



Novel Organotin(IV) Complexes, Derived from Chiral Benzimidazoles: Synthesis, Molecular Structure and Spectral Properties

A. AKREMI^{*1}, A. NOUBIGH² and M. J. A. ABUALREISH³

^{1,2,3}Department of Chemistry, Faculty of Sciences, Northern Border University, Arar 91431, Kingdom of Saudi Arabia.

^aDepartment of Chemistry, Faculty of Science, El Manar University, Tunis, Tunisia. (permentant address)

^bLaboratory of Physical Chemistry of Materials , Preparatory Institute for Scientific and Technical Studies of La Marsa, 2070, Carthage University, Tunisia. (permentant address)

^cDepartment of Chemistry, Faculty of Science and Technology, Omdurman Islamic University, Sudan. (permentant address).

*Corresponding author E-mail: akrimimi@gmail.com

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ABSTRACT

The synthesis of homoleptic five-coordinate heteroaryl tin(IV) compounds using three chiral *N*-heterocyclic substituents, 2-(1-aminoethyl)benzimidazole (1), 2-(pyrrolidin-2-yl) benzimidazole (2) and 2-(1-amino-2-mercaptopropyl)benzimidazole (3) ligands is described. It has been found that ligands 1 and 2 behave in the bidentate *N,N* donor fashion, however, ligand 3 behave in the bidentate *N, S* donor. Overall ligands furnished, with moderate yields, their corresponding complexes $[(CH_3)_2Sn(C_9H_{10}N_3)Cl]$ (4), $[(CH_3)_2Sn(C_9H_{12}N_3)Cl]$ (5) and $[(CH_3)_2Sn(C_9H_{10}N_3S)Cl]$ (6). The characterization of all compounds by various spectroscopic methods UV-Vis, FT-IR, NMR, RX and elemental analyses provided insights into the diversity of complex formation.

Keywords: Five-coordinate, Heteroaryl tin(IV), Chiral benzimidazoles, Bidentate, Moderate yields.

INTRODUCTION

The organotin(IV) compounds have been widely investigated during the last few decades due to its multifaceted picture comprising a broad spectrum of biocidal properties, catalytic activity, use as stabilizers and appealing structural diversity¹⁻¹¹.

Structural studies have always been prominent in organotin chemistry, and particularly

the structural changes which occur between the solution and solid states. The tin atom in the complexes can be penta-coordinated¹²⁻¹⁴ or hexa-coordinated¹⁵⁻¹⁸ and the complexes often show fluxional stereochemical behavior^{16,19}.

On the other hand, benzimidazoles are known to exhibit a wide range of pharmacological properties including antiviral and antibacterial activities²⁰⁻²³. Another feature of the benzimidazole ligands is functionalization at the non-coordinated



nitrogen of the benzimidazole moiety, which provides a mode for modification of their properties.

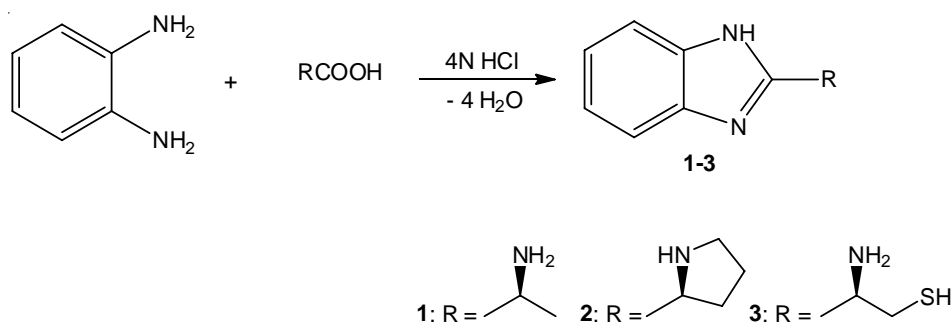
In addition, chiral organometallic complexes exhibit various pharmacological properties. The binding of chiral drugs to DNA usually shows stereoselectivity, which affect their pharmacokinetic profiles and biochemical activities²⁴⁻²⁶.

