Journal of Organometallic Chemistry 694 (2009) 269–277

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Hypervalent triphenyl and diphenyl tin coordination compounds derived from 2-(1H-benzimidazol-2-yl)phenol

Adriana Esparza-Ruiz, Adrián Peña-Hueso, Iris Ramos-García, Aurora Vásquez-Badillo, Angelina Flores-Parra *, Rosalinda Contreras

Department of Chemistry, Cinvestav (Centro de Investigacion y de Estudios Avanzados), A.P. 14-740, 07000 México D.F., Mexico

ARTICLE INFO

Article history:
Received 4 September 2008
Received in revised form 22 October 2008
Accepted 22 October 2008
Available online 30 October 2008

Keywords:
2-(1H-benzimidazol-2-yl)phenol
Hypervalent organotin compounds
^{119}Sn NMR

ABSTRACT

Reactions of 2-(1H-benzimidazol-2-yl)phenol (**1**) and $SnPh_3Cl$, $SnPh_2Cl_2$ and $SnCl_4$ were investigated. One tetracoordinated triphenyltin(IV) compound: triphenyltin-2-(1H-benzimidazol-2-yl)phenolate] (**3**) and its adducts: [O → Sn] dimethylsulfoxide triphenyltin-[2-(1H-benzimidazol-2-yl)phenolate] (**4**), [O → Sn] aqua triphenyltin-[2-(1H-benzimidazol-2-yl)phenolate] (**5**) [O → Sn] ethanol triphenyltin-[2-(1H-benzimidazol-2-yl)phenolate] (**6**), [N → Sn] pyridine triphenyltin-[2-(1H-benzimidazol-2-yl)phenolate] (**7**), where **1** acts as a monodentate ligand bound through the phenol oxygen, were obtained. In the pentacoordinated compounds **4**–**7**, the tin atom has tbp geometry. The three phenyl groups are in equatorial positions, whereas the benzimidazole and the Lewis base are in apical positions. Two hexacoordinated tin compounds: diphenyltin-bis[2-(1H-benzimidazol-2-yl-κN)phenolate-κO] (**8**), dichlorotin-bis[2-(1H-benzimidazol-2-yl-κN)phenolate-κO] (**9**) bearing two bidentate ligands are reported. The coplanar ligands in **8** and **9** form six membered rings by oxygen and nitrogen coordination. The tin geometry is *all-trans* octahedral. In **8** the two phenyl groups, and in **9** the two chlorine atoms are perpendicular to the plane of the ligands. Compounds were identified in solution mainly by ^{1}H, ^{13}C and ^{119}Sn NMR and in the solid state by X-ray diffraction analysis.

1. Introduction

We are currently investigating the chemistry of organotin compounds derived from polyfunctional planar aromatic ligands, such as diphenolamines [1], diphenoloxamides [2–4] and thiolamines derived from benzimidazole [5,6]. The rigid framework of the aromatic ligands allows the synthesis of hypervalent tin compounds having diverse structures and inter- and intramolecular weak interactions. The relevance of these compounds is based on their structure and tin hypervalence, as well as on the wide number of applications of tin compounds as biocides and plaguicides [7–13] and antiinflamatories [14] along with the well known biocidal and pharmacological activities of benzimidazole derivatives [15–17] and to their potential as anticancer, antibacterial [18,19] or DNA intercalating agents [20].

2. Results and discussion

2.1. General comments

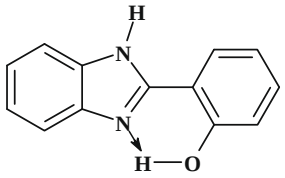
Herein we report a series of tin derivatives of 2-(1H-benzimidazol-2-yl)phenol (**1**). The ligand is a polyfunctional molecule suitable for the synthesis of structurally diverse coordination compounds which are influenced by the strong intramolecular hydrogen bond O–H···N (H···N distance is 1.63 Å) which affords a planar tetracyclic structure, as was found in solid state (Scheme 1) [21]. Previous preparation of phosphorus [22] and boron [23] heterocycles derived from **1** and the tris-chelate cobalt(III) complex obtained by bidentate coordination of **1** [21] suggest that the reaction of **1** with tin reagents could give the structures depicted in Scheme 2. However, their resulting derivatives, described in Schemes 3 and 5 were not the structures which had been expected as we will discussed later. Reactions of R_2SnX_2 (X = OR, Cl; R = Me, Et, Bu, C_6H_5) and ligand **1** were previously reported, however the products were only characterized by elemental analysis, UV and IR, [24] therefore, a detailed structural analysis was justified. We have performed the reactions of ligand **1** with $(C_6H_5)_3SnCl$, $(C_6H_5)_2SnCl_2$ and $SnCl_4$, and the corresponding characterizations of the products were carried out by NMR and X-ray diffraction.

2.2. Reaction of **1** with $SnPh_3Cl$

The equimolar reaction of $SnPh_3Cl$ with the sodium salt (**2**) of compound **1** was performed in dry THF. The (THF-d_8) solution of the reaction product **3** presented a ^{119}Sn NMR signal at −88.5 ppm, which corresponded to a tetracoordinated $Sn(Ph)_3OR$

* Corresponding author. Tel.: +55 5061 3720; fax: +55 5061 3389.
E-mail address: aflores@cinvestav.mx (A. Flores-Parra).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.10.037

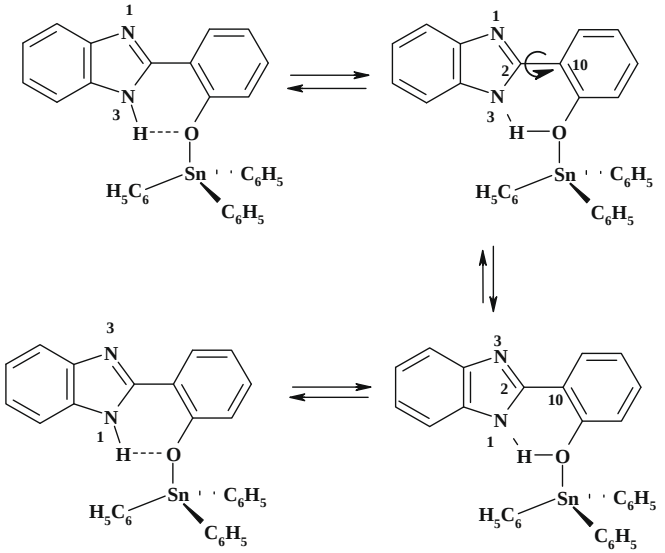


Scheme 1. 2-(1H-benzimidazol-2-yl)phenol (**1**).

