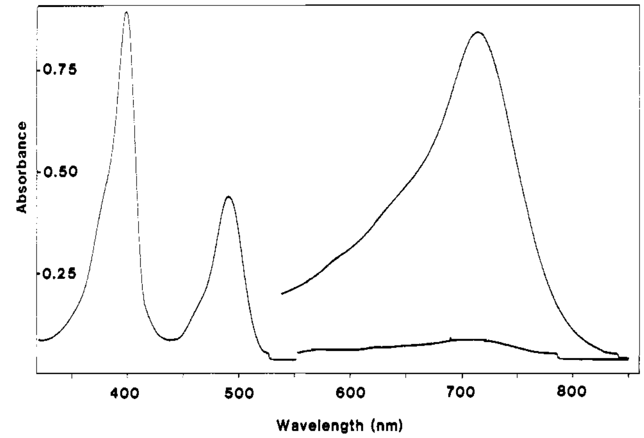

Figure 1. UV-visible spectrum of (TPP)Sn in toluene.

Due to the absence of axial ligand, no characteristic vibration is expected in IR spectroscopy. The absence of the strong IR absorptions in the two ranges 280–300 cm^{-1} and 560–570 cm^{-1} corresponding to Sn–Cl and Sn–OH vibrators, respectively,[4,5] permits one to check the purity of complexes. In addition no N–H band around 3300 cm^{-1} of the free base was also detected.

Electronic spectral data (Table I) of the tin(II) porphyrins belong to the p-type hyperporphyrin class, as expected for divalent group 14 porphyrins.[23] The spectrum of (TPP)Sn is reported on Figure 1. All the complexes exhibit two major absorptions in the Soret region and a broad Q band in the range 693–695 nm for the tetraarylporphyrins and at 595 nm for (OEP)Sn. The spectrum reported by Landrum[11] for (TPP)Sn shows three absorptions in the Soret region and several Q bands. The strongest peak around 420 nm may be due to the presence of (TPP)H$_2$, as also demonstrated by the presence of the characteristic Q bands of this latter ligand. According to Gouterman[23] the extra band

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Table IV. Mössbauer Parameters for (P)Sn and (P)SnFe(CO)$_4$ Derivatives[a]

	^{119}Sn				^{57}Fe			
compd	T, K	δ, ±0.005 mm·s^{-1}	Δ, ±0.01 mm·s^{-1}	Γ_1, Γ_2, mm·s^{-1}	T, K	δ, ±0.005 mm·s^{-1}	Δ, ±0.01 mm·s^{-1}	Γ_1, Γ_2, mm·s^{-1}
(OEP)Sn[b]	80	2.830	1.20	0.80, 0.80				
(Pc)Sn[c]	77	2.88	1.44					
(OEP)SnFe(CO)$_4$[b]	80	1.389	1.17	0.79, 0.79	95	−0.081	2.27	0.31, 0.32
(TpNEt$_2$PP)SnFe(CO)$_4$[b]	80	1.358	1.17	0.84, 0.78	80	−0.083	2.24	0.21, 0.24
(Pc)SnFe(CO)$_4$[d]	77	1.32 (1)	1.37 (1)	0.94 (2)	77	−0.10 (1)	2.26 (1)	0.34 (1)
(Pc)SnCl$_2$[c]	77	0.30	0.99					

[a] δ, isomer shift; Δ, quadrupole splitting, Γ, full line width. [b] Present work. [c] From ref 30. [d] From ref 20.

Table V. ^{1}H NMR Data[a] for (P)Sn Complexes

			protons of R^1			protons of R^2		
compd	R^1	R^2		m/i[b]	δ		m/i[b]	δ
(TPP)Sn	C$_6$H$_5$	H	o-H	br/8	8.10		s/8	8.91
			m-H	br/8	7.48			
			p-H	br/4	7.43			
(TmTP)Sn	m-CH$_3$C$_6$H$_4$	H	o-H	br/8	7.97		s/8	9.21
			m-H	br/4	7.41			
			p-H	d/4	7.35			
			m-CH$_3$	s/12	2.33			
(TpTP)Sn	p-CH$_3$C$_6$H$_4$	H	o-H	br/8	8.05		s/8	9.26
			m-H	d/8	7.25			
			p-CH$_3$	s/12	2.40			
(TMP)Sn	o,p,o'-(CH$_3$)$_3$C$_6$H$_2$	H	o-H	s/4	7.13		s/8	8.93
			m'-H	s/4	7.10			
			p-CH$_3$	s/12	2.05			
			o-CH$_3$	s/12	1.67			
			o'-CH$_3$	s/12	2.42			
(OEP)Sn	H	CH$_2$CH$_3$		s/4	10.39	α-CH$_2$	br/8	4.04
						α'-CH$_2$	br/8	3.97
						β-CH$_3$	t/24	1.84