The present work describes the synthesis and characterization of three tin(IV) compounds derived

from chiral bidentate ligands 2-(1-aminoethyl)benzimidazole (1), 2-(pyrrolidin-2-yl)benzimidazole (2) and tridentate ligand 2-(1-amino-2-mercaptopyrpylyl) benzimidazole(3) (Scheme 1).

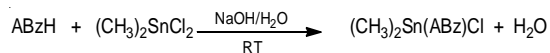
RESULTS AND DISCUSSIONS

2-Alkylaminobenzimidazoles (ABzH) 1-3 have been synthesized from reaction of *o*-phenylenediamine with L(+)-alanine, L(+)-proline and L(+)-cysteine respectively (Scheme 1)²⁷.



Scheme 1. The synthesis of ligands 1-3

Organotin complexes ($\text{Me}_2\text{SnABzCl}$) 4-6 were prepared by reaction of 2-Alkylaminobenzimidazole derivatives (ABzH) 1-3 with Me_2SnCl_2 in aqueous alkaline medium at room temperature (Scheme 2). The composition of isolated complexes was confirmed by the findings obtained from elemental analyses. It has been found that in all ABzH 1-3, one chloride was substituted by monoanionic ligands and yielded their corresponding mononuclear complexes. Thus, ligands (1) and (2) behave in the Bidentate *N, N* donor fashion, however, ligand 3 behave in the bidentate *N, S* donor. This result may be explained by the considerable simultaneous acidic and nucleophile behavior of sulfur in mercaptan group²⁹ (Table 1). Characterization of synthesized complexes and their nature of bonding were examined by spectroscopic investigations.

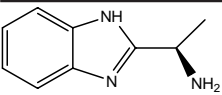
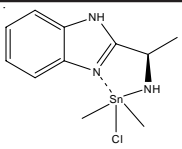
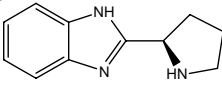
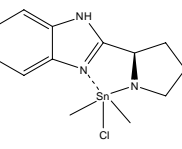
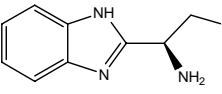
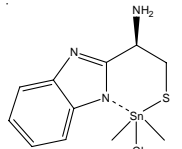


Scheme 2. Synthesis of complexes 4-6 with 2-alkylaminobenzimidazoles (ABzH)

FT-IR

All ligands (ABzH) 1-3 display broad medium stretching vibrational band ($\nu(\text{N}-\text{H})$) at 3450 cm^{-1} , which does not change on complexation²⁸. However, as well used as hydrochloride benzimidazoles, the broad bands at $3150\text{-}2400 \text{ cm}^{-1}$ corresponding to $\nu(\text{N}^+-\text{H})$ stretching vibration disappear after reaction to create new bands at $500\text{-}600 \text{ cm}^{-1}$ related to $\text{Sn}-\text{C}$ stretching vibration. Thus, a medium or relatively weak band at 1625 cm^{-1} with a small shoulder at 1522 cm^{-1} due to stretching vibration of $\text{C}=\text{N}$, were considerably become larger and sharper (1633 and 1507 cm^{-1}) confirming the complexation with tin atom in all complexes 4-6²⁸. Moreover, the medium intensity band at 2525 cm^{-1} , assigned to the $\nu(\text{S}-\text{H})$ vibration in the free ligand 3, has not been observed in the spectra of the corresponding complex (6), while, a short band has been appeared in the 421 cm^{-1} range assigned to the $\nu(\text{Sn}-\text{S})$ (Fig. 1). The above discussed data are in agreement with the deprotonation of the thiolic group after coordination on the tin center²⁹.

Table 1: Synthesized organotin complexes 4-6

ABzH	Proposed complex structure	Time reaction (mn)	Yield %
 1	 4	5	43
 2	 5	2	56
 3	 6	2	72