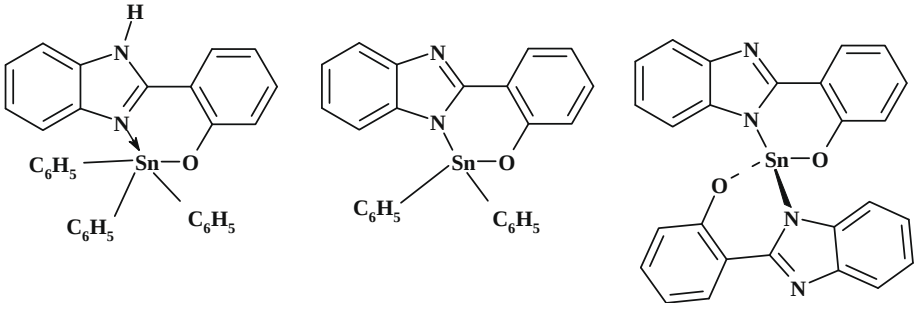
tin atom, as it was confirmed by comparison with $Sn(Ph)_3O$-1-naphtyl (−91.8 ppm) [25,26]. The chemical shift indicated that the reaction involved the substitution of the OH proton by the tin atom and that N → Sn coordination was absent, which was confirmed by comparison with the ^{119}Sn resonance (−189.9 ppm) of a pentacoordinated tin derivative of $Sn(Ph)_3$-8-hydroxyquinoline where a similar O–Sn bond was formed together with a strong intramolecular N → Sn coordination [25,26]. An explanation for the lack of N → Sn intramolecular coordination in compound **3** was found in the strong hydrogen bond between the N–H and the oxygen of the O-$SnPh_3$ group, which stabilizes the tautomer with the N-lone pair on the opposite side to the tin coordination, Scheme 3. The tin resonance of compound **3** in THF showed that THF was not significantly coordinated to the tin atom at room temperature.

The structure of **3** was confirmed by its ^1H spectrum (dry THF-d_8) which showed the N–H proton at 12.62 ppm and by the ^{13}C spectrum where the C10, C11 and C12 signals were shifted to higher frequencies when compared with those of **1**, due to the O–Sn bond formation. The simplicity of benzimidazole protons in the ^1H spectrum of **3** at room temperature [one signal at 7.80 ppm for H4 and H7 and another at 7.15 ppm for H5 and H6] indicated the fast N–H tautomerism between N1 and N3. This phenomenon was also observed in the ^{13}C spectrum which showed only three signals for the phenylene carbons atoms [C4–C7 (114.4); C5–C6 (122.3) and C8–C9 (137.9 ppm)]. The N–H bond dissociation and tautomerism could be assisted by the O–H hydrogen bond, promoting the C2–C10 bond rotation, and the exchange of the N1 and N3 positions, Scheme 4.

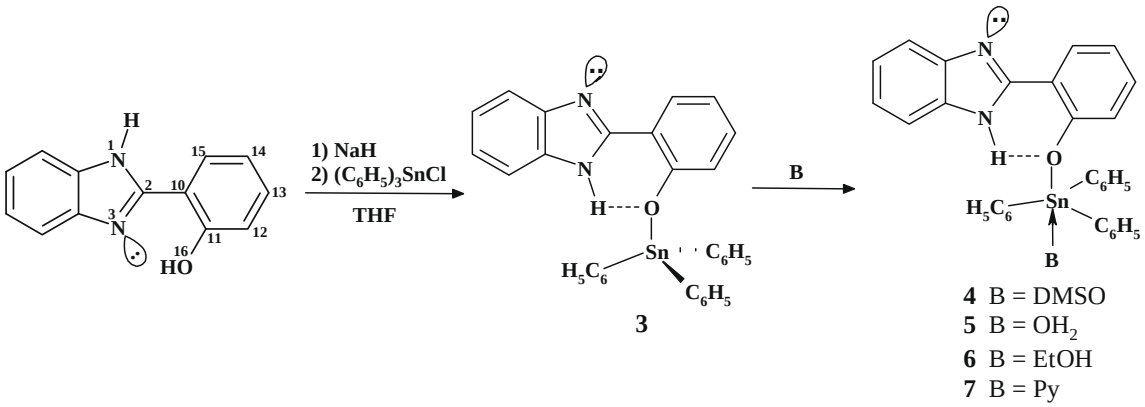
Lewis base additions (DMSO, H_2O/DMSO, EtOH, or pyridine) to compound **3** resulted in the corresponding pentacoordinated compounds **4–7** (Scheme 3) which were analyzed in solution. The ^{119}Sn



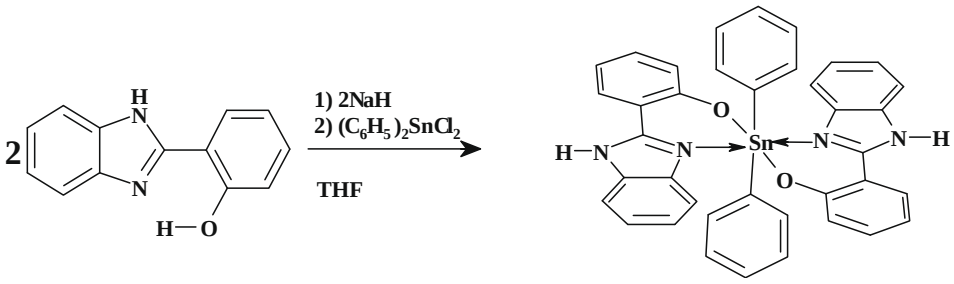
Scheme 4. Proton tautomerism in compound **3**.



Scheme 2. Expected compounds derived from ligand **1** and Ph_3SnCl, Ph_2SnCl_2 and $SnCl_4$.



Scheme 3. Tin compounds synthesized from ligand **1** and Ph_3SnCl.



Scheme 5. Synthesis of compound **8**.

NMR spectrum of compound **3** dissolved in anhydrous DMSO gave a signal at −265.5 ppm, for the DMSO coordinated compound **4**. A similar experiment in wet DMSO, showed two signals (−227.8 and −265.5 ppm), where the second one was assigned to **4**, and the first to the coordinated water compound **5**. Addition of ethanol gave complex **6** (−223.2 ppm) and pyridine afforded complex **7** (−218.8 ppm), Table 1. The tin pentacoordination was also confirmed from the coupling constants values $^{1}J(^{119/117}Sn–^{13}C)$ = 786.4/753.3 Hz measured at the ^{13}C spectrum of **6**. The ^{1}H spectra of compounds **4–7** showed the characteristic hydrogen bound N–H signals [12.62 to 13.25 ppm], Table 1.

Compounds **4–7** afforded suitable crystals for X-ray diffraction analyses, Fig. 1. In all structures, the tin atom is pentacoordinated with tbp geometry. The three phenyl groups are in equatorial positions, whereas the benzimidazole and the Lewis base are in apical positions. The ligand presented two intramolecular hydrogen bonds (N–H···O and C–H···N) which maintain its planar conformation. All the crystals were of good quality, except compound **4** which was poor. However the structure was determined with clarity. The crystal data for compounds **4–6** and for **7–8** are in Tables 2 and 3, respectively. Selected bond lengths and angles for **4–7** are in Table 4 and for **8** in Table 5.

Intermolecular interactions are observed in **5**, formed through the H_2O molecule coordinated to tin, Fig. 2. The crystal lattice of **6** shows intramolecular H···O bonds and an intermolecular N1 H36 bond [2.10(5) Å] forms a polymer, Fig. 3. Compound **7** crystallized with two independent molecules [**7a** and **7b**] in the asymmetric cell which differs slightly in the Sn–Ph bonds conformations, Fig. 4.

