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Mechanochemical synthesis and characterization of tri-organotin(IV) complexes of 4-aminobenzoic acid and 4-cyanobenzaldehyde as potential antifungal agents

Q. M. Amua, E. N. Iornumbe, and E. C*. Oggah

[1]Department of Chemistry, Inorganic Research Group, Joseph Sarwuan Tarka University, P.M.B 2373 Makurdi, 970001, Nigeria.

*Correspondence E-mail: ecaiphas@gmail.com

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Abstract

Mechanochemical synthesis of organotin (IV) complexes using green chemistry approaches reduces environmental pollutants by eliminating solvents and catalysts, while also improving energy efficiency. In this study, four organotin (IV) complexes were synthesized and characterized, specifically with tributyltin (IV)-4-aminobenzoic acid and dibutyltin (IV)-4-cyanobenzaldehyde as ligands. Various analytical techniques were employed for their characterization. FTIR results confirmed the formation of the complexes, with Sn-O and Sn-N bands appearing at ca. 750 cm^{-1} in the spectra of the respective complexes. Thermogravimetric analysis (TGA) indicated the presence of water of hydration and the incorporation of ligands. Additionally, the complexes' calcination temperatures and heat capacities were evaluated using Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). For example, complexes B1, B3, and B4 exhibited high specific heat capacities of approximately 23.48, 30.46, and 25.22 J/g°C, respectively. This indicates that these complexes are the most thermally stable among all those synthesized, making them promising candidates for biological applications. X-ray fluorescence analysis revealed that the percentage of Sn content in B3 was 13.57 % (0.14 mmol), which is lower than that in B4, where the Sn content was 13.85 % (0.15 mmol). These findings indicate that the mechanosynthesis of complex compounds is more effective with longer reaction times. Notably, the synthesized organotin (IV) complexes have shown promising activity against certain fungal strains. For example, complex B2 exhibited greater efficacy against Aspergillus flavus compared to the standard drug. This finding suggests that these complexes could serve as potential candidates for the development of novel antifungal agents.

Keywords: Mechanosynthesis, Characterization, Thermal analysis, Antifungal studies, Complexes.

Introduction

Organometallic compounds contain at least one metal-carbon bond, in which the carbon is part of an organic group [1]. Due to their diverse industrial applications, they have been studied extensively. Organotin compounds have contributed immensely to the research and understanding of organometallic compounds, which began in 1949. This has resulted in their application across various fields. Comprehensive studies on the structural properties and the changes observed in both the solution and solid states of organotin compounds have been documented [2].

Solvents and Catalytic synthesis of organotin (IV) compounds have been exhaustively exploited by synthetic researchers [1-3] and have shown several shortcomings such as hazardous, toxic, increase in the cost of synthesis, low yields, prolonged reaction times, harsh reaction conditions, and requiring excess amounts of catalysts [4]. Solvent and catalyst-free syntheses are gaining importance as tools for the synthesis of a wide variety of useful and important compounds with the number of reactions conducted under these conditions increasing [5]. This is due to operational simplicity, high yields, mild reaction conditions, non-purification; and shorter reaction time which has made Solvent and catalyst-free synthesis a promising alternative to obtain a wide range of organotin(IV) compounds [6,7]. Eliminating solvent and catalyst in the design, synthesis, and characterization of organotin(IV) compounds with fascinating biological activity and broad applications in the last few decades has been the subject of immense interest to researchers and plays a significant role in addressing and transporting the molecule to the target, interactions with biomolecules and pathogenic resistance [6-8].

Mechanochemical synthesis is a developing method for synthesizing compounds by utilizing mechanical forces such as compression, continuous deformation, fractures, shear, or friction [8-10]. This pollution-free method has been utilized for synthesizing various materials, including metals, metal oxides, metal-organic frameworks, organic compounds, and carbon nanotubes with high-yield and low-cost synthesis often the advantage [11]. By using this synthetic approach, the limitations of conventional methods can be circumvented to explore the synthesis of new compounds that may show enhanced efficacy against microbes. Characterizing the synthesized compounds will yield valuable insights into their structural features, and biological activities [8, 11].

Although a wide range of research works concerning the synthesis of organotin(IV) complexes and biological properties have been conducted, the mechanochemical synthetic approach which often proves to be more efficient than the conventional approach remains a novel strategy in this regard [12-14]. Herein, we report the synthesis of tri-organotin(IV) complexes of tributyltin(IV)-4-aminobenzoic acid and dibutyltin(IV)-4-cyanobenzaldehyde by mechanochemical strategies, their thermal and spectroscopic characterization as well as antifungal assays. The study aim to investigate the structural features of the synthesized organotin(IV) complexes and their antifungal potentials.