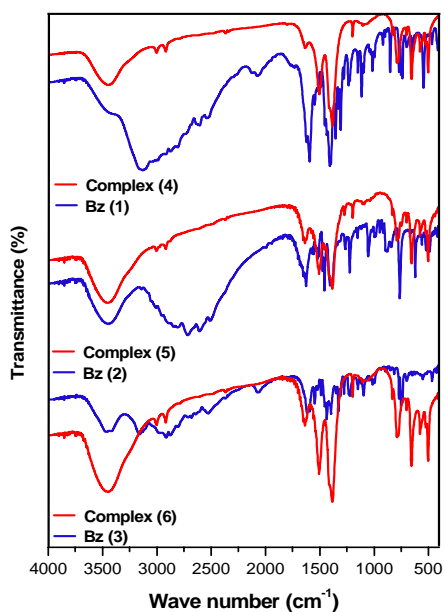


Fig. 1. Infra-red spectra of synthesized compounds

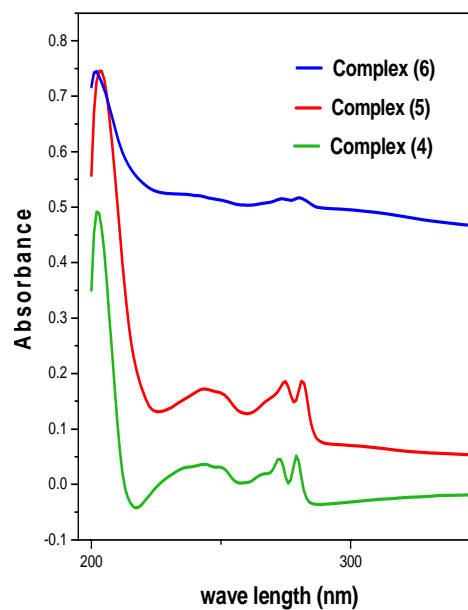


Fig. 2. Ultra-violet spectra of synthesized complexes

UV-Vis studies

The solutions of complexes 4-6 were prepared with DMSO at room temperature, and their concentration was 1×10^{-5} mol/L. The spectrum showed the general appearance of absorption maxima for 2-alkylaminobenzimidazole moiety³⁰ (Figure. 2).

NMR spectroscopy

¹H NMR spectroscopy

The ¹H NMR spectra of tin complexes were measured in DMSO-*d*₆ solution and exhibited signals with chemical shift values in accordance with their proposed structures. All complexes 4-6

spectra showed signals at 10.8-10.5, 7.6-7.1, 4.31-4.62, and 1.50 which were assigned to the NH proton, chiral CH, and the $\text{CH}_3\text{-Sn}^{31}$, correspondingly. The latter signals confirm simultaneously the presence of the tryptophan moiety in the complexes 4-6³², and the non-coordination of -NH- group of tryptophan moiety on the tin atom²⁸. In addition, the ligands (1) and (3) revealed NH_2 proton signal at 1.61-1.76 ppm³³ which has disappeared in the complexes (4) and (5) respectively, indicating coordination of the -NH_2 group on the tin atom. Moreover, the ligand (2) showed NH (pyrrolidine group) proton signal at 2.16³⁴ which has disappeared in the complex (5) suggesting probably coordination of -NH- moiety to the atom center. In complex (5), the ^1H NMR signals at 1.80-2.40, 3.09-3.30, and 4.64 ppm indicates the presence of pyrrolidine group³⁴. Furthermore in complex (6), cysteine moiety was confirmed by the presence of signals at 2.57 and 4.08 ppm³³. Thus, the appearance of signals at 1.63-1.78 indicates the presence of -NH_2 group which confirms coordination of the deprotonated thiolate group on the tin center instead of the latter amino group²⁹.

^{119}Sn NMR spectroscopy

To investigate the ligand-binding modes to the tin atom in solution³⁵, ^{119}Sn NMR spectra was measured. It is generally recognized that ^{119}Sn chemical shifts are very sensitive either to the coordination modes and ligand types³⁶. Thus, a range of δ values from +200 to -60 have been reported for four-coordinated, -90 to -190 for five-coordinated and -210 to -400 for six-coordinated diorganotin(IV) complexes in solution³⁷. The chemical shift values for the synthesized compounds 4-6 are -186, -204, and -207 ppm, respectively confirming the penta-coordination mode.