2.3. Reaction of *1* with $SnPh_2Cl_2$

The sodium anion of ligand **1** was reacted with a half equivalent of Ph_2SnCl_2. The ^{119}Sn spectrum of the reaction mixture showed a ^{119}Sn resonance at −573 ppm, characteristic of a hexacoordinated tin atom. The elemental analysis and the TOF high resolution mass spectrum [MS(TOF), Calc. $(C_{32}H_{23}N_4O_2Sn)^+$ 615.0837 amu. Exp. 615.0848 amu (error = 1.7 ppm)] showed that compound **8** contains a tin atom with two deprotonated benzimidazole ligands and two phenyl groups, Scheme 5. From different THF solutions crystals of two polymorphs of **8** were obtained and analyzed by X-ray diffraction [polymorph **8a** is monoclinic, ($P2_1$) whereas **8b** is triclinic ($P\bar{1}$)].

Both polymorphs contain one molecule of **8** and two of THF. The tin atom is hexacoordinated with *all-trans* octahedral geometry. Four of the six positions are occupied by two bidentate planar ligands bound by the oxygen and one nitrogen and lie in the same plane. The two other positions are occupied by two phenyl groups perpendicular to the plane of the ligands, Fig. 5. The tin bonds lengths: Sn–O (∼2.11 Å), and Sn–C (∼2.17 Å) are characteristic of covalent bonds, whereas Sn–N (∼2.28 Å) correspond to strong coordination bonds, Scheme 5. The molecule is rigid due to the π-delocalization and cooperative intramolecular hydrogen bonds. Each phenol oxygen atom becomes pentacoordinated due to its hydrogen bonds to three C–H groups, Fig. 6. The acidic N–H protons are bound to the THF oxygen (2.15 Å), Fig. 7.

Crystals of compound **8** are insoluble in polar and non polar solvents, therefore, their characterization in solution was performed before its precipitation or crystallization. An explanation for this insolubility could be found in the crystal packing of **8**, where the ligands form a staircase framework stabilized by intermolecular π-stacking with other molecules. The Sn-phenyl groups contribute to the close packing of the molecules by C–H···π-interactions, The oxygen atoms of the THF molecules form bifurcated hydrogen bonds with the ligands covering the labile protons of the molecules, therefore the crystals offer C–H and aromatic rings surfaces which could explain the crystals insolubility, Figs. 7 and 8.

Table 1
^{119}Sn, ^{1}H and ^{13}C selected NMR Data (δ, ppm) of compounds **3–7**.

Compound	δ ^{119}Sn {solvent}	δ ^{1}H	δ $^{13}C_i$ [$^{1}J(^{13}C,^{119/117}Sn)$]	δ $^{13}C_o$ [$^{2}J(^{13}C,^{119/117}Sn)$]	δ $^{13}C_m$ [$^{3}J(^{13}C,^{119/117}Sn)$]	δ $^{13}C_p$ [$^{4}J(^{13}C,^{119}Sn)$]
$(C_6H_5)_3SnCl$	−47.0 {$CDCl_3$}	–	136.2 [613.8/586.4]	134.2 [49.3]	130.6 [64.3/61.7]	133.4 [13.4]
$(C_6H_5)_3SnCl$	−226.8 {DMSO-d_6}	–	143.8 [810.6]	136.1 [47.9]	128.5 [71.3]	129.1 [14.6]
$(C_6H_5)_3SnCl$	− 203.5 {pyridine}	–	143.3 [783.2]	137.0 [45.9]	129.1 [70.3]	129.8 [14.6]
3	−88.5 {THF-d_8}	N–H 12.62	140.5	136.4 [44.6]	128.4	129.3
4	−265.5 {DMSO-d_6}	N–H 13.25	142.1	136.1 [43.9]	128.9	129.5
5	−227.8 {DMSO-d_6}	O–H 11.84 N–H 13.25	142.1	136.1 [43.9]	128.9	129.5
6	−223.2 {$CDCl_3$}	O-H 11.51 N–H 12.78	142.9 [786.4/753.3]	136.1 [46.9]	128.2 [69.2]	128.9
7	−218.8 {$CDCl_3$}	N–H 12.62	140.2	136.6 [43.7]	129.1 [67.9]	130.0

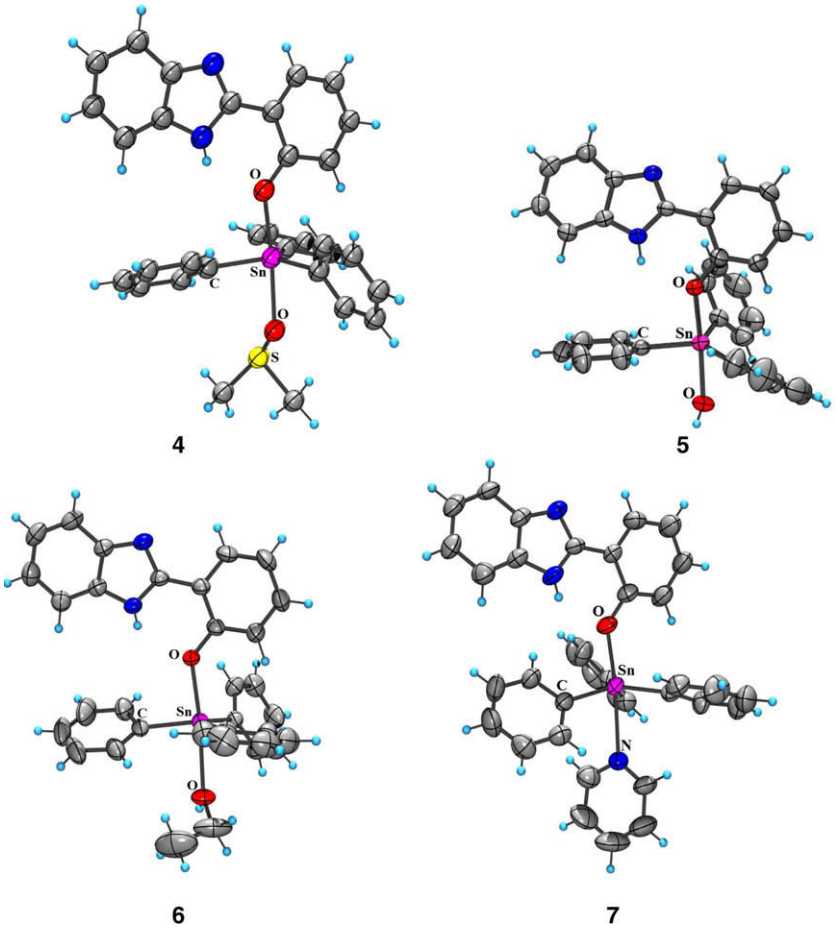


Fig. 1. ORTEP diagrams for compounds **4–7**.

2.4. Reaction of *1* with tin tetrachloride

One equivalent of $SnCl_4$ was added to two equivalents of the sodium anion of ligand **1** dissolved in THF at −60 °C, and then stirred at room temperature for three days. From the solution, the ^{119}Sn spectrum showed a signal for a hexacoordinated compound **9** (−614 ppm). The solvent was evaporated and a very insoluble white powder was obtained which was purified by washing with water, THF and MeOH. The elemental analysis of the solid corresponds to a molecule with two deprotonated ligands, a tin and two chlorine atoms. Some crystals were formed in a THF solution after the addition of a few drops of DMSO. The structure of compound **9** was determined even though the crystal was disordered. Compound **9** is similar to **8**. In **9** the two Sn–Cl bonds atoms are perpendicular to the plane formed by the benzimidazoles, Fig. 9. The quality of the crystals prevents the reporting of accurate angles and bond lengths.