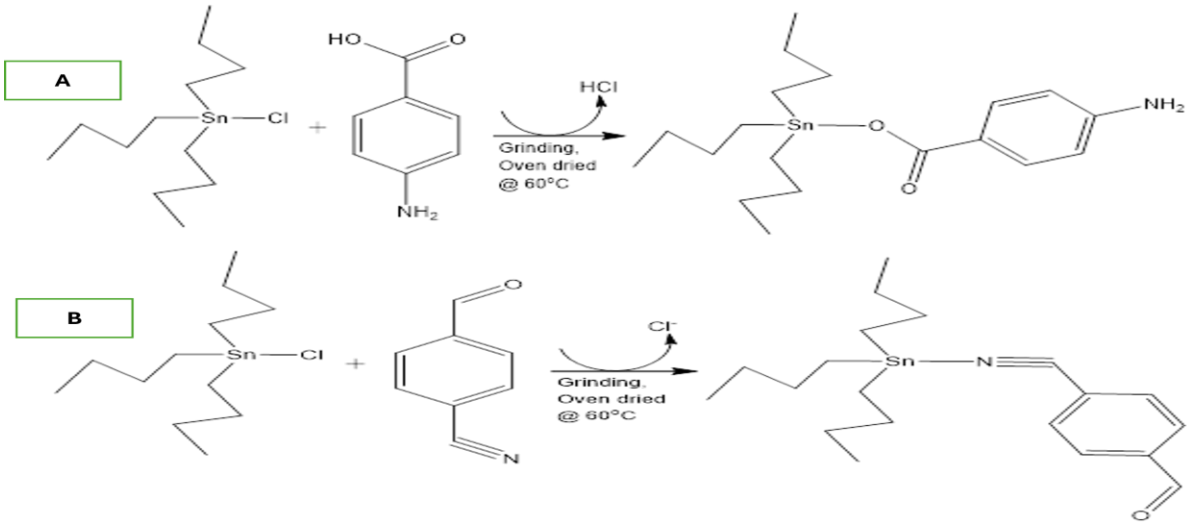
Materials and Methods

Chemicals

All chemicals and solvents used were of analytical grade, obtained from Sigma-Aldrich, and used without further purification.

Synthesis of the complexes, tributyltin(IV)-4-aminobenzoate (B1 and B2) and tributyltin(IV)-4-cyanobenzaldehyde (B3 and B4)

The complexes were synthesized using a procedure described in the literature [8]. Tributyltin(IV)-4-aminobenzoate (B1 and B2) was prepared by the addition of Bu_3SnCl (0.999g) to 4-aminobenzoic acid (0.4213 g) in a mortar and was ground using a pestle for 10 min. Instantly, a yellow-orange compound was formed. The resulting compound was oven-dried at 60℃ (Scheme 1a). Similarly, dibutyltin(IV)-4-cyanobenzoate (B3 and B4) was synthesized by the addition of Bu_3SnCl (0.999 g) to 4-cyanobenzaldehyde (0.452 g) in a mortar and ground using a pestle for 10 min, upon which a white compound was formed instantly. The resulting compound was oven-dried at 60℃ (Scheme 1b).



Scheme 1. Synthesis of the complexes, tributyltin(IV)-4-aminobenzoate (A) and tributyltin(IV)-4-cyanobenzaldehyde (B)

Instrumentation and General Characterization

The infrared spectral data of the synthesized organotin(IV)carboxylates were run as KBr discs and displayed on Perkin Elmer 3000 MX FT-IR spectrophotometer spectrum BX with spectrum version 5.3.1 software version All spectra were recorded from 4000 to 400 cm^{-1} using the Pelkin Elmer 3000 MX spectrometer. The IR spectra were analyzed using the spectroscopic software Win-IR Pro Version 3.0 with a peak sensitivity of 2 cm^{-1}. The ultraviolet spectra of the prepared complexes were obtained using acetone as solvent from Perkin Elmer UVD-2690 UV-VIS double beam PC scanning spectrophotometer (UV-Winlab 2.8.5.04) software version. Powdered samples of the organotin(IV) complexes were pelletized and sieved to 0.074 mm and they were later taken in an aluminium alloy grid (35 mm x 50 mm) on a flat glass plate and were covered with a paper on wearing hand gloves, the samples were compacted by gently pressing them with the hand. Each sample was run through the Rigaku D/Max-IIIC X-ray diffractometer produced diffractions at a scanning rate of 2 0/min in the 2 to 50 0 at room temperature with a CuKa radiation set at 40 kV and 20 mA. The diffraction data (d value and relative intensity) were obtained.

Thermogravimetric analyses (TGA) is a technique in which, upon heating a substance, its weight increases or decreases. The TGA of the organotin(IV)carboxylates sample was carried out by using TA Instruments TGA Q50 thermal analyzer at a heating rate of 5 ℃/min and in an atmosphere up to 650 ℃. A small sample of about 15 mg was loaded into the ceramic crucible to avoid the effect of mass and heat transfer limitation. The atmosphere nitrogen continuously flowed into the inner part of the heating chamber during the thermal degradation process. The samples were subjected to the pre-adjusted heating program from room temperature to 650℃. The respective TGA data resulted during the experiment and the thermograms were recorded which will reveal changes in the structure and other important properties of organotin(IV)carboxylates being studied. Thermogravimetric analysis (TGA) and Differential

Thermal Analysis (DTA) were carried out using TA Instruments TGA Q50 thermal analyzer at a heating rate of 5 ℃/min and in an atmosphere up to 650 ℃ with measurements from 30 to 800 °C in the atmosphere to determine the changes that occurred during the heat treatment of the metal complexes. DTA was done on the organotin complexes to determine some important energetics that are crucial for studying heat transport mechanisms in various solid-state compounds. Tin content analysis of the complexes was determined by x-ray fluorescence using an X-ray Phillips MagiX fluorescence spectrophotometer (Philips, Amsterdam, The Netherlands) with an X-ray source of 1 kW and a Rh anode in a helium atmosphere. The quantification method can analyze from 0.0001 % to 100 % tin.