XRD analysis

The XRD powder diffraction spectra of synthesized complexes were recorded with a scan rate about $0.02^\circ \text{ min}^{-1}$ and range $2\theta = 5\text{-}55$ degree (Fig. 3). The registered spectra revealed peak with maxima at $2\theta = 12.48\text{-}12.42$, $d = 7.23\text{-}7.05 \text{ \AA}$, and $\text{FWHM} = 0.2503\text{-}0.2435$ (Fig. 4). All data are summarized in Table 2. The obtained results demonstrate closer parameters regarding to the first (maxima) peaks of XRD spectra for all complexes.

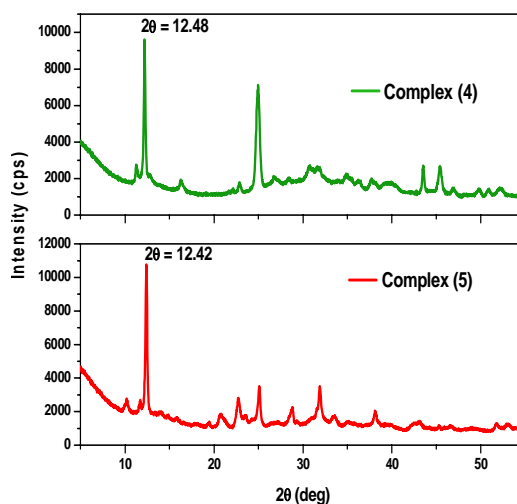


Fig. 3. XRD powder spectra of Sn Complex (4) and (5)

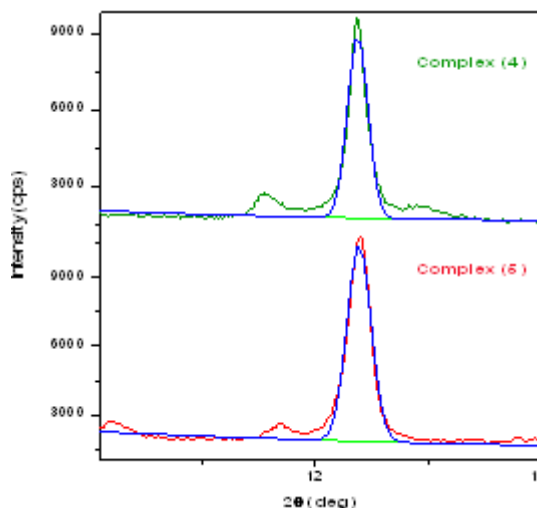


Fig. 4. Determining of FWHM and peak area parameter from the first peak (maxima) of Complex (4) and (5) by Origin software

Table 2: First peak (maxima) parameters of XRD spectra

	First peak (maxima) parameters			
	FWHM	Peak area	2θ	d-spacing [Å]*
Complex 4	0.2435	1883.7	12.48	7.23
Complex 5	0.2503	2289.1	12.42	7.10
Complex 6	0.2488	2161.4	12.45	7.05

(*) d-spacing [Å] values were obtained by X'pert High Score software.

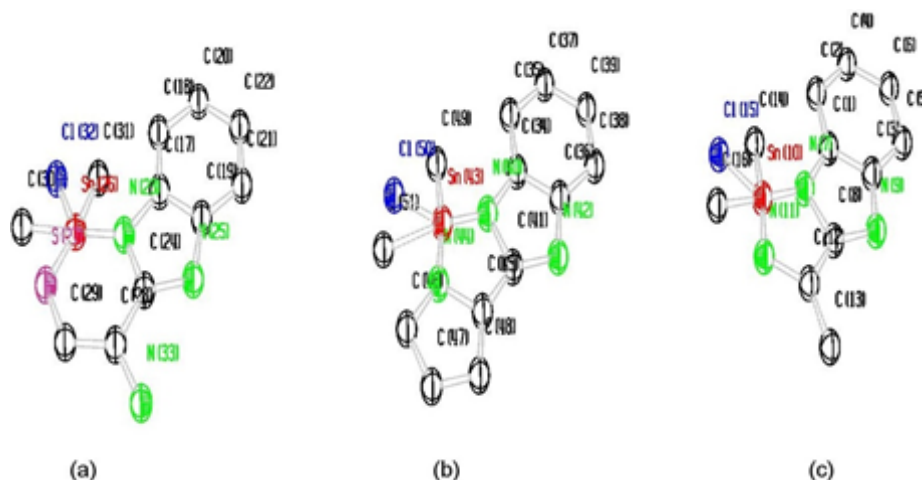


Fig. 5. Refined ORTEP drawing of the X-ray proposed structure of compounds: (a) complex (6), (b) complex (5), and (c) complex (4). Hydrogen atoms have been omitted

