

Crystal structure and two-stage hydrolysis of dimethoxo(*meso*-tetra(4-methoxyphenylporphyrinato))tin(IV), Sn(tmpp)(OMe)₂

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In this work, we determine the crystal structure of dimethoxo(*meso*-tetra(4-methoxyphenylporphyrinato))tin(IV), Sn(tmpp)(OMe)₂ (**1**). Experimental results indicate that the tin atom has an octahedral geometry. The geometry around the tin center has Sn(1)–O(5) = 2.020(6), Sn(1)–O(6) = 2.003(7) Å and an average Sn(1)–N = 2.10(1) Å. The two methoxo groups are unidentately coordinated to the tin(IV) atom. Two-stage hydrolysis of Sn(tmpp)(OMe)₂ in CDCl₃ was observed by ¹H and ¹³C NMR spectroscopy. Compound (**1**) crystallizes in the space group *P*2₁/*n* with *a* = 14.7492(1), *b* = 19.2022(3), *c* = 16.0806(2) Å, β = 94.104(1)°, and *Z* = 4.

KEY WORDS: Crystal structure; tin porphyrin; two-stage hydrolysis; methanolate; *trans* equivalent axial ligand.

Introduction

Previously, we reported the two-stage hydrolysis of dimethoxo(*meso*-tetraphenylporphyrinato)tin(IV), Sn(tpp)(OMe)₂,¹ dimethoxo(*meso*-tetra-*p*-tolylporphyrinato)tin(IV), Sn(tptp)(OMe)₂,² and dimethoxo(*meso*-tetraphenylporphyrinato)germanium(IV), Ge(tpp)(OMe)₂.³ Dimethoxo(*meso*-tetra(4-methoxyphenylporphyrinato))tin(IV), Sn(tmpp)(OMe)₂, (**1**) is a homolog of the previous three complexes. Complex (**1**) might undergo a similar two-stage hydrolysis reaction in the presence of water. The X-ray structure of this hydrolytically unstable complex (**1**) is reported here.

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Experimental

Synthesis of Sn(tmpp)(OMe)₂ (**1**)

Sn(tmpp)(OH)₂ (**3**) was prepared by substituting *meso*-tetraphenylporphyrin, tpp, with *meso*-tetra(4-methoxyphenylporphyrin), tmpp, in the preparation Sn(tpp)(OH)₂ as described elsewhere.^{4,5} Crystals of compound (**1**) were obtained by allowing methanol to diffuse into a nearly saturated solution of Sn(tmpp)(OH)₂ (**3**) in CH₂Cl₂. The crystal (**1**) was dissolved in CDCl₃ (99.8% from Aldrich) for the ¹H and ¹³C NMR measurements. Tables 1 and 2 summarize the ¹³C and ¹H NMR data.

Spectroscopy

¹H and ¹³C NMR spectra were recorded at 400.13 and 100.61 MHz on a Bruker AM-400 spectrometer in CDCl₃. ¹³C NMR data are relative to the center line of CDCl₃ at 77.0 ppm. ¹H NMR data are relative to CDCl₃ at 7.24 ppm.

Table 1. ^{13}C Chemical Shifts (δ) of Compounds **1–3** and MeOH in CDCl_3 at 24°C at 100.61 MHz^{a,b}

Compound	C_4	C_α	$\text{C}_{2,6}$	C_1	C_β	C_{meso}	$\text{C}_{3,5}$	O–Me	Axial M–OMe
$\text{Sn}(\text{tmpp})(\text{OMe})_2(\mathbf{1})$	159.8	147.2	136.1	133.9	132.4	121.1	112.5	55.6	44.6
$\text{Sn}(\text{tmpp})(\text{OMe})(\text{OH})(\mathbf{2})$	159.8	147.5	136.3	133.9	132.3	121.3	112.5	55.6	44.6
$\text{Sn}(\text{tmpp})(\text{OH})_2(\mathbf{3})$	159.8	146.9	136.2	133.9	132.6	120.9	112.5	55.6	—
MeOH	—	—	—	—	—	—	—	50.3	—

^a Chemical shifts in ppm relative to the center line of CDCl_3 at 77.0 ppm.