3. Summary

Expected compounds, in Scheme 2, were not found, and in their place five new triphenyltin compounds were synthesized, where **1** acts as a monodentate ligand, bound through the phenol oxygen. The monodentate benzimidazole forms a planar tetracyclic structure, due to the strong intramolecular N–H···O hydrogen bond. Compound **3** in dry THF is tetracoordinated. It is very reactive and in the presence of Lewis bases or water traces gives the H_2O, EtOH, DMSO and pyridine pentacoordinated tin adducts **4–7**. $SnPh_2Cl_2$ and $SnCl_4$ reactions afford molecules with two coplanar benzimidazoles, where the tin is included in the plane of the ligands. The coordination produces six membered rings. The hexacoordinated tin has *all-trans* octahedral geometry.

4. Experimental

4.1. General comments

Vacuum line techniques were employed for all manipulations of air and moisture sensitive compounds. THF was dried by distillation from Na-benzophenone under a N_2 atmosphere prior to use. Dry $CDCl_3$, DMSO-d_6, THF-d_8, $SnPh_3Cl$, $SnPh_2Cl_2$ and $SnCl_4$ were purchased from Aldrich and used without further purification. The melting points were obtained on a Mel-Temp II apparatus and are uncorrected. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett–Packard HP 5989 spectrometer. High resolution mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source. Elemental analyses were performed on Eager 300 or on Flash 1112 Thermo Finnigan equipment. NMR spectra were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Advance 300 MHz. ^1H, ^{13}C [Ξ 25.145020, $Si(CH_3)_4$], ^{15}N [Ξ 10.136767, CH_3NO_2] and ^{119}Sn [Ξ = 37.290 $Sn(CH_3)_4$]. ^{119}Sn spectra were obtained by single pulse with broad decoupling experiments. The assignment of ^1H and ^{13}C data were based on 2D experiments: $^1H/^1H$ COSY, $^1H/^{13}C$ HETCOR and $^1H/^{13}C$ COLOC. IR spectra were obtained in KBr disc using a FT Spectrum GX Perkin–Elmer spectrometer.

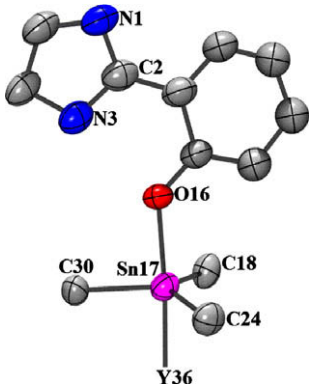
Table 2
Crystal data and structure refinement for compounds **4–6**.

Compounds	**4**	**5**	**6**
Empirical formula	$C_{33}H_{30}N_2O_2SSn$	$C_{35}H_{34}N_2O_3Sn$	$C_{33}H_{30}N_2O_2Sn$
Formula weight	637.37	649.36	605.3
Temperature (K)	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	10.0488 (3)	10.18670 (10)	9.80120 (10)
b (Å)	30.0103 (10)	19.2769 (3)	10.7383 (2)
c (Å)	10.0271 (4)	15.8509 (3)	15.9763 (3)
α (°)	90	90	71.6371 (7)
β (°)	99.893 (2)	91.7559 (7)	77.2214 (7)
γ (°)	90	90	62.9023 (7)
Volume (Å^3)	2978.88 (18)	3111.15 (8)	1414.66 (4)
Z	4	4	2
Calculated ρ (mg/m^3)	1.421	1.386	1.421
μ (mm^{-1})	0.96	0.86	0.94
$F(000)$	1296	1328	616
Crystal size (mm)	0.5 × 0.05 × 0.05	0.3 × 0.2 × 0.15	0.5 × 0.5 × 0.2
Crystal color	Colourless prism	Light brown prism	Orange prism
θ range	2.057–28.378	2.571–27.859	3.408–27.465
Limiting indices	$-12 \le h \le 12$; $-39 \le k \le 33$; $-20 \le l \le 20$	$-11 \le h \le 13$; $-13 \le l \le 13$ $-13 \le k \le 13$;	$-12 \le h \le 12$; $-25 \le k \le 22$; $-19 \le l \le 20$
Reflections collected	11352	39453	23525
Independent reflections	6644	7400	6370
$[R_{(int)}]$	0.125	0.07	0.032
Completeness to θ	25.3°, 96.8%	27.9°, 99.7%	25.8°, 99.5%
Observed reflections	2173	3219	5353
T_{max}, T_{min}	0.9532, 0.9532	0.88, 0.85	0.83, 0.76
Goodness-of-fit (GOF) on F^2	0.7652	1.0979	1.0684
R (all data)	0.3189	0.0838	0.0343
wR (all data)	0.3579	0.0565	0.0417
Final R_1	0.1222 ($I > 2.5\sigma$)	0.0249 ($I > 3.0\sigma$)	0.0268 ($I > 3.0\sigma$)
Final wR_2	0.1279	0.0285	0.036

Table 3
Crystal data and structure refinement for compounds **7–8**.

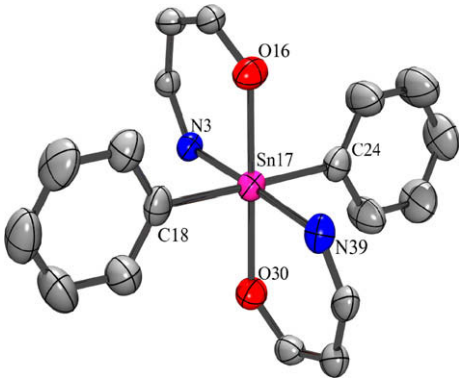
Compounds	**7**	**8a**	**8b**
Empirical formula	$C_{36}H_{29}N_3OSn$	$C_{38}H_{28}N_4O_2Sn \cdot 2(C_4H_8O)$	$C_{38}H_{28}N_4O_2Sn \cdot 2(C_4H_8O)$
Formula weight	638.34	835.57	835.57
Temperature (K)	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	Pn	$P2_1$	$P\bar{1}$
a (Å)	9.7034 (2)	9.7634 (2)	9.7521 (3)
b (Å)	17.6907 (3)	20.7618 (3)	9.7643 (3)
c (Å)	17.4471 (3)	9.7963 (2)	10.4988 (4)
α (°)	90	90	87.6687 (15)
β (°)	93.7878 (7)	92.9310 (10)	85.8673 (15)
γ (°)	90	90	87.0848 (15)
Volume (Å^3)	2988.43 (10)	1983.17 (6)	995.14 (6)
Z	4	2	1
Calculated ρ (mg/m^3)	1.419	1.399	1.394
μ (mm^{-1})	0.89	0.69	0.69
$F(000)$	1296	860	430
Crystal size (mm)	0.2 × 0.17 × 0.1	0.15 × 0.08 × 0.08	0.23 × 0.15 × 0.12
Crystal color	Light brown prism	Colorless prism	Colorless prism
θ range	3.447–27.504	3.48–27.489	1.946–30.411
Limiting indices	$-12 \le h \le 12$; $-22 \le k \le 22$; $-12 \le l \le 12$	$-12 \le h \le 12$; $-22 \le l \le 22$ $-13 \le k \le 13$;	$-10 \le h \le 13$; $-24 \le k \le 26$; $-14 \le l \le 13$
Reflections collected	13205	8781	14285
Independent reflections	12973	8781	5167
$[R_{(int)}]$	0.024	0	0.087
Completeness to θ	26.7°, 99.5%	25.6°, 98.8%	26.8°, 96.4%
Observed reflections	8084	6344	2315
T_{max}, T_{min}	0.915, 0.8561	0.946, 0.946	0.92, 0.65
Goodness-of-fit (GOF) on F^2	1.018	1.0211	1.0284
R (all data)	0.0788	0.0701	0.1106
wR (all data)	0.0504	0.0659	0.1169
Final R_1	0.0359 ($I > 3.0\sigma$)	0.0403 ($I > 3.0\sigma$)	0.0468 ($I > 3.0\sigma$)
Final wR_2	0.0367	0.0454	0.0603

Table 4
Selected bond lengths (Å) and angles (°) for compounds **4–7**.