[a] Spectra recorded in C$_6$D$_6$ at 294 K with SiMe$_4$ as internal reference. [b] m, multiplicity; i, intensity; s, singlet; d, doublet; br, broad peak.

I is observed at 394–398 nm for the tetraarylporphyrins and at 386 nm for (OEP)Sn, while the band II is located close to 490 nm for the tetraarylporphyrins and at 495 nm for (OEP)Sn. This supplementary absorption (band I) is due to the charge-transfer transition $a_{2u}(np_z) \rightarrow e_g(\pi^*)$ from the metal to the macrocycle ring, since the 5p$_z$ orbital of the tin atom contains one electron doublet. The ratio of the molar absorptivities for the Soret and the extra bands (ϵ(I)/ϵ(II)) clearly demonstrates the more basic is the macrocycle, the greater is the hyperporphyrin character. The basicity of the macrocycle increases the electron density on the metal center implying a greater intensity for the transition $a_{2u}(5p_z) \rightarrow e_g(\pi^*)$; indeed, the strongest absorption is observed for the octaethylporphyrin complex.

^{1}H NMR spectra of the studied complexes are those of diamagnetic metalloporphyrins.[24] The chemical shifts are summarized in Table V, and the ^{1}H NMR spectrum of (OEP)Sn at 294 K in C$_6$D$_6$ is given in Figure 2. The meso proton resonance signal of the octaethylporphyrin ligand appears at 10.39 ppm, while methylene and methyl protons are located in the range 3.97–4.04 and 1.84 ppm, respectively. The splitting of the α-CH$_2$ peaks results from the nonequivalence of the two sides of the macrocycle, which may be due to the out-of-plane position of the tin atom. These results are comparable to those published for the (P)SnFe(CO)$_4$ complexes.[17] For this series it was established by X-ray diffraction that the divalent tin atom is pentacoordinated and located out of the macrocycle plane. The splitting of the α-CH$_2$ signals is much more important for (OEP)Sn than for (OEP)SnFe(CO)$_4$, indicating a larger metal–four-nitrogen plane distance in (OEP)Sn.

Surprisingly the ^{1}H NMR data for the tetraarylporphyrin derivatives at room temperature exhibit no splitting for the ortho protons of the phenyl groups. Such a result is not in agreement with the expected nonequivalence of both sides of the macrocycle, but it is well-known that the free rotation of the phenyl ring can induce the equivalence of ortho protons of tetraphenylporphyrin derivatives.[25,26] Therefore, the influence of the temperature on the NMR spectrum has been studied and spectra of (TpTP)Sn in deuterated toluene have been recorded from 253 to 313 K. At room temperature the ortho proton resonance appears as a broad signal at 8.05 ppm. At a temperature lower than 273 K the signal for ortho protons is split into two broad singlets that give two well-resolved doublets at about 253 K. The same behavior is also noticed for meta protons. At room temperature the resonance signal appears as a doublet located at 7.25 ppm, while at 253 K these protons become nonequivalent and a double doublet is observed. This variable-temperature study (Figure 3) clearly demonstrates the out-of-plane displacement of the tin atom. On the NMR spectrum of (TMP)Sn the o-methyl groups give two singlets at 1.67 and 2.42 ppm. The steric hindrance of methyl groups prevents rotation of the phenyl ring[25,26] and can explain this important splitting. On the basis of the ^{1}H NMR data, it is impossible to discriminate between a monomeric or a dimeric

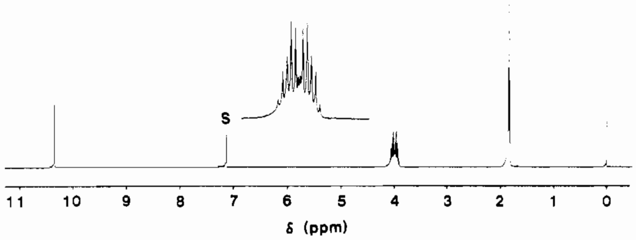

Figure 2. ^{1}H NMR spectrum of (OEP)Sn at 294 K in C$_6$D$_6$. (S = nondeuterated solvent).