^b When water is present in a CDCl_3 solution of $\text{Sn}(\text{tmpp})(\text{OMe})_2(\mathbf{1})$, resonances due to $\text{Sn}(\text{tmpp})(\text{OMe})(\text{OH})(\mathbf{2})$ and $\text{Sn}(\text{tmpp})(\text{OH})_2(\mathbf{3})$ develop. The contamination peak (**2–3**) in NMR spectrum can be interpreted in terms of the two-stage hydrolysis of compound (**1**).

Crystallography

Table 3 presents crystal data and other information for $\text{Sn}(\text{tmpp})(\text{OMe})_2 \cdot \text{CH}_2\text{Cl}_2$. Measurements were taken on a Siemens SMART CCD diffractometer using monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were based on 9220 symmetry-equivalent reflections using the SHELXTL-PC program package with ($T_{\text{min,max}} = 0.573, 0.928$). The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares. All nonhydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen-atom positions were located on a difference map and included in the structure-factor calculation. Selected bond distances and angles for compound (**1**) are given in Table 4. Final coordinates and equivalent isotropic displacement coefficients for all non-hydrogen atoms are listed in Table 5. The vigorous thermal motion of CH_2Cl_2 causes the extremely large temperature factors of the carbon and chlorine atoms. Hence, C–Cl bond was fixed at 1.767 Å in the refinement. This fixation

explains the large residual electron density peak at Cl(1).

Results and discussion

Molecular structure of $\text{Sn}(\text{tmpp})(\text{OMe})_2 \cdot \text{CH}_2\text{Cl}_2$

Figure 1 illustrates the skeletal framework of complex (**1**), $\text{Sn}(\text{tmpp})(\text{OMe})_2 \cdot \text{CH}_2\text{Cl}_2$. This structure has a six-coordinate tin with four nitrogen atoms of the porphyrinato group and the two OMe-ligands. Bond distances (Å) are $\text{Sn}(1)–\text{O}(5) = 2.020(6)$, $\text{Sn}(1)–\text{O}(6) = 2.003(7)$, $\text{O}(5)–\text{C}(49) = 1.36(2)$, $\text{O}(6)–\text{C}(50) = 1.30(2)$, and the mean $\text{Sn}–\text{N} = 2.10(1) \text{ Å}$. CH_2Cl_2 from the solvent is trapped during crystal growth.

The geometry about Sn(1) is a slightly distorted octahedron. The tin atom lies 0.027(3) Å from the 24-atom porphyrin plane (C_{20}N_4), resulting in a mean $\text{O}(5)–\text{Sn}(1)–\text{N}$ (or $\text{O}(6)–\text{Sn}(1)–\text{N}$) bond angle of $89.7(6)$ (or $90.3(6)^\circ$) and the $\text{O}(5)–\text{Sn}(1)–\text{O}(6)$ bond angle of $174.0(3)^\circ$. The dihedral angles between the

Table 2. Proton chemical shift (δ) of compounds **1–3** and MeOH in CDCl_3 at 24°C at 400.13 MHz^a

Compound	β -H	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	OMe	M–OMe	Sn–OH
$\text{Sn}(\text{tmpp})(\text{OMe})_2(\mathbf{1})$	9.14 (5.2 Hz) ^b	8.24 (m) ^c	7.34 (m)	—	4.11	–2.16 (69.1 Hz) ^b	—
$\text{Sn}(\text{tmpp})(\text{OMe})(\text{OH})(\mathbf{2})$	9.14	8.23	7.33	—	4.11	–2.15	–7.45
$\text{Sn}(\text{tmpp})(\text{OH})_2(\mathbf{3})$	9.15	8.24 (8.6) ^d	7.34 (8.6) ^d	—	4.11	—	–7.5
MeOH	—	—	—	—	3.07	—	—
$\text{Ge}(\text{tpp})(\text{OMe})_2$	9.02	8.28 (m)	7.79 (m)	—	—	–2.57	—

^a Chemical shift in ppm relative to CDCl_3 at 7.24 ppm; M is Sn for compounds **1**, **2**, **3** and Ge for complex $\text{Ge}(\text{tpp})(\text{OMe})_2$.