Bond lengths	4	5	6	7a	7b
C2–N1	1.31(2)	1.330(4)	1.333(3)	1.330(7)	1.330(8)
C2–N3	1.39(3)	1.367(4)	1.355(4)	1.351(8)	1.351(8)
C8–N1	1.39(3)	1.386(5)	1.388(4)	1.396(7)	1.385(8)
C9–N3	1.40(3)	1.372(4)	1.372(4)	1.385(9)	1.362(9)
C18–Sn	2.11(2)	2.129(4)	2.132(3)	2.114(7)	2.127(8)
C24–Sn	2.13(2)	2.126(4)	2.122(3)	2.126(6)	2.122(7)
C30–Sn	2.15(2)	2.122(3)	2.123(3)	2.112(6)	2.117(7)
O(N)36–Sn	2.32(1)	2.349(2)	2.505(2)	2.559(5)	2.541(6)
O16–Sn	2.12(1)	2.125(2)	2.105(2)	2.101(4)	2.113(5)
Bond angles	**4**	**5**	**6**	**7a**	**7b**
O(N)36–Sn–C30	87.8(6)	90.1(1)	86.4(1)	83.2(2)	84.6(2)
O(N)36–Sn–C24	87.3(6)	86.3(1)	84.07(9)	86.2(2)	86.8(2)
C30–Sn–C24	118.9(8)	125.0(1)	121.1(1)	122.7(2)	117.7(3)
O(N)36–Sn–O16	176.0(5)	176.5(1)	174.39(8)	173.1(2)	172.9(2)
C30–Sn–O16	88.3(6)	86.8(1)	87.98(9)	89.9(2)	88.3(2)
C24–Sn–O16	94.2(6)	94.2(1)	98.7(1)	97.3(2)	96.0(2)
O(N)36–Sn–C18	83.2(7)	86.9(1)	86.93(9)	86.1(2)	84.1(2)
C30–Sn–C18	118.4(8)	113.3(1)	118.5(1)	113.7(2)	115.9(3)
C24–Sn–C18	121.4(8)	121.2(2)	118.8(1)	121.5(2)	124.4(3)
O16–Sn–C18	99.1(7)	95.8(1)	95.88(9)	96.9(2)	99.5(2)

Table 5
Selected bond lengths (Å) and angles (°) for compound **8**.



Bond lengths	8a	8b
Sn–O16	2.114(4)	2.112(4)
Sn–O30	2.105(4)	
Sn–N3	2.284(4)	2.299(4)
Sn–N39	2.288(4)	
Sn–C18	2.167(5)	2.176(6)
Sn–C24	2.152(5)	
Bond angles	**8a**	**8b**
N3–Sn–O16	83.3(2)	82.8(2)
N3–Sn–C18	90.6(2)	91.0(2)
O16–Sn–C18	90.0(2)	91.4(2)
N3–Sn–C24	88.7(2)	89.0(2)
O16–Sn–C24	88.7(2)	88.6(2)
C18–Sn–C24	178.6(2)	179.9(1)
N3–Sn–O30	95.9(2)	97.2(2)
O16–Sn–O30	179.2(2)	179.9(1)
C18–Sn–O30	89.9(2)	88.6(2)
C24–Sn–O30	91.4(2)	91.4(2)
N3–Sn–N39	178.0(5)	179.9(1)
O16–Sn–N39	98.7(4)	97.2(2)
C18–Sn–N39	89.3(2)	89.0(2)
C24–Sn–N39	91.4(2)	91.0(2)
O30–Sn–N39	82.1(4)	82.8(2)

4.2. Syntheses

4.2.1. Triphenyltin [2-(1H-benzimidazol-2-yl)phenolate] (**3**)

Compound **1** (200 mg, 0.95 mmol) and NaH (26 mg, 1.08 mmol) were dissolved in dry THF (40 mL) and the reaction mixture was stirred for 1 h at r.t., then $(C_6H_5)_3SnCl$ (367 mg, 0.95 mmol) was added and the mixture stirred for 12 h. It was filtered and the solvent evaporated under vacuum. A light brown crystalline powder was obtained which corresponded to compound **3**. NMR (THF-d_8), δ (ppm), ^{1}H: 7.80 (2H, H-4, H-7), 7.15 (2H, H-5, H-6), 6.86 (H-12), 7.45 (H-13), 6.79 (H-14), 7.95 (H-15), 12.62 (N–H); [$SnPh_3$] group: 7.50 (6H, H_o), 7.36 (6H, H_m), 7.35 (3H, H_p). ^{13}C: 152.4 (C2), 114.4 (C4, C7), 122.3 (C5, C6), 137.9 (C8, C9), 114.5 (C10), 160.1 (C11), 118.3 (C12), 131.0 (C13), 118.3 (C14), 126.0 (C15); $SnPh_3$ group: 140.9 ($3C_i$), 136.4 ($6C_o$), 128.4 ($6C_m$), 129.3 ($3C_p$).

4.2.2. [O → Sn] dimethylsulfoxide triphenyltin-[2-(1H-benzimidazol-2-yl)phenolate] (**4**)

Compound **3** was dissolved in DMSO-d_6, and the adduct **4** characterized by NMR. From the NMR tube, crystals suitable for X-ray diffraction analyses were formed. NMR (DMSO-d_6), δ (ppm). ^{1}H: 7.87 (2H, H-4, H-7), 7.10 (2H, H-5, H-6), 6.60 (H-12), 6.75 (H-13), 6.65 (H-14), 8.13 (H-15), 11.92 (N–H); [$SnPh_3$] group: 7.55 (6H, H_o), 7.36 (9H, 6H$_m$ and 3H$_p$). ^{13}C: 152.1 (C2), 114.4 (C4, C7), 121.3 (C5, C6), 136.7 (C8, C9), 161.9 (C11), 120.0 (C12), 130.2 (C13), 118.0 (C14), 128.2 (C15); $SnPh_3$ group: 142.1 ($3C_i$), 136.1 ($6C_o$), 128.9 ($6C_m$), 129.4 ($3C_p$).

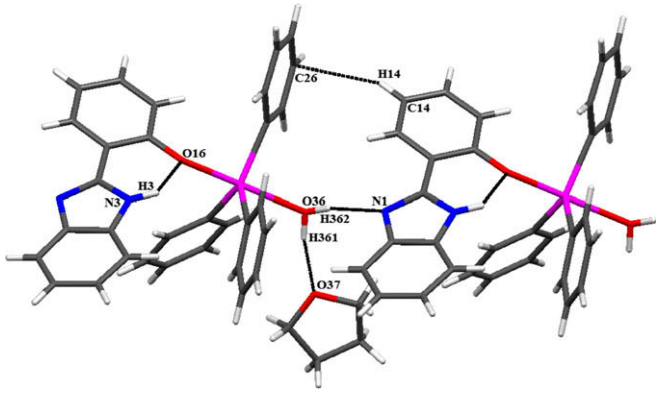


Fig. 2. Interactions in the lattice of **5**. [Distances: O16···H3 = 2.09 Å, O37···H361 = 1.86(4) Å, N1···H362 = 1.96(5) Å and C26···H14 = 2.85 Å].