Antifungal Activity Assay

Isolates of the microbes will be obtained from the Microbiology Department, Ahmadu Bello University, Zaria. Agar-well diffusion techniques were adopted to determine the antifungal activity of the complexes. Sabouraud dextrose agar (SDA) was used as a culture medium prepared according to the manufacturer's instructions, sterilized at 121 ℃ for 15 minutes, poured into sterile petri dishes under an aseptic hood, and allowed to cool and solidify. The sterile medium was seeded with 0.1 mL of standard inoculums of the test fungi and spread evenly over the surface of the medium using a sterile swab. A well will be cut at the centre of each inoculated medium using a standard cork borer of 6 mm diameter and 200 µg/mL of the test compounds dissolved in DMSO was introduced into their respective wells. Other wells supplemented with standard antifungal drugs; fulcin and fluconazole were used as controls. After allowing for diffusion, the media was incubated immediately at 30 ℃ for 7 days and checked daily for inhibition zone (the area where the fungi will be unable to grow), then it indicated the compounds tested showed antifungal activity [15].

The minimum inhibition concentrations (MICs) of the test complexes were obtained using the broth dilution method. Sabouraud dextrose broth was prepared in a test tube, sterilized at 121 ℃ for 15 minutes, and allowed to cool. Furthermore, serial dilution of test organotin compounds in sterile broth was made to obtain the concentrations of 200 µg/mL, 100 µg/mL, 50 µg/mL, 25 µ/mL and 12.5 µg/mL. In addition, 1.5 × 105 CFU/mL of test fungi in normal saline was prepared and introduced into each of the concentrations and incubated at 30 ℃ for 7 days. The test tubes were observed for turbidity (growth) and the lowest concentration of a compound in the broth which showed no turbidity was recorded as a minimum inhibition concentration. To ascertain whether the test fungi could be killed completely, or their growth would be only inhibited, minimum fungicidal concentration (MFC) was determined. The content of MIC in the serial dilution was subcultured onto the prepared medium and incubated at 30 ℃ for 7 days and plates were observed for colony growth. The MFC was the plate with the lowest concentration of the complex without colony growth [15].

Results and Discussion

Physical Properties of the Metal Complexes

The physical properties of the organotin complexes are shown in Table 1. It was observed that B1 and B2 were light orange while B3 and B4 were white. Good yields were also obtained for the complexes (73.85 – 95.28 %), with the highest yield recorded for complexes B3 and B4 (91.64 and 95.28 %), while complex B1 gave the lowest percentage yield (73.85 %). The longer reaction time factor is observed to be responsible for the higher yield obtained for B2 and B4. The complexes were formed according to Schemes

Table 1. Physical properties of the synthesized organotin complexes

Complex	Formula weight ($gmol^{-1}$)	Decomposition temperature (°C)	Colour	Yield (%)
Bu_3SnAM-30 (**B1**)	427.05	151−154	Light orange	73.85
Bu_3SnAM-60 (**B2**)	427.05	107−110	Light orange	78.33
Bu_3SnCN-30 (**B3**)	421.13	88–91	White	91.64
Bu_3SnCN-60 (**B4**)	421.13	97–98	White	95.28

FT-IR Studies

The study of infrared spectral data of the reported complexes has proven to offer sufficient evidence to understand better the coordinating modes in the organotin complexes. Thus, the FTIR analyses were carried out on the synthesized metal complexes with the spectra data presented in Table 2 and the spectra shown in Figure 1. The absorption band due to ν(C=O) was observed at 1697 – 1695 cm^{-1} in the spectra of the organotin complexes indicating the incorporation of the ligands to form the complexes [16].

Table 2: FTIR spectra data for the synthesized organotin complexes

Complex/bands (cm^{-1})	N-H; C-H	-CN-	C=O	C-O	Sn-C	Sn-O; Sn-N
Bu_3SnAM-30 (**B1**)	2954	-	1695	1367	655	735
Bu_3SnAM-60 (**B2**)	2954	-	1691	1389	664	744
Bu_3SnCN-30 (**B3**)	2962	2251	1611	1318	659	766
Bu_3SnCN-60 (**B4**)	2954	2237	1607	1318	664	762