^b $^n\text{J}(\text{Sn}–\text{H})$ coupling constant in Hz, $n = 4$ for β -H and $n = 3$ for M–OMe.

^c m = multiplet.

^d $^3\text{J}(\text{H}–\text{H})$ coupling constants in Hz.

Table 3. Crystal data for compound Sn(tmpp)(OMe)₂·CH₂Cl₂

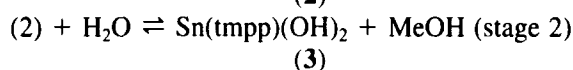
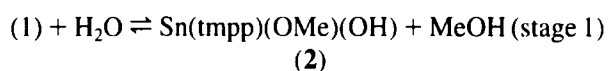
Compound	Sn(tmpp)(OMe) ₂ ·CH ₂ Cl ₂
Color/shape	Black/columnar
Empirical formula	C ₅₁ H ₄₄ Cl ₂ N ₄ O ₆ Sn
Formula weight	998.5
Temperature	296K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions (7846 reflections with 5 < 2θ < 50 deg)	<i>a</i> = 14.7492(1) Å <i>b</i> = 19.2022(3) Å <i>c</i> = 16.0806(2) Å β = 94.104(1)°
Volume	4542.6(10) Å ³
<i>Z</i>	4
Density (calculated)	1.460 mg/m ³
Absorption coefficient	0.736 mm ⁻¹
Diffractometer/scan	Siemens SMART/CCD area detector
Radiation/wavelength	MoKα(graphite monochrome)/ 0.71073 Å
<i>F</i> (000)	2040
Crystal size	0.22 × 0.25 × 0.70 mm
2θ range	2.5 to 55.8°
Index ranges	-18 ≤ <i>h</i> ≤ 19, -19 ≤ <i>k</i> ≤ 24, -17 ≤ <i>l</i> ≤ 20
Reflections collected	25906
Independent/ observed refls	9781 (<i>R</i> _{int} = 0.0509)/4078 (<i>I</i> ≥ 3.0σ(<i>I</i>))
Absorption correction	semiempirical
Range of relat. transm. factors	0.928 and 0.573
Refinement method	Full-matrix least-squares
Computing	SHELXTL PLUS(VMS)
No. of parameters varied	577
Goodness-of-fit on <i>F</i> ²	0.85
Weights	[σ ² (<i>F</i>) + 2.3 × 10 ⁻³ <i>F</i> ²] ⁻¹
Final <i>R</i> indices [<i>I</i> > 3σ(<i>I</i>)]	<i>R</i> = 0.0603, <i>R</i> _w = 0.0644
Largest diff. peak and hole	1.75 and -0.89eÅ ⁻³

mean plane of the skeleton (C₂₀N₄) and the planes of the phenyl group are 122.6° [C(24)], 79.7° [C(30)], 95.6° [C(36)] and 83.1° [C(42)].

The central hole's radius (C₁'...N, the distance from the geometrical centre C₁' of the mean plane of the 24-atom core to the porphyrinato-core N atoms) is 2.10(1) Å. This distance is larger than 2.01 Å suggested by Collins and Hoard.⁶ Hence, the tin (IV) atom is bonded in a highly expanded porphyrinato core (C₂₀N₄). The central hole's radius for (1) is shorter than the 2.106(6) Å in Sn(tpp)(OH)₂,⁷ and 2.132(9) Å in Sn(tpp)(OAc)₂,⁸ but larger than the 2.078(7) Å in Sn(tpp)(NO₃)₂,⁸ and 2.074(5) Å in Sn(tpp)(ClO₄)₂.¹⁰ The crystal data show no evidence for the intermolecular hydrogen bonds.