4.2.3. [O → Sn] aqua triphenyltin-[2-(1H-benzimidazol-2-yl)-phenolate] (**5**)

Compound **3** (100 mg) was slowly crystallized in 20 mL of wet THF (3 weeks) to give brown pale crystals, (82 mg, 80%). At 148 °C crystals lost solvent, they solidify again at 168 °C, and do not melt below 340 °C. NMR (DMSO-d_6), δ (ppm), ^{1}H: 7.87 (2H, H-4, H-7), 7.10 (2H, H-5, H-6), 6.60 (H-12), 6.75 (H-13), 6.65

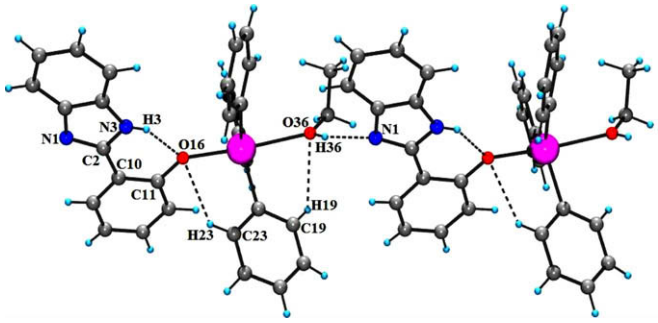


Fig. 3. Some H-bonds in the lattice of **6**. [Distances: O16···H3 = 2.19(4) Å, O16···H23 = 2.62(4) Å, O36···H19 = 2.59(5) Å and N1···H36 = 2.10(5) Å].

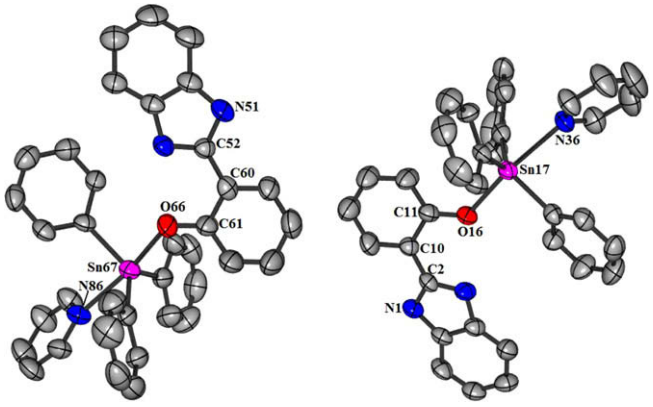


Fig. 4. ORTEP diagram of **7a** (right) and **7b** (left).

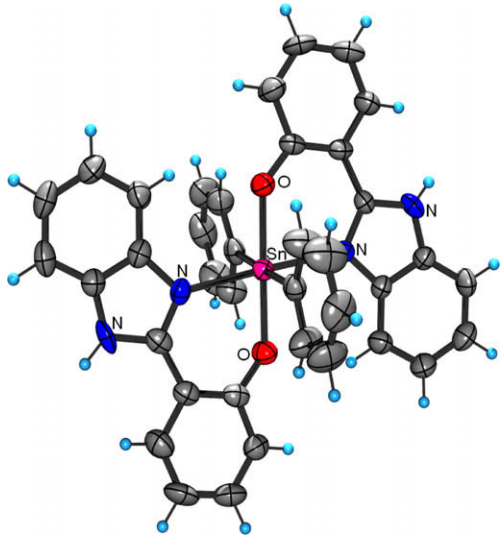


Fig. 5. ORTEP diagram of **8**.

(H-14), 8.13 (H-15), 13.25 (N–H); $SnPh_3$ group: 7.55 (6H, H_o), 7.36 (9H, 6H$_m$ and 3H$_p$); H_2O: 11.51 (2H). ^{13}C: 152.1 (C2), 114.4 (C4, C7), 121.3 (C5, C6), 136.7 (C8, C9), 114.5 (C10), 161.9 (C11), 120.0 (C12), 130.2 (C13), 118.0 (C14), 128.2 (C15); $SnPh_3$ group: 142.1 (3C$_i$), 136.1 (6C$_o$), 128.9 (6C$_m$), 129.4 (3C$_p$). M.S.: *m*/*z* (%): 560(0.1) [M−H_2O], 483(0.3) [M−Ph], 351(100) [M−L]. IR (KBr, *ν* cm^{-1}):

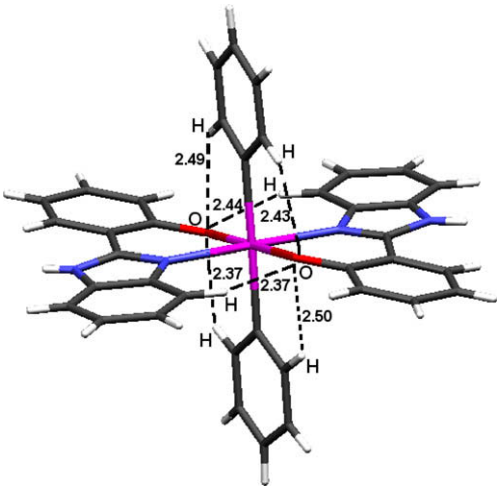


Fig. 6. Intramolecular interactions of compound **8**.

1603 (C=N), 731 (Sn–O). Anal. Calc. for $C_{31}H_{24}N_2OSn \cdot THF \cdot 2H_2O$: C, 63.00; H, 5.44; N, 4.20. Found: C, 63.36; H, 5.41; N, 3.98%.

*4.2.4. [O → Sn] ethanol triphenyltin-[2-(1H-benzimidazol-2-yl)-phenolate] (**6**)*

Compound **3** (100 mg) dissolved in EtOH afforded colorless crystals (85 mg, 79%). Dec at 310 °C. M.S.: *m*/*z* (%): 605(0.1) [M]$^+$, 559(1.1) [M−EtOH]$^+$, 210(100) [M−$SnPh_3EtOH$]$^+$. IR (KBr, *ν* cm^{-1}): 1653 (C=N), 733 (Sn–O). NMR ($CDCl_3$), *δ* (ppm) ^{1}H: 7.72 (2H, H-4, H-7), 7.12 (2H, H-5, H-6), 6.59 (H-12), 6.95 (H-13), 6.61 (H-14), 8.13 (H-15), 12.78 (N–H); $SnPh_3$ group: 7.92 (6H, H$_o$), 7.34 (6H, H$_m$) 7.33 (3H, H$_p$); EtOH: 3.60 (2H, CH_2), 0.88 (3H, CH_3), 11.51 (1H, OH). ^{13}C: 152.5 (C2), 114.2 (C4, C7), 122.3 (C5, C6), 136.8 (C8, C9), 114.4 (C10), 160.8 (C11), 119.0 (C12), 130.9 (C13), 117.2 (C14), 126.9 (C15); $SnPh_3$ group: 142.9 (3C$_i$), 136.1 (6C$_o$), 128.2 (6C$_m$), 128.9 (3C$_p$); EtOH: 57.4 (CH_2), 18.2 (CH_3). Anal. Calc. for $C_{31}H_{24}N_2OSn \cdot C_2H_6O$: C, 65.48; H, 5.00; N, 4.63. Found: C, 65.03; H, 5.20; N, 4.41%.