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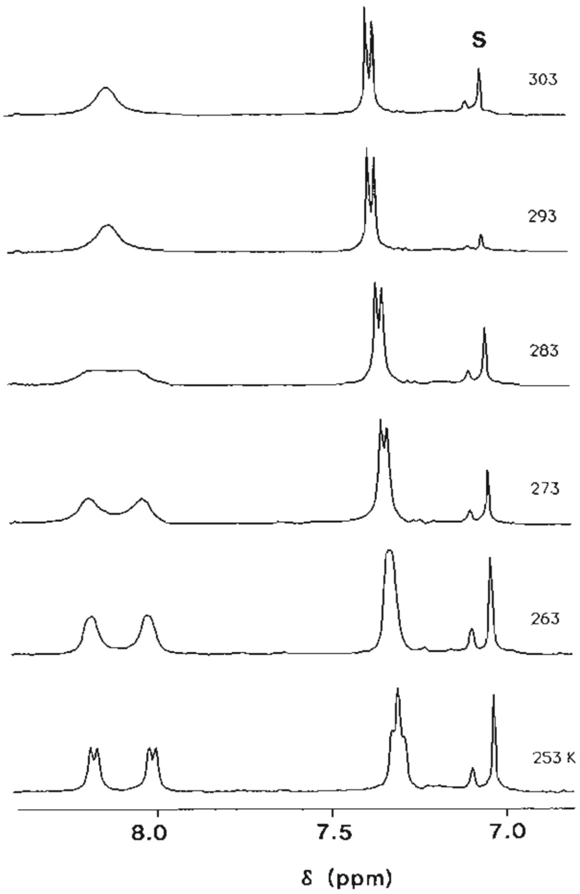

Figure 3. ^{1}H NMR spectra of (TpTP)Sn in the range 233–303 K. (S = nondeuterated solvent).

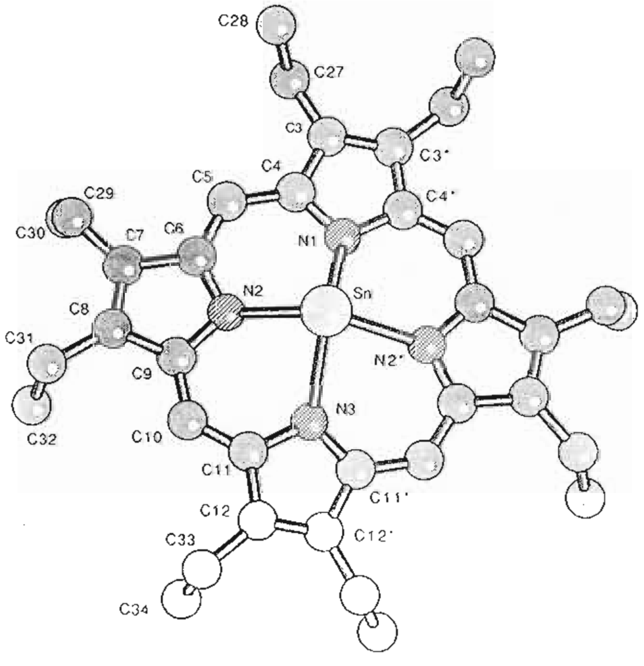

Figure 4. PLUTO view of (OEP)Sn.

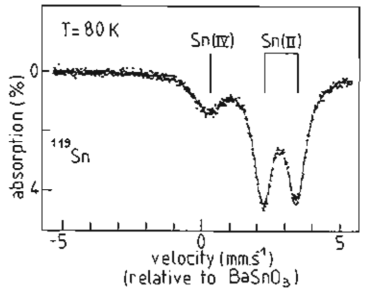

Figure 5. ^{119}Sn Mössbauer spectrum of (OEP)Sn.