Two-stage hydrolysis of Sn(tmpp)(OMe)₂(1)

The δ(M-CH₃) shift from -2.57 to -2.16 ppm is due to substituting Ge for Sn. Sn(tmpp)(OMe)₂(1) is sensitive to hydrolysis. The hydrolysis of (1) shown in Fig. 2 may be interpreted as two-stage reactions.



The ¹³C and ¹H NMR resonances of compounds (2) and (3) are shown in Tables 1 and 2, respectively. The methanol resulting from the hydrolysis of compounds (1) and (2) shown in stages 1 and 2 is found to be at δ = 3.07 ppm from ¹H NMR (shown in Table 2) and 50.3 ppm from ¹³C NMR measurement (shown in Table 1). The chemical shift of the methanol product at δ = 3.07 ppm is similar to the shift at δ = 3.08 ppm for the hydrolysis of Sn(tpp)(OMe)₂,¹ but is differ-

Table 4. Selected bond distances (Å) and bond angles (°) for [Sn(tmpp)(OMe)₂·CH₂Cl₂]

Sn(1)-O(5)	2.020(6)	Sn(1)-N(1)	2.105(7)
Sn(1)-O(6)	2.003(7)	Sn(1)-N(2)	2.100(7)
O(5)-C(49)	1.36(2)	Sn(1)-N(3)	2.113(8)
O(6)-C(50)	1.30(2)	Sn(1)-N(4)	2.073(7)
O(5)-Sn(1)-N(1)	87.6(3)	N(1)-Sn(1)-N(2)	90.0(3)
O(5)-Sn(1)-N(2)	90.1(3)	N(1)-Sn(1)-N(3)	179.2(3)
O(5)-Sn(1)-N(3)	92.0(3)	N(1)-Sn(1)-N(4)	89.8(3)
O(5)-Sn(1)-N(4)	89.2(3)	N(2)-Sn(1)-N(3)	89.3(3)
O(6)-Sn(1)-N(1)	86.7(3)	N(2)-Sn(1)-N(4)	179.3(3)
O(6)-Sn(1)-N(2)	91.7(3)	N(3)-Sn(1)-N(4)	90.9(3)
O(6)-Sn(1)-N(3)	93.7(3)	O(6)-Sn(1)-O(5)	174.0(3)
O(6)-Sn(1)-N(4)	89.0(3)	Sn(1)-O(5)-C(49)	125.6(8)
		Sn(1)-O(6)-C(50)	125.3(9)