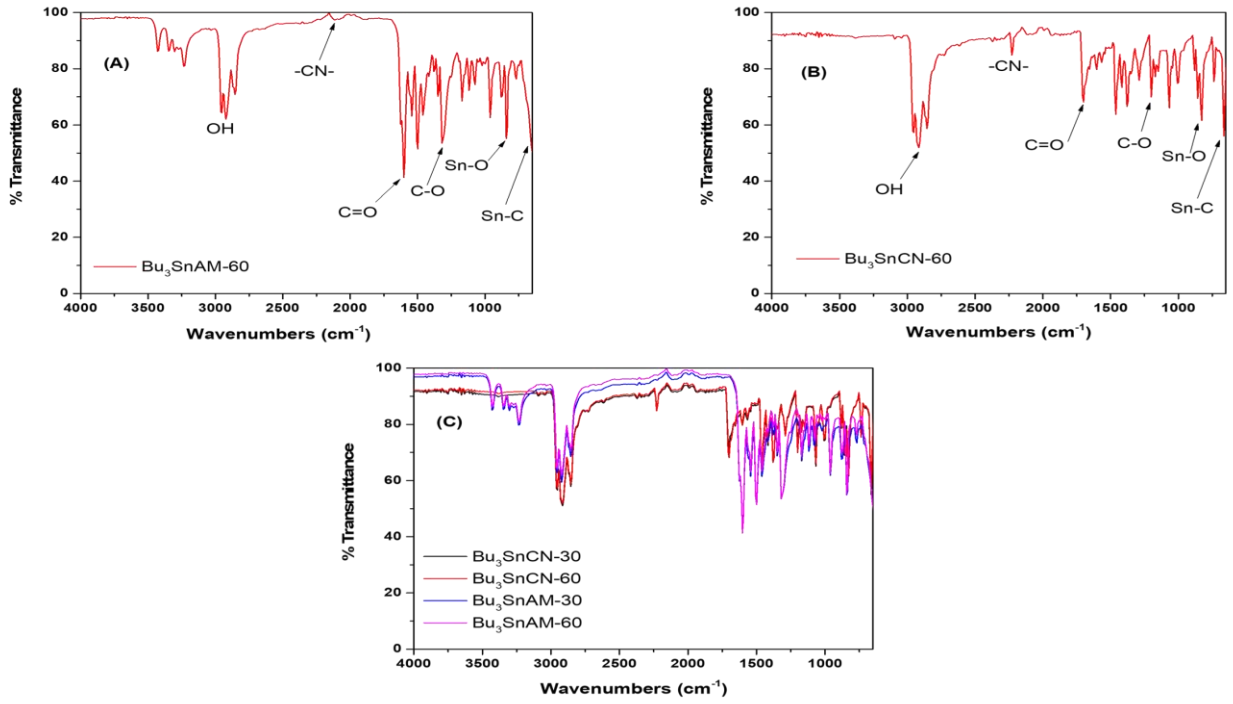


Figure 1. FTIR spectrum of B2 (A), B4 (B), and stacked spectra of B1, B2, B3, and B4

This is supported by the vibrational frequencies (2954 cm^{-1}) in the spectra of both B1 and B2 which are credited to the ν(N-H) group. The fact that the peaks appeared in a similar position rationalizes the similarity of B1 and B2 which is only different in the reaction time. The presence of bands at ca. 2251 and 2237 cm^{-1} for B3 and B4 respectively suggest the presence of the cyanide functional group (-CN-) in their structure. Interestingly, bands associated with the organometallic bond were observed at ca. 655 – 664 cm^{-1} in the spectra of the complex compounds while peaks observed in the range of 735 – 766 cm^{-1} were ascribed to Sn-O/Sn-N vibration in the respective aminobenzoic hydroxide and cyanobenzaldehyde complexes. The findings in the present study are consistent with those of other researchers for similar kinds of materials [16, 17].

Differential Thermal Analysis Studies

Differential thermal analysis (DTA) is a technique in which the difference in temperatures between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. Thus, the DTA analysis of the organotin complexes was carried out from 30 to 800 °C in atmosphere (Table 3). From the DTA plots (Figure 2), exothermic and endothermic events taking place within the samples have been analyzed over a programmed range of temperatures. During the endothermic process in the DTA thermogram, the temperature of a sample falls behind the reference temperature, and a down peak is observed whereas in the exothermic process, the sample temperature exceeds the reference temperature, and a minimum is observed on the graphical plot. The analysis was done between 30 °C and 800 °C with air as the atmosphere for all samples and data presented in Table 4.4. The DTA curve of B1 showed an endothermic peak at about 244 °C, corresponding to the evaporation of the absorbed water [18]. Two other endothermic peaks at approximately 308 and 384 °C occur in DTA, which might be associated with the decomposition of organic residues. The appearance of an exothermic peak at ca. 514 °C suggests completion of the reaction and hence 514 °C has been assigned as the calcination temperature.

Table 3. Differential thermal analysis data (◦C) of the synthesized organotin complexes

Complex	Endothermic peaks	Exothermic peaks	Calcination temperature
Bu_3SnAM-30 (**B1**)	244, 308, 384	514	514
Bu_3SnAM-60 (**B2**)	182, 313, 390	534	534
Bu_3SnCN-30 (**B3**)	280, 374	486	486
Bu_3SnCN-60 (**B4**)	213, 387	568	568