Calorimetric measurements

The differential scanning calorimetry measurements of synthesized complexes were recorded on heating between 200 and 800 K with a scanning rate 5 K min⁻¹ (Fig. 6). The first thermogram showed the combustion of organic part of complex (4) which located at 592 K. The values of enthalpy and entropy were resulted from the peak area are as follow: $\Delta H = -774.8$ kJ/mol and $\Delta S = -1.5$ kJ mol⁻¹ K⁻¹.

The second thermogram revealed the combustion of complex (5), which was achieved in three steps; at 473, 568, and 638 K, correspondently. The values of enthalpy and entropy were determinate from the peak area are as follow: $\Delta H = -668$ kJ/mol and $\Delta S = -1.2$ kJ mol⁻¹ K⁻¹.

The third thermogram displayed the combustion of complex (6), which was completed in three steps located at 555 K, 588 K, and 652 K, respectively. The values of enthalpy and entropy

were obtained from the peak area are as follow: $\Delta H = -664$ kJ/mol and $\Delta S = -1.3$ kJ mol⁻¹ K⁻¹.

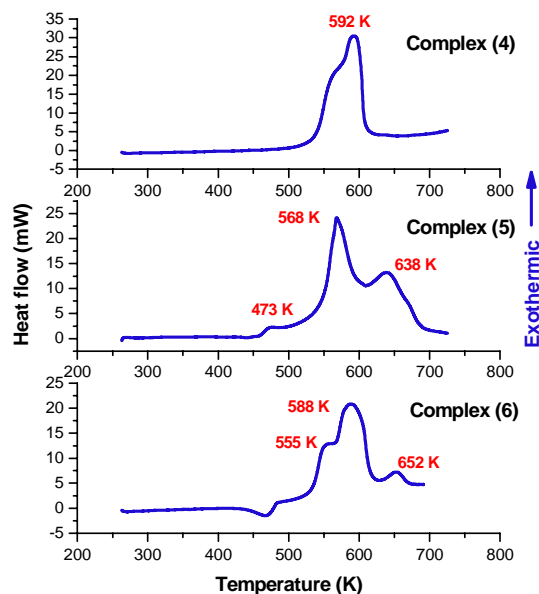


Fig. 6. DSC measurements of complexes 4-6

recorded by Bruker Avance 300 spectrometer (Bruker, France) at 300 and 75 MHz, respectively. Chemical shifts were reported in ppm from internal TMS for ¹H, ¹³C and ¹¹⁹Sn. Elemental analysis was obtained by means an Exeter Analytical CE-440 Elemental instrument (Exeter Analytical, UK). X-ray spectra were recorded by an Oxford X-calibur Gemini diffractometer (Santa Clara, California, USA) equipped with EOS CCD detector using

EXPERIMENTAL

Apparatus and materials

The melting point of complexes was recorded by a differential scanning calorimetric instrument (DSC 131 evo-Setaram, France). The IR spectra were measured using a Nicolet iS5 Infrared Spectrometer in KBr (Thermo Scientific, USA.). ¹H-NMR, ¹³C-NMR and ¹¹⁹Sn spectra were

monochromated Mo K α radiation ($k = 0.71073 \text{ \AA}$) at room temperature. Dimethyltin dichloride, *o*-phenylenediamine, L(+)-alanine, L(+)-proline, and L(+)-cysteine were purchased from Sigma-Aldrich and used as received.

Typical Procedure for the synthesis of complexes 4-6

ABZH 1-3 (5 mmol) were taken in 10 mL aqueous solution of NaOH (5 mmol) and stirred at room temperature for 20 minutes. After that, an aqueous solution of dimethyltin dichloride (5.5 mmol) was added dropwise with continuous stirring. After couple of minutes stirring, a pale yellow powder was precipitated, which was filtered out, washed simultaneously with water and ethanol and recrystallized from a mixture ethanol/DMSO (95/5).