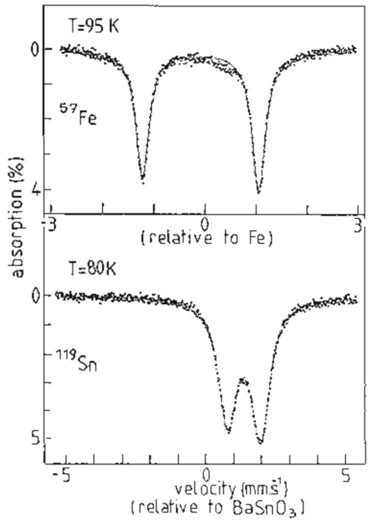

Figure 6. Mössbauer spectra of (OEP)SnFe(CO)$_4$.

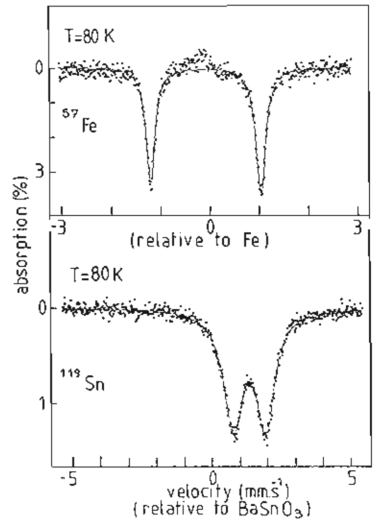

Figure 7. Mössbauer spectra of (TpNEt$_2$PP)SnFe(CO)$_4$.

structure for these type complexes. Therefore, the X-ray structure of (OEP)Sn was performed.

Figure 4 is the PLUTO view of (OEP)Sn, and Table VI gives the bond distances and angles of the molecule. (OEP)Sn is a monomeric species in the solid state, the minimum van der Waals contact between two adjacent molecules being 3.55 Å (meso C10 and CH$_2$ of an ethyl group C31). The coordination polyhedron of the tin atom is very similar to that of the lead atom in (tetra-*n*-propylporphinato)lead(II).[27] As expected for such heavy elements, the out-of-plane position is the main feature of these structures: Pb(II) and Sn(II) lie respectively at 1.174 and 1.018 Å from the four-nitrogen plane. Furthermore, this latter value compares with that of Sn(II) in (Pc)Sn[28] (1.11 Å) and is about 0.2 Å larger than that observed in (OEP)SnFe(CO)$_4$[17] and (TPP)SnMn(CO)$_4$HgMn(CO)$_5$.[16]

The ^{119}Sn Mössbauer spectrum of (OEP)Sn recorded at 80 K is shown in Figure 5. A strong symmetrical doublet characteristic of Sn(II) appears at $\delta = 2.83$ mm·s^{-1}, and the signal close to 0.2 mm·s^{-1} is due to Sn(IV) porphyrin, presumably (OEP)Sn(OH)$_2$

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Table VI. Bond Distances (Å) and Bond Angles (deg) for (OEP)Sn[a]

Sn–N1	2.276 (4)	C7–C8	1.357 (6)
Sn–N2	2.277 (3)	C7–C29	1.497 (7)
Sn–N3	2.286 (4)	C8–C9	1.445 (6)
N1–C4	1.367 (5)	C8–C31	1.510 (6)
N2–C6	1.373 (5)	C9–C10	1.379 (5)
N2–C9	1.378 (5)	C10–C11	1.385 (7)
N3–C11	1.376 (5)	C11–C12	1.435 (6)
C3–C4	1.443 (6)	C12–C12*	1.359 (7)
C3–C3*	1.355 (6)	C12–C33	1.493 (7)
C3–C27	1.530 (7)	C27–C28	1.486 (8)
C4–C5	1.399 (6)	C29–C30	1.532 (7)
C5–C6	1.382 (5)	C31–C32	1.510 (7)
C6–C7	1.453 (5)	C33–C34	1.493 (9)
N1–Sn–N2	78.58 (9)	C6–C7–C8	106.4 (3)
N2–Sn–N3	78.41 (9)	C6–C7–C29	125.6 (4)
N2–Sn–N2*	127.3 (1)	C8–C7–C29	128.1 (4)
Sn–N1–C4	124.5 (2)	C7–C8–C9	107.6 (3)
Sn–N2–C6	123.5 (2)	C7–C8–C31	127.6 (4)
Sn–N2–C9	123.9 (2)	C9–C8–C31	124.8 (3)
Sn–N3–C11	124.1 (2)	N2–C9–C8	109.5 (3)
C4–N1–C4*	106.0 (4)	N2–C9–C10	124.5 (3)
C6–N2–C9	106.5 (3)	C8–C9–C10	126.0 (4)
C11–N3–C11*	106.5 (4)	C9–C10–C11	127.7 (4)
C3*–C3–C4	106.8 (4)	N3–C11–C10	124.4 (3)
C3*–C3–C27	128.4 (5)	N3–C11–C12	109.6 (4)
C4–C3–C27	124.9 (4)	C10–C11–C12	126.0 (4)
N1–C4–C3	110.2 (3)	C11–C12–C12*	107.1 (4)
N1–C4–C5	124.4 (3)	C11–C12–C33	124.2 (4)
C3–C4–C5	125.4 (4)	C12*–C12–C33	128.5 (4)
C4–C5–C6	127.5 (4)	C3–C27–C28	110.9 (5)
N2–C6–C5	124.3 (3)	C7–C29–C30	113.0 (4)
N2–C6–C7	110.0 (3)	C8–C31–C32	112.5 (4)
C5–C6–C7	125.5 (4)	C12–C33–C34	112.4 (5)