Table 5. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

Atom	$U_{eq} = 1/3 \sum_j U_{ij} a_i a_j \cdot a_i \cdot a_j$			
	x/a	y/b	z/c	U_{eq}
Sn(1)	0.2157(1)	0.1277(1)	0.2414(1)	0.045(1)
Cl(1)	0.2380(6)	0.1080(6)	0.7515(5)	0.266(6)
Cl(2)	0.2313(7)	0.2564(5)	0.7851(6)	0.224(5)
O(1)	-0.3117(5)	0.1237(4)	0.5060(5)	0.075(3)
O(2)	0.5105(5)	0.1136(4)	0.7599(5)	0.079(3)
O(3)	0.7455(4)	0.1314(5)	-0.0196(5)	0.074(3)
O(4)	0.0575(5)	0.1293(4)	-0.2855(4)	0.075(3)
O(5)	0.2149(5)	0.0226(3)	0.2399(4)	0.060(2)
O(6)	0.2044(5)	0.2316(4)	0.2352(5)	0.071(3)
N(1)	0.0775(5)	0.1240(4)	0.1986(4)	0.043(2)
N(2)	0.1789(5)	0.1269(5)	0.3652(5)	0.050(2)
N(3)	0.3540(6)	0.1307(5)	0.2858(5)	0.063(3)
N(4)	0.2515(5)	0.1273(5)	0.1191(5)	0.053(2)
C(1)	0.0055(6)	0.1257(5)	0.2491(6)	0.051(3)
C(2)	0.0120(6)	0.1242(5)	0.3369(5)	0.047(3)
C(3)	0.0924(6)	0.1221(5)	0.3898(6)	0.052(3)
C(4)	0.0983(7)	0.1127(5)	0.4789(6)	0.058(4)
C(5)	0.1866(7)	0.1129(5)	0.5056(6)	0.056(4)
C(6)	0.2392(6)	0.1213(5)	0.4354(6)	0.050(3)
C(7)	0.3347(6)	0.1245(5)	0.4359(5)	0.047(3)
C(8)	0.3884(6)	0.1278(5)	0.3664(5)	0.046(3)
C(9)	0.4862(6)	0.1270(5)	0.3689(6)	0.050(3)
C(10)	0.5083(6)	0.1293(6)	0.2859(6)	0.057(3)
C(11)	0.4265(5)	0.1296(5)	0.2353(5)	0.047(3)
C(12)	0.4200(7)	0.1302(6)	0.1474(6)	0.056(3)
C(13)	0.3402(6)	0.1293(5)	0.0925(6)	0.051(3)
C(14)	0.3349(7)	0.1290(6)	0.0043(5)	0.059(3)
C(15)	0.2459(7)	0.1279(6)	-0.0235(5)	0.058(3)
C(16)	0.1925(6)	0.1271(6)	0.0479(5)	0.050(3)
C(17)	0.0972(6)	0.1253(5)	0.0475(5)	0.050(3)
C(18)	0.0441(6)	0.1258(5)	0.1163(5)	0.049(3)
C(19)	-0.0526(6)	0.1288(5)	0.1139(6)	0.052(3)
C(20)	-0.0769(6)	0.1284(5)	0.1936(6)	0.052(3)
C(21)	-0.0746(6)	0.1255(5)	0.3802(5)	0.049(3)
C(22)	-0.1403(7)	0.0753(5)	0.3671(6)	0.061(4)
C(23)	-0.2192(7)	0.0755(5)	0.4107(7)	0.062(4)
C(24)	-0.2333(6)	0.1271(6)	0.4665(6)	0.056(3)
C(25)	-0.1692(7)	0.1799(5)	0.4785(6)	0.056(3)
C(26)	-0.0910(6)	0.1783(5)	0.4359(6)	0.053(3)
C(27)	0.3849(6)	0.1225(5)	0.5201(5)	0.048(3)
C(28)	0.3927(7)	0.1826(5)	0.5675(6)	0.055(3)
C(29)	0.4359(7)	0.1820(5)	0.6490(6)	0.056(3)
C(30)	0.4693(6)	0.1198(6)	0.6806(6)	0.055(3)
C(31)	0.4628(7)	0.0599(5)	0.6347(7)	0.059(4)
C(32)	0.4201(7)	0.0611(5)	0.5540(6)	0.056(3)
C(33)	0.5078(6)	0.1296(6)	0.1038(5)	0.049(3)
C(34)	0.5532(7)	0.1899(6)	0.0886(7)	0.066(4)
C(35)	0.6311(8)	0.1890(6)	0.0459(8)	0.073(4)
C(36)	0.6659(6)	0.1272(7)	0.0207(6)	0.060(3)
C(37)	0.6224(9)	0.0678(7)	0.0327(10)	0.098(6)
C(38)	0.5428(10)	0.0687(6)	0.0775(10)	0.098(6)
C(39)	0.0486(6)	0.1250(5)	-0.0387(5)	0.052(3)
C(40)	0.0403(8)	0.0644(5)	-0.0826(6)	0.061(4)
C(41)	0.0032(7)	0.0624(5)	-0.1659(6)	0.055(3)