[(CH₃)₂Sn(C₉H₁₀N₃)Cl] (4)

M.p. 480-482 K; Calc. for C₁₁H₁₆ClN₃Sn (%): C, 38.36; H, 4.68; N, 12.20. Found: C, 38.34; H, 4.66; N, 12.18; Selected IR data (KBr) [ν/cm^{-1}]: 3449 $\nu(\text{NH})$; 1633 and 1507 $\nu(\text{C}=\text{N})$; 780 $\nu(\text{Ar})$; 576 $\nu(\text{Sn}-\text{C})$; 500 $\nu(\text{Sn}-\text{N})$. UV-Vis (EtOH) [$\lambda_{\text{max}}/\text{nm}$]: 202, 272, 279. ¹H NMR (DMSO-*d*₆, ppm): 1.5 (CH₃-Sn) 4.3 (-CH); 7.6-7.2 (Harom); 10.8 (BzNH). ¹³C NMR (DMSO-*d*₆, ppm): 151 (C=N); 114-128 (Carom); 46 (CH); 22 (-CH₃), 8.1 (CH₃-Sn). ¹¹⁹Sn NMR (DMSO-*d*₆, ppm): -186.

[(CH₃)₂Sn(C₉H₁₂N₃)Cl] (5)

M.p. 453-455 K; Calc. for C₁₃H₁₈ClN₃Sn (%): C, 42.15; H, 4.90; N, 11.34. Found: C, 42.14; H, 4.88; N, 11.32; Selected IR data (KBr) [ν/cm^{-1}]: 3451 $\nu(\text{NH})$; 1637 and 1507 $\nu(\text{C}=\text{N})$; 792 $\nu(\text{Ar})$; 579 $\nu(\text{Sn}-\text{C})$; 500 $\nu(\text{Sn}-\text{N})$. UV-Vis (EtOH) [$\lambda_{\text{max}}/\text{nm}$]: 203, 274, 281. ¹H NMR (DMSO-*d*₆, ppm): 1.5 (CH₃-Sn); 1.4-2.4 (m, -CH₂-CH₂-); 3.1-3.3 (CH-NH-CH₂-); 4.6 (-CH); 7.1-7.6 (Harom), 10.5 (BzNH). ¹³C NMR

(DMSO-*d*₆, ppm): 154 (C=N); 115-129 (Carom); 46 (CH); 21 (-CH₃); 8.4 (CH₃-Sn). ¹¹⁹Sn NMR (DMSO-*d*₆, ppm): -204.

[(CH₃)₂Sn(C₉H₁₀N₃S)Cl] (6)

M.p. 485-487 K; C₁₁H₁₆ClN₃SSn (%): C, 35.09; H, 4.28; N, 11.16. Found: C, 35.08; H, 4.26; N, 11.15; Selected IR data (KBr) [ν/cm^{-1}]: 3450 $\nu(\text{NH})$; 1636 and 1507 $\nu(\text{C}=\text{N})$; 788 $\nu(\text{Ar})$; 576 $\nu(\text{Sn}-\text{C})$; 501 $\nu(\text{Sn}-\text{N})$. UV-Vis (EtOH) [$\lambda_{\text{max}}/\text{nm}$]: 201, 273, 280. ¹H NMR (DMSO-*d*₆, ppm): 1.4 (CH₃-Sn) 2.6 (CH₂-SH) 4.0 (-CH); 7.1-7.6 (Harom), 10.6 (BzNH). ¹³C NMR (DMSO-*d*₆, ppm): 154 (C=N); 117-130 (Carom); 44 (CH); 23 (-CH₃); 8.2 (CH₃-Sn). ¹¹⁹Sn NMR (DMSO-*d*₆, ppm): -207.

CONCLUSION

Chiral penta-coordinate organotin(IV) complexes were successfully prepared and characterized using different analytical techniques. The obtained spectroscopic data were accordant with the proposed structures of products. The complexes (4) and (5) were resulted *via N,N* coordination to tin atom by their analogous ligands (1) and (2), respectively, whereas, the complex (6) was achieved by *N,S* chelation of tin center. The XRD spectra of compounds revealed closer parameters about the first (maxima) peak. DSC studies showed that the decomposition of the complexes proceeded *via* exothermic combustion.

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