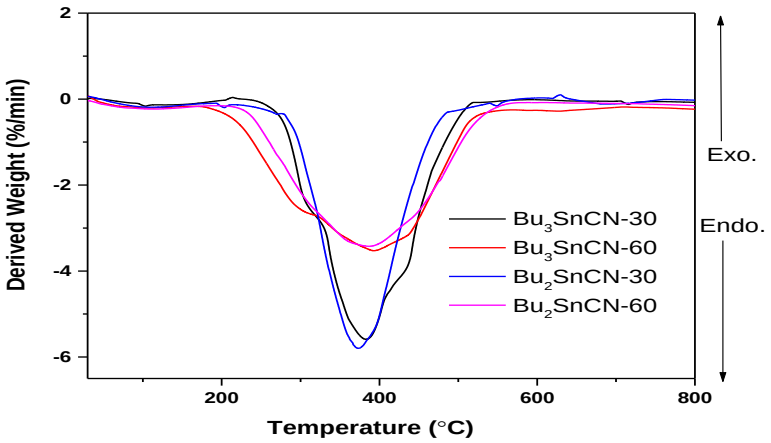


Figure 2. DTA thermograms of the organotin complexes

The DTA plot of B2 appeared to have an endothermic peak assignable to absorbed water evaporation at about 182 °C and two other endothermic peaks at ca. 313 and 390 °C which can be ascribed to the decomposition of organic residues. Again, an exothermic peak appeared at about 534 °C which can be assigned to the degradation of impurities and completion of the reaction. The peak at 534 °C thus forms the calcination temperature of B1. Interestingly, a similar pattern was observed in the thermograms of B3 and B3 except that only two endothermic peaks were observed in these scenarios. This could be ascribed to structural differences in the compounds and fewer impurities in the latter group. Consequently, 486 and 568 °C were assigned to be the calcination temperatures of the complexes B3 and B4 respectively [19].

Thermogravimetric Analysis

The interpretation of the variation in the mass of a sample with a temperature change is done by thermogravimetric analysis [20]. It is usually done on samples to identify the changes in weight percent for temperature change. Thermal analysis techniques have been applied extensively in studying the thermal behaviour of metal complexes. Thus, thermogravimetric analysis (TGA) was carried out from 30 to 800 °C in the atmosphere to determine the changes that occurred during the heat treatment of the metal complexes. Table 4 shows the thermogravimetric data of the organotin complexes while their respective thermograms are presented in Figure 3.

Table 4. Thermogravimetric analysis data of the synthesized organotin complexes

Complex	% H_2O	% CN	% Residue
Bu_3SnAM-30 (**B1**)	0.74	82.14	17.12
Bu_3SnAM-60 (**B2**)	1.91	89.04	9.05
Bu_3SnCN-30 (**B3**)	1.18	73.95	24.87
Bu_3SnCN-60 (**B4**)	2.11	76.77	21.12

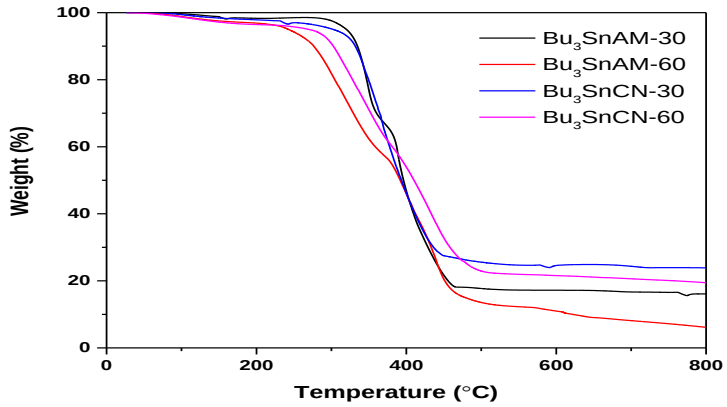


Figure 3. DTA thermograms of the organotin complexes

The thermogram of the organotin complexes showed that an onset degradation temperature occurred at ca. 234, 306, 310, and 281 °C for B1, B2, B3, and B4 respectively. This mass loss has been attributed to dehydration with the loss of H_2O molecules representing about 0.74, 1.91, 1.18, and 2.11 % respectively for the organotin complexes. This may rationalize the presence of water for hydration or crystallization in all the metal complexes [21]. Furthermore, the second step of mass losses was observed in the thermograms at ca. 275 – 164, 315 – 462, 325 – 450, and 285 – 490 °C for B1, B2, B3, and B4 respectively. This represents two events which are the decomposition of organic matter (Ligand) and the formation of the residues (SnO_2) [22]. Thus, the percentage composition of ligand and residues in the organotin complexes were observed to be 82.14 and 17.12 %, 89.04 and 9.05 %, 73.95 and 24.87 %, and 76.77 and 21.12 % for B1, B2, B3, B4 respectively.

It is important to observe that the percentage mass loss attributed to B1 is lower than that of B2 even though the complexes are the same except for their reaction time (30 min reaction time for B1 and 60 min for B2). This may infer that a longer reaction time is most appropriate for the mechanochemical approach to the synthesis of metal complexes. These thermal events further justify the formation of the organometallic complexes, an observation that is in concomitance with literature reports for similar kinds of materials [23].

Differential Scanning Calorimetry Studies

Differential scanning calorimetry (DSC) methods are commonly used to determine non-isothermal transformation indices. This procedure allows us to measure the quantity of heat absorbed from or emitted to the surroundings per unit time during isothermal procedures or heating and cooling [24]. This way, the heat capacities, melting points, transition temperatures, and more can be measured. This information can provide further insights into phase transitions, crystallization processes, and other related phenomena. These thermodynamic parameters are crucial for studying heat transport mechanisms in various solid-state compounds. Thus, the thermodynamic properties of synthesized organotin complexes have also been investigated to understand their energetics and determine some thermodynamic parameters (Table 5).