Table 5. Continued

Atom	$U_{eq} = 1/3 \sum_j U_{ij} a_j^* a_j \cdot a_i$			U_{eq}
	x/a	y/b	z/c	
C(42)	-0.0247(6)	0.1230(6)	-0.2032(6)	0.056(3)
C(43)	-0.0175(9)	0.1840(6)	-0.1595(7)	0.076(4)
C(44)	0.0191(8)	0.1859(5)	-0.0773(7)	0.066(4)
C(45)	-0.3251(9)	0.1742(8)	0.5690(9)	0.093(5)
C(46)	0.5133(10)	0.1713(8)	0.8116(7)	0.096(6)
C(47)	0.7732(9)	0.0712(9)	-0.0612(9)	0.099(6)
C(48)	-0.0602(8)	0.0678(7)	-0.3346(6)	0.072(4)
C(49)	0.2787(12)	-0.0191(8)	0.2791(11)	0.117(7)
C(50)	0.2419(12)	0.2751(9)	0.2889(13)	0.121(8)
C(51)	0.1927(10)	0.1890(4)	0.7167(7)	0.141(9)

ent from the shift of 3.39 ppm for Sn(ttp)(OMe)₂ and 3.34 ppm for Ge(tp)(OMe)₂.³ The upfield shift of ~ -0.29 ppm (from 3.37 ± 0.03 to 3.08 ± 0.01 ppm) for complex (1) and Sn(tp)(OMe)₂ might come from some hydrogen-bonding complexation of methanol to the methoxo ligands in these two complexes. The ring current effect causes $\delta(CH_3-OH)$ to be slightly upfield from this value.

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Supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been

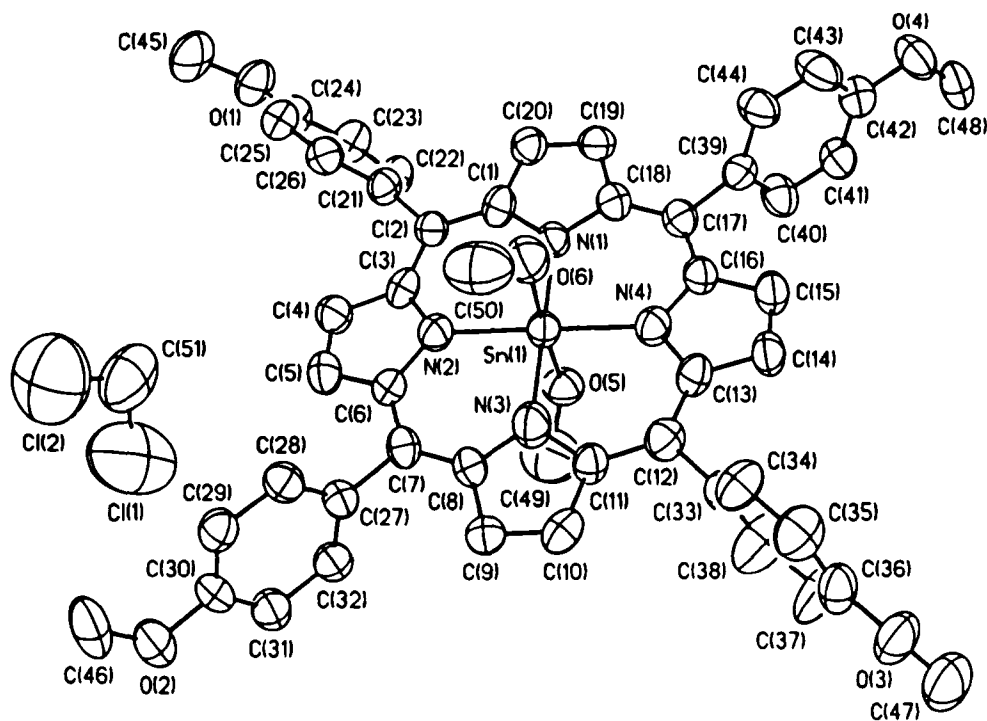


Fig. 1. Molecular configurations and atom-labeling schemes for Sn(tmpp)(OMe)₂·CH₂Cl₂, with ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