*4.2.5. [N → Sn] pyridine triphenyltin-[2-(1H-benzimidazol-2-yl)-phenolate] (**7**)*

To a solution of **3** (100 mg) in THF (10 mL) two equivalents of dried pyridine were added and the solution was kept aside for few days. Brown pale crystals were obtained (90 mg, 82%,). M.S.: *m*/*z* (%): 482(0.1) [M−Py and Ph]$^+$, 405(0.1) [M−Py and 2Ph]$^+$, 351(17.0) [M−L]$^+$, 210(6.0) [M−Ph_3Sn]$^+$, 78(100) [M−LPh_3Sn]$^+$. IR (KBr, *ν* cm^{-1}): 1620 (C=N), 739 (Sn–O), 545 (Sn–C), 455 (Sn–N). NMR ($CDCl_3$), *δ* (ppm) ^{1}H: 7.77 (2H, H-4, H-7), 7.16 (2H, H-5, H-6), 6.62 (H-12), 6.96 (H-13), 6.63 (H-14), 8.25 (H-15), 12.62 (N–H); $SnPh_3$ group: 7.72 (6H, H$_o$), 7.40 (6H, H$_m$), 7.45 (3H, H$_p$); [Py]: 8.39 (2H, H$_o$), 7.27 (2H, H$_m$), 7.70 (1H, H$_p$). ^{13}C: 153.1 (C2), 114.7 (C4, C7), 122.1 (C5, C6), 140.29 (C8, C9), 116.8 (C10), 161.4 (C11), 120.0 (C12), 131.0 (C13), 117.9 (C14), 128.1 (C15); $SnPh_3$ group: 140.2 (3C$_i$), 136.6 (6C$_o$), 129.1 (6C$_m$), 130.0 (3C$_p$); [Py]: 149.4 (2C$_o$), 124.3 (2C$_m$), 137.1 (C$_p$). Anal. Calc. for $C_{36}H_{29}N_3OSn$: C, 67.74; H, 4.58; N, 6.58. Found: C, 67.60; H, 4.44; N, 6.44%.

*4.2.6. Diphenyltin-bis[2-(1H-benzimidazol-2-yl-κN)phenolate-κO] (**8**)*

To a solution of **1** (250 mg, 1.2 mmol) in 40 mL of THF, NaH was added (68 mg, 2.8 mmol). The reaction mixture was stirred for 2 h. Then Ph_2SnCl_2 (145 mg, 0.6 mmol) was added and the mixture was stirred for 3 days. The soluble phase in THF was evaporated under

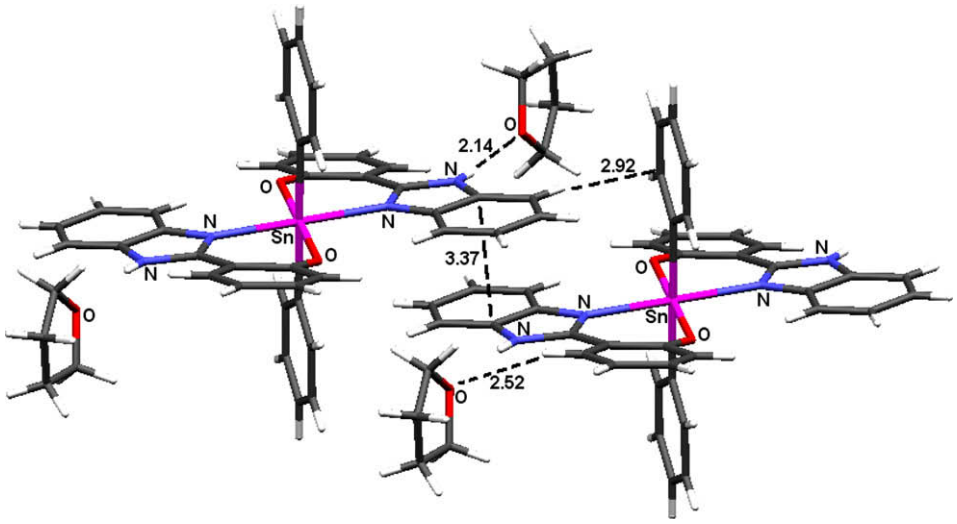


Fig. 7. Intermolecular interactions in the crystal of **8b**.

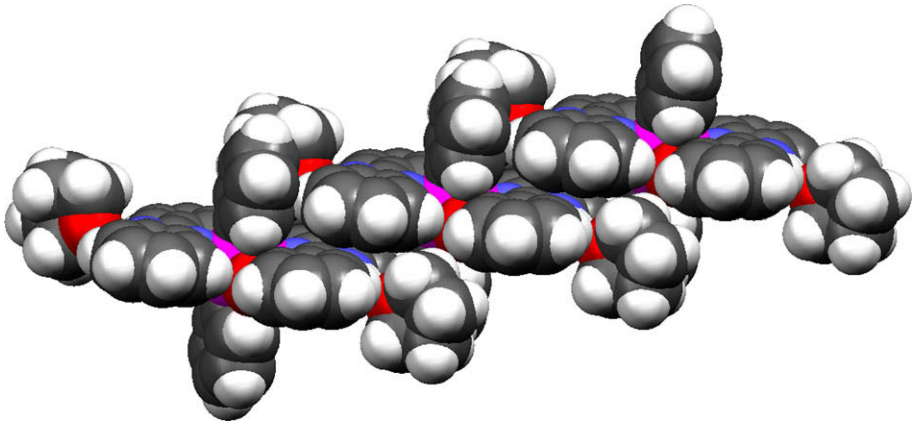


Fig. 8. Close staircase packing in compound **8b**.

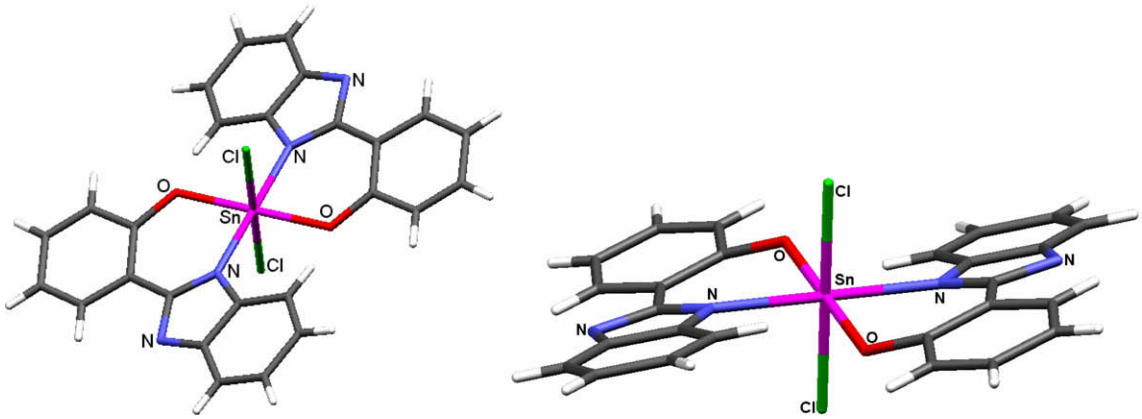


Fig. 9. Views of the crystalline structure of compound **9**.

vacuum to give a light brown powder which after crystallization in THF, affords colorless crystals. Dec ≈ 300 °C. NMR (THF-d_8): δ ^{119}Sn −573. IR (KBr, ν cm^{-1}): 1604 (C=N), 747 (Sn–O), 455 (Sn–N). M.S. (TOF), Calc. $(C_{32}H_{23}N_4O_2Sn)^+$ 615.0837 amu. Exp. 615.0848 amu (error = 1.7 ppm). Anal. Calc. for $C_{38}H_{28}N_4Sn \cdot 2THF \cdot 2H_2O$: C, 63.39; H, 5.55; N, 6.43. Found: C, 63.29; H, 5.24; N, 6.04%.