Table 5. Differential scanning calorimetric analysis of the synthesized organotin complexes

Complex	Melting range T_i (°C)	T_f (°C)	Fusion temperature (°C)	C_p ($KJg^{-1}°C^{-1}$)	Crystallization temperature (°C)
Bu_3SnAM-30 (**B1**)	151.26	154.46	222.89	23.48	252.34
Bu_3SnAM-60 (**B2**)	107.01	110.81	224.53	1.38	283.71
Bu_3SnCN-30 (**B3**)	88.22	91.27	252.21	30.46	287.82
Bu_3SnCN-60 (**B4**)	97.80	98.33	210.08	25.22	284.54

Figure 4 shows the DSC curves of the synthesized organotin complexes. The complexes all exhibited endothermic processes. The area of the endothermic peak corresponds to the heat of fusion and the peak temperature corresponds to the melting point. The melting ranges (Ti and Tf) temperatures of fusion, and temperatures of crystallization of the complexes are given in Table 4.6. The heat capacities Cp of the complexes were calculated from DSC results and are all presented. It can be observed from the DSC data that the range of melting temperatures occurred at approximately similar domains in the respective curves of the organotin complexes. This could suggest that the synthesized metal complexes have similar structural architectures, hence their decomposition patterns as supported by TGA results [24]. This claim is further supported by the values of temperatures of fusion of the complexes which are in similar domains at ca. 88 – 154 °C and crystallization which was observed at ca. 133 – 251 °C. Interestingly, the specific heat capacities of the synthesized complexes fall

in the range of ca. 1.38 – 30.46 $KJg^{-1}°C^{-1}$ which is similar to complexes reported by other researchers [17, 24]. It is important to note however that, some of the complexes have very high specific heat capacities.

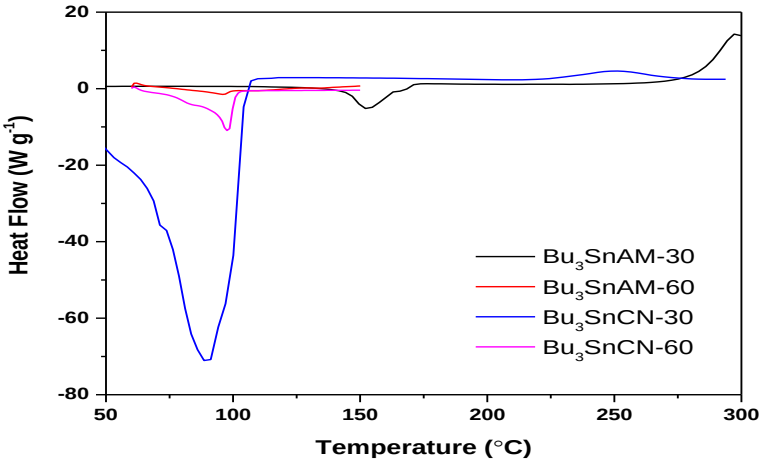


Figure 4. Stacked DSC thermograms of B1, B2, B3, and B4

This suggests that such complexes with a high specific heat capacity require a greater change in energy to change their temperatures. For instance, B1, B3, and B4 demonstrated very high specific heat capacities ca. 23.48, 30.46, and 25.22 $Jg^{-1}°C^{-1}$ respectively. This suggests that these complexes are the most thermally stable among all the synthesized complexes which rationalizes them as potential candidates for biological applications [17].

X-Ray Fluorescence Analysis

The amounts of tin in the complexes were determined by XRF measurements as shown in Table 6. Certain conclusions can be drawn from these data considering that the metal centres coordinated to the ligand moieties via the hydroxyl and cyano ends respectively. A comparison of the complexes of the two ligands studied showed a better reaction efficiency for cyanobenzaldehyde complexes as the metals were loaded more than the corresponding aminobenzoic hydroxide analogue.

Table 4.7 X-ray fluorescence data for the tin content analysis of the organotin complexes

Complex	SnO_2 (%)	Sn (%)	Sn (mmol)
Bu_3SnAM-30 (**B1**)	3.82	3.01	0.03
Bu_3SnAM-60 (**B2**)	3.73	2.94	0.02
Bu_3SnCN-30 (**B3**)	17.22	13.57	0.14
Bu_3SnCN-60 (**B4**)	17.58	13.85	0.15

This could suggest that steric requirements are a relevant factor in the coordination ability of these ligands [25]. Interestingly, the % Sn content in B3 (13.57 %, 0.14 mmol) was less than that in B4 (13.85 %, 0.15 mmol). This again suggests that the mechanosynthesis of the complex compounds is more effective with a longer reaction time. For instance, the synthesis of B3 proceeded for only 30 minutes, while B4 was allowed to react for 60 minutes. The results here agree with that of TGA and DTA.

Powder X-ray Diffraction Studies

The powder x-ray diffraction (PXRD) pattern of the organotin complexes, B3 and B4 was recorded by employing Bruker d8 Advance X-ray diffractometer, using CuKα radiation (λ = 1.5406 Å), 40 kV- 40mA, 2θ/θ scanning mode. Data was taken for the 2θ range of 10 to 70 degrees with a step of 0.0202 degrees. The PXRD data and its analysis are given in Table 6 while the diffractograms are presented in Figure 5. The diffractograms of the complexes showed similar peaks with similar Miller indices. This indicates that the complexes, B3 and B4 are the same materials with only reaction time differentiating them.