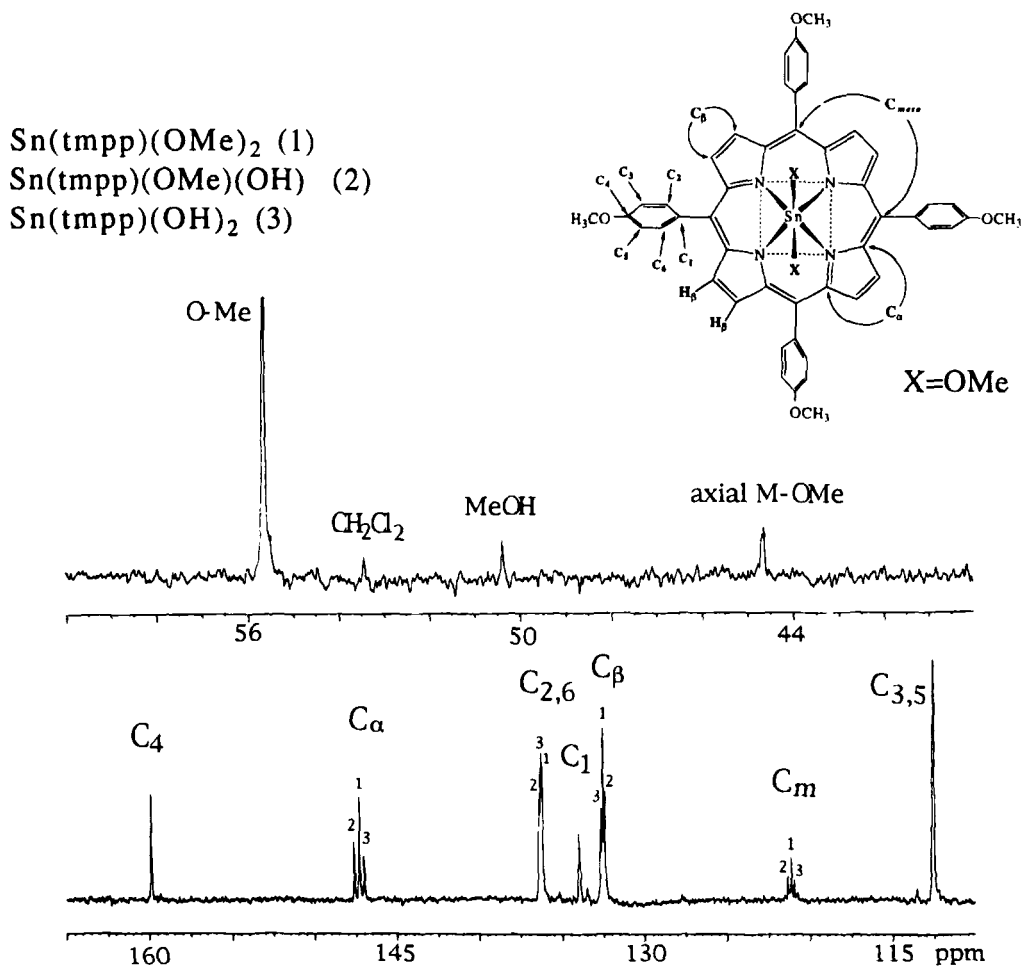


Fig. 2. The 100.61 MHz ^{13}C broad band NMR spectrum for $\text{Sn}(\text{tmpp})(\text{OMe})_2(1)$ hydrolysis in CDCl_3 at 24°C after reaction time of several minutes.

deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5362. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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