*4.2.7. Dichlorotin-bis[2-(1H-benzimidazol-2-yl-κN)phenolate-κO] (**9**)*

To a solution of **1** (500 mg, 2.4 mmol) in 60 mL of THF, NaH was added (69 mg, 2.9 mmol). The reaction mixture was stirred for 2 h and cooled to −60 °C and $SnCl_4$ (0.14 mL, 1.2 mmol) was added. The mixture was stirred for 3 days at r.t., then the solvent was evaporated under vacuum. A white powder was obtained, that

was washed with water, THF and MeOH. M.p. > 400 °C. IR (KBr, ν cm^{-1}): 1605 (C=N), 1246 (C–O), 750 (Sn–O). Anal. Calc. for $C_{26}H_{18}N_4O_2SnCl_2 \cdot 2H_2O$: C, 48.49; H, 3.44; N, 8.70. Found: C, 48.46; H, 3.49; N, 8.41%.

4.3. Crystallographic study

Data were measured on a Nonius Kappa CCD instrument with CCD area detector using graphite-monochromated Mo Kα radiation at 293 K, Intensities were measured using $\varphi + \omega$*scans (tables).* Crystals of **5**, **6** and **8** were obtained from THF, **7** from a $CDCl_3$–DMSO-d_6 mixture and **4** from DMSO-d_6. In the asymmetric unit of **5** and **8** there was also THF molecules non-coordinated to tin. All structures were solved using direct methods with SHELX-97 GM [27]. The refinement for all structures (based on F^2 of all data) was performed by full matrix least-squares techniques with crystals 12.84 [28]. All non-hydrogen atoms were refined anisotropically, the NH protons of **5**–**8** and those of the H_2O and EtOH of **5** and **6** were located in the difference map and their positions refined. The N–H of **4** was located in the difference map and including as riding atom.

Acknowledgments

Financial support from Conacyt-Mexico and Cinvestav is acknowledged as well as Conacyt-Mexico scholarships for A.E.-R. and A.P.-H., and J. Guthrie for valuable discussions.

Appendix A. Supplementary material

CCDC 692913, 692911, 692910, 692912, 692914, 692915 contains the supplementary crystallographic data for **4**, **5**, **6**, **7**, **8a**, **8b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.037.

References

[1] C. Camacho-Camacho, H. Tlahuext, H. Nöth, R. Contreras, Heteroatom Chem. 9 (1997) 321.
[2] R. Contreras, V.M. Jiménez-Pérez, C. Camacho-Camacho, M. Güizado-Rodríguez, B. Wrackmeyer, J. Organomet. Chem. 604 (2000) 229.
[3] V.M. Jiménez-Pérez, C. Camacho-Camacho, M. Güizado-Rodríguez, H. Nöth, R. Contreras, J. Organomet. Chem. 614/615 (2000) 283.
[4] V.M. Jiménez-Pérez, A. Ariza-Castolo, A. Flores-Parra, R. Contreras, J. Organomet. Chem. 691 (2006) 1584.
[5] A. Peña-Hueso, A. Esparza-Ruiz, I. Ramos-García, A. Flores-Parra, R. Contreras, J. Organomet. Chem. 693 (2008) 492.
[6] A. Esparza-Ruiz, A. Peña-Hueso, I. Ramos-García, A. Flores-Parra, R. Contreras, J. Organomet. Chem. 693 (2008) 2739.
[7] I. Wharf, Appl. Organomet. Chem. 14 (2000) 34.
[8] I. Wharf, H. Lamparski, R. Reeleder, Appl. Organomet. Chem. 11 (1997) 969.
[9] X. Song, Q. Duong, E. Mitrojorgji, A. Zapata, N. Nguyen, D. Strickman, J. Glass, G. Eng, Appl. Organomet. Chem. 18 (2004) 363.
[10] M. Jain, S. Maanju, R.V. Singh, Appl. Organomet. Chem. 18 (2004) 471.
[11] M. Jain, R.V. Singh, Appl. Organomet. Chem. 17 (2003) 616.
[12] A. Chaudhary, M. Agarwal, R.V. Singh, Appl. Organomet. Chem. 20 (2006) 295.
[13] S.K. Kamruddin, T.K. Chattopadhyaya, A. Roy, E.R.T. Tiekink, Appl. Organomet. Chem. 19 (1996) 513.
[14] M. Nath, S. Pokharia, G. Eng, X. Song, A. Kumar, Eur. J. Med. Chem. 40 (2005) 289.
[15] W.L. Drew, R.C. Miner, G.I. Marousek, S. Chou, J. Clin. Virol. 37 (2006) 124.
[16] I. Omar, T.M. O'Neill, S. Rossall, Plant Pathol. 55 (2006) 92.
[17] A. Joubert, X.-W. Sun, E. Johansson, C. Bailly, J. Mann, S. Neidle, Biochem. 42 (2003) 5984.
[18] A.V. Dolzhenko, W.-K. Chui, J. Heterocyclic Chem. 43 (2006) 95.
[19] A.V. Dolzhenko, W.-K. Chui, A.V. Dolzhenko, Heterocyclic Chem. 43 (2006) 1513.
[20] A.D. Settimo, G. Primofiore, F.D. Settimo, A.M. Marini, S. Taliani, S. Salerno, L.D. Via, J. Heterocyclic Chem. 40 (2003) 1091.
[21] X. Quezada-Buendía, A. Esparza-Ruiz, A. Peña-Hueso, N. Barba-Behrens, R. Contreras, A. Flores-Parra, S. Bernés, S.E. Castillo-Blum, Inorg. Chim. Acta 361 (2008) 2759.
[22] J. Hernández-Díaz, A. Flores-Parra, R. Contreras, Heteroatom Chem. 15 (2004) 307.
[23] A. Esparza-Ruiz, Ph.D. Thesis, Cinvestav Mexico, 2007.
[24] P.C. Vyas, N. Kaur, P. Vyas, A.K. Kaushal, Asian J. Chem. 7 (1995) 571.
[25] J. Holeček, A. Lyčka, R. Wagener, Collect. Czech., Chem. Commun. 51 (1986) 2116.
[26] B. Wrackmeyer, Ann. Rep. NMR Spectrosc. 38 (1999) 203.
[27] Sheldrick, SHELX-97-2 Users Manual, University of Göttingen, Germany, 1977.
[28] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Crystallogr. 36 (2003) 1487.