Table 6. Some important lattice parameters of Bu_2SnCN-30 (B3) and Bu_2SnCN-60 (B4)

Sample	2θ (◦)	θ (◦)	Cos θ (◦)	FWHM (◦)	FWHM (rad)	δ (nm)	*Hkl*
Bu_3SnCN-30 (**B3**)	6.89	3.45	0.9982	0.26	0.0045	30.81	110
Bu_3SnCN-60 (**B4**)	7.36	3.68	0.9979	0.24	0.0042	33.01	110

FWHM = full width at half maximum, δ = Average crystallite size, *hkl* = Miller index of the most prominent peak, rad = radians

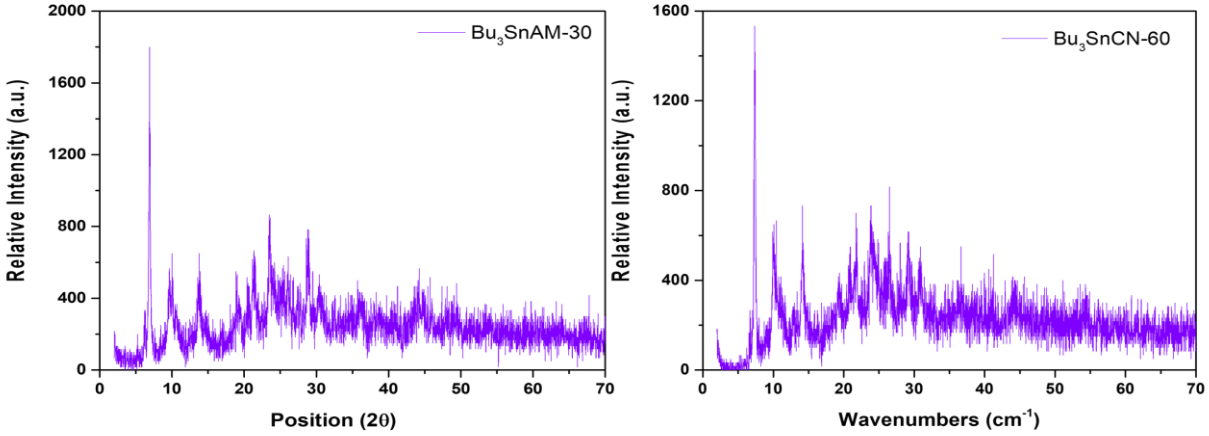


Figure 5. X-ray diffractogram of B3 (left) and that of B4 (right)

Furthermore, the most prominent peaks in the thermograms of B3 and B4 occurred at 2θ values of 6.89 and 7.36◦ degrees with d-spacings of 12.73 and 12.03 nm respectively. These peaks were used to estimate the average crystallite size of the organotin complexes by employing the Debye-Scherrer formula, $\delta = 0.9\lambda / \beta \cos\theta$, where λ is the wavelength of the X-rays used for diffraction and β is full width at half maximum (FWHM) of the peak [26]. The average crystallite sizes of B3 and B4 were thus estimated to be 30.81 and 33.01 nm respectively. This observation provides evidence that the organotin complexes were formed with relatively high crystallinity as evidenced by the appearance of six narrow and high-intensity peaks in the diffractograms. Consequently, a monoclinic Bravais lattice system is proposed for the complexes under investigation. Some of the low-intensity peaks observed in the diffractogram have been identified to be due to ligands, which might not have reacted completely and hence remained in the sample in minute quantity [27].

It is important to note that the average crystallite size of B3 (30.81 nm) is less than that of B4 (33.01 nm). This suggests that the mechanosynthesis of the complex compounds is better with a longer reaction time than not since the synthesis of B3 was allowed to proceed for only 30 min but 60 min for that of B4. The results of XRF, TGA, and DTA support this. Thus, the obtained structural data allow us to propose the structural formula of the studied organotin complexes as presented in Figure 6.

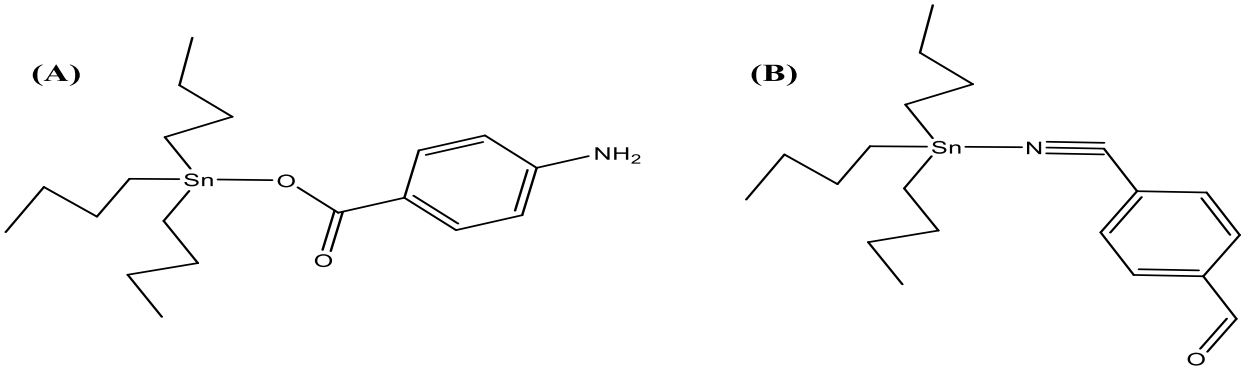


Figure 6. Proposed structure of (A) tributyltin(IV)-4-aminobenzoate complex and (B) of tributyltin(IV)-4-cyanobenzaldehyde complex

Biological Activities

A comparative evaluation of the antimicrobial activity of the ligands, L1 and L2, and the synthesized organotin(IV) complexes, B2 and B4 was carried out [15] against three fungi strains (Figure 6 and Table 7). The result showed that L1 is inactive against Candida albicans but active against the other fungi strains. However, B2, a complex formed from L1, demonstrated interesting activity against all the studied fungi strains. This may infer that the microbial activity of L1 is induced and increased in coordination with the metal center, and B2 has shown an interesting potential for the development of broad-spectrum antifungal agents. This can further be rationalized by the fact that B2 demonstrated better activity against Aspergillus flavus than the standard drug. On the other hand, L2 showed no activity against all the microbes but its complex, B4 demonstrated slight activity against Candida albicans and Aspergillus niger.