[a] Starred atoms are related to the corresponding nonstarred atoms by the mirror plane.

as an oxidation product. The ^{119}Sn and ^{57}Fe spectra of (OEP)SnFe(CO)$_4$ and (TpNEt$_2$PP)SnFe(CO)$_4$, where TpNEt$_2$PP is the dianion of tetrakis(*p*-(diethylamino)phenyl)porphyrin, also appear in Figures 6 and 7. In each case the signal is a doublet.

The Mössbauer parameters of (OEP)Sn, (OEP)SnFe(CO)$_4$, and (TpNEt$_2$PP)SnFe(CO)$_4$ and for comparison those of (Pc)Sn and (Pc)SnFe(CO)$_4$[20] are listed in Table IV. The ^{119}Sn isomer shifts are equal to 1.39 mm·s^{-1} and 1.36 mm·s^{-1} for the pseudo tin(II) complexes of (OEP)SnFe(CO)$_4$ and (TpNEt$_2$PP)SnFe(CO)$_4$, respectively. These values range between the isomer shifts observed for Sn(IV) complexes[29] ($\delta_{\mathrm{Sn(IV)}} \approx 0$ mm·s^{-1}) and for Sn(II) complexes ($\delta_{\mathrm{Sn(II)}} \approx 3$ mm·s^{-1}). On the other hand, the ^{57}Fe isomer shifts of these metal–metal derivatives (Table IV) are close to -0.10 mm·s^{-1} and are characteristic of an iron atom in a zero oxidation state. As a comparison, the isomer shift of Fe(0) in Fe(CO)$_5$[30] is equal to -0.09 mm·s^{-1}.

The quadrupole splitting values at the Fe and Sn nuclei permit one to assign a +II oxidation state for the tin atom of the (P)SnFe(CO)$_4$ complexes. Hence, the iron quadrupole splittings are equal within 0.02 mm·s^{-1}, leading to the same zero oxidation state and coordination scheme for this latter atom whatever the nature of the P ligand. Furthermore, the tin quadrupole splittings are almost the same for (P)Sn (1.20 and 1.44 mm·s^{-1}) and for (P)SnFe(CO)$_4$ (1.17 and 1.37 mm·s^{-1}). Thus, the tin atom is five-coordinated in both series, the fifth "coordination site" being either the 5p$_z$ lone pair for (P)Sn or the Fe(CO)$_4$ group for (P)SnFe(CO)$_4$.

The lower value of the isomer shift for the (P)SnFe(CO)$_4$ complexes can be explained by the Sn → Fe, electron transfer, which decreases the s electron density on the tin nucleus. It also explains the iron Mössbauer parameters values[17] and the shorter Sn–N distances for (P)SnFe(CO)$_4$ (≈2.19 Å) than for (P)Sn (≈2.28 Å). Thus, the tin atom is in a formal +II oxidation state in (P)SnFe(CO)$_4$ with the Sn–Fe bond having an important covalent character.

Supplementary Material Available: Tables of hydrogen atom fractional coordinates, anisotropic temperature factors, least-squares planes, and crystallographic data (6 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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