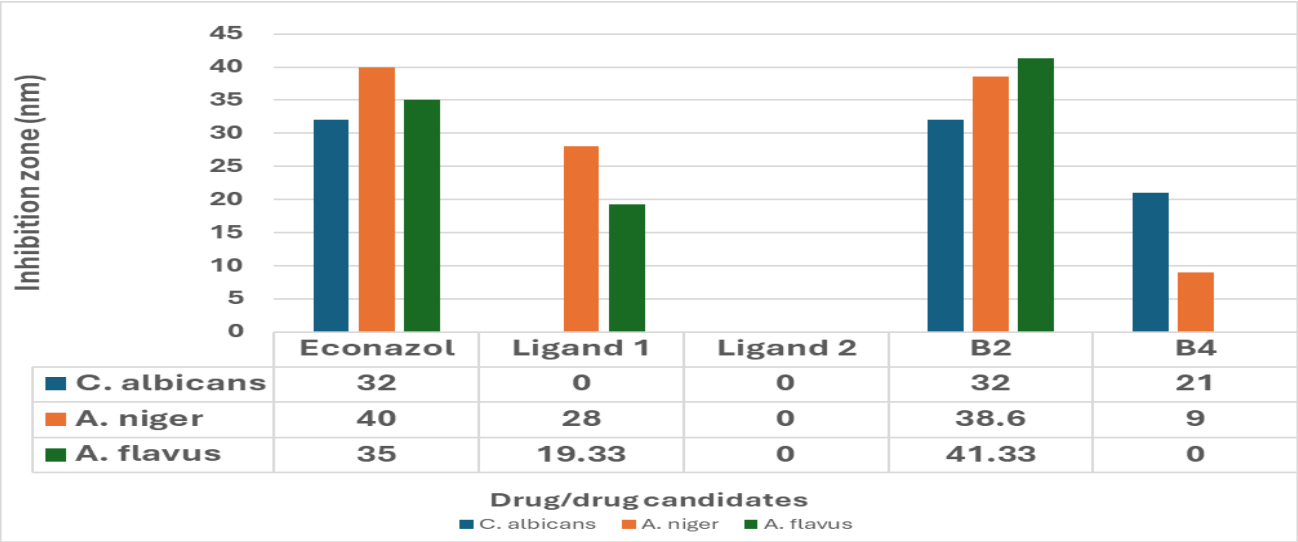


Figure 6. Inhibition zone of the ligands and organotin(IV) complexes

Table 7. Minimum Inhibitory Concentration (mg/mL) of the drug candidates against the Test Organisms

Test organism	L1	L2	B2	B4
Candida albicans	ND	ND	12.50	50.00
Aspergillus niger	25.00	ND	25.00	100.00
Aspergillus flavus	50.00	ND	25.00	ND

KEY: ND = Not determined for MIC

Thus, this activity is rather induced than otherwise. It, therefore, becomes important to observe that both aminobenzoic acid and cyanobenzaldehyde are important moieties in determining the antifungal activity of the organotin(IV) complexes under study. Based on the minimum inhibitory and fungicidal concentrations, B2 proved to be the best drug candidate in this study as it showed the lowest concentration (12.5 and 25.00 mg/mL respectively) capable of inhibiting the growth and causing the death of Candida albicans.

Conclusions

Four organotin(IV) complexes of tributyltin(IV)-4-aminobenzoate and dibutyltin(IV)-4-cyanobenzoate have been synthesized and characterized using diverse analytical techniques. FTIR results confirmed formation of the complexes with Sn-O and Sn-N bands appearing at Ca 750 cm^{-1} in the spectrum of the respective complexes. The presence of water of hydration and ligand incorporation was determined by TGA studies with calcination temperatures and heat capacities of the complexes evaluated by DTA and DSC. For instance, B1, B3, and B4 demonstrated very high specific heat capacities ca. 23.48, 30.46, and 25.22 $Jg^{-1}°C^{-1}$ respectively, suggesting that these complexes are the most thermally stable among all the synthesized complexes which rationalizes them as potential candidates for biological applications. X-ray fluorescence analysis showed that the % Sn content in B3 (13.57 %, 0.14 mmol) was less than that in B4 (13.85 %, 0.15 mmol). This suggests that the mechanosynthesis of the complex compounds is more effective with a longer reaction time. Interestingly, the synthesized organotin(IV) complexes have demonstrated interesting activity against some fungal strains. For instance, B2 demonstrated better activity against *Aspergillus flavus* than the standard drug. This suggests these complexes to be potential materials for the development of future antifungal agents.

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