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New dimeric and supramolecular organotin(IV) complexes with a tridentate schiff base as potential biocidal agents

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ABSTRACT

The paper describes the synthesis and structural characterization of six new diorganotin(IV) compounds 1–6, [R_2SnL] and a monoorganotin(IV) derivative, C_4H_9SnClL (7). Here L = N′-(5-bromo-2-oxidobenzylidene)-N-(oxidomethylene)hydrazine ligand with ONO tridentate chelation capability and R = CH_3 (**1**), C_2H_5 (**2**), n-C_4H_9 (**3**), C_6H_5 (**4**), C_8H_{17} (**5**), $tert$-C_4H_9 (**6**), The packing diagram offers a supramolecular structure for **1** and a dimeric structure for **4** with distorted square-pyramidal and distorted trigonal geometry, respectively. The different geometry of **1** than **4** can be attributed to the presence of intermolecular non-covalent Sn—O and Sn—H interactions in the former. The antifungal, antibacterial, antiurease and antileishmanial activities of these complexes proved them to be active biologically and may be formulated as new metal-based drugs in future.

1. Introduction

Schiff base ligands received instant and enduring popularity not only they have played a seminal role in the development of modern coordination chemistry [1], but they can also be found at key points in the development of inorganic chemistry [2], catalysis [3,4] medicinal imaging [5], optical materials [6], and thin films [7,8]. The chemistry of organotin(IV) has been the area of interest for many years because of their industrial and biomedical applications [9]. Several organotin(IV) complexes have been found as affective antifouling [10], anti-microbial [11] and antiviral agents. Organotin(IV) complexes with schiff base ligands have been an area of focus owing to their anti-tumor activities [12–20]. In addition to this, the complexes belonging to this class also present interesting structural diversities [21]. Keeping in view all these points and as an extension of our previous work, we synthesized and characterized seven new organotin(IV) derivatives of a ONO tridentate schiff base, N′-(5-bromo-2-oxidobenzylidene)-N-(oxidomethylene)hydrazine, and carried out their antifungal, antibacterial, antiurease and antileishmanial activities. This paper is unique in the sense that the antiurease and antileishmanial activities for organotin(IV) schiff bases are scantly available in the literature and the given article may be the first step in this direction. The profound antileishmanial activities demand further investigations on these complexes to be used as antileishmanial agents in future.

2. Experimental

2.1. Chemicals

Organotin(IV) dichlorides, dioctyltin(IV) oxide, butyltin(IV) chloridedihydroxide, 5-bromo-2-hydroxybenzaldehyde and formic hydrazide were procured from Aldrich. The organic solvents (toluene, chloroform, hexane, ethanol etc.) were used of Merck, Germany and were dried *in situ* using standard procedures [22] and freshly collected prior to use.

2.2. Instrumentation

The melting points were determined on an electrothermal melting point apparatus, model MP-D Mitamura Rieken Kogyo

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(Japan) by using capillary tubes and are uncorrected. The infrared (IR) spectra were recorded as neat liquids, using NaCl cells or as KBr pellets for solids on a Bio-Rad Excaliber FT-IR, model FTS 300 MX spectrophotometer (USA) in the frequency range of 4000–400 cm^{-1}. Multinuclear NMR (^1H, ^{13}C, and ^{119}Sn) spectra were recorded on a Bruker ARX 300 MHz-FT-NMR and a Bruker 400 MHz-FT-NMR spectrometers Switzerland using $CDCl_3$ as an internal reference. Chemical shifts (δ) are given in ppm and coupling constants (J) are given in Hz. The multiplicities of signals in ^1H NMR are given with chemical shifts; (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

The mass spectra were recorded on a MAT-311A Finnigan (Germany). The m/z values were evaluated assuming that H = 1, C = 12, N = 14, O = 16, Cl = 35 and Sn = 120. The X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer, equipped with a 4 K CCD detector set 60.0 mm from the crystal. The crystals were cooled to 100 ± 1 K using the Bruker KRYOFLEX low-temperature device and Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). Generator settings were 50 kV/40 mA. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods using the program *DIRDIF* or SIR2004. Final refinement on F^2 carried out by full-matrix least squares techniques using SHELXL-97, a modified version of the program *PLUTO* (preparation of illustrations) and *PLATON* package.

2.3. Syntheses

2.3.1. Synthesis of N′-(5-bromo-2-hydroxybenzylidene)formohydrazide (H_2L)

An ethanolic solution of 5-bromo-2-hydroxybenzaldehyde 3.35 g (16.65 mmol) was added slowly to the solution of formic hydrazide 1.0 g (16.65 mmol), in ethanol with constant stirring at room temperature. The mixture was refluxed for 1 h and on cooling yellow crystalline solid was obtained (Scheme 1a). m.p. 256–258 °C. Yield 80% (3.236 g). *Anal.* Calc. for $C_8H_7BrN_2O_2$ (M = 242): C, 39.53; H, 2.90; N, 11.53 Found: C, 39.50; H, 2.89; N, 11.57%. IR (cm^{-1}): 1706 ν(C=O), 3185 ν(NH), 1098 ν(N–N), 1609 ν(C=N), 3410 ν(OH)$_{Phenolic}$.

2.3.2. Synthesis of Dimethyltin(IV) [N′-(5-bromo-2-oxidobenzylidene)-N-(oxidomethylene)hydrazine]; (**1**)

A 250 mL two-necked flask containing 100 mL toluene, equipped with a reflux condenser was charged with N′-(5-bromo-2-hydroxybenzylidene)formohydrazide 0.73 g (3.0 mmol), and triethylamine 0.84 mL (6.0 mmol) along with a magnetic bar. To the solution of triethylammonium salt of the ligand, dimethytin(IV) dichloride (0.66 g, 3.0 mmol) in dry toluene was added drop wise into the flask with stirring at room temperature. The solution turned yellow, it was stirred for 5 h at room temperature. The white precipitates of Et_3NHCl formed during the reaction were filtered. The filtrate was concentrated by rotary evaporator to obtain yellow solid. The product was recrystallized from $CHCl_3$/n-hexane (4:1) mixture (Scheme 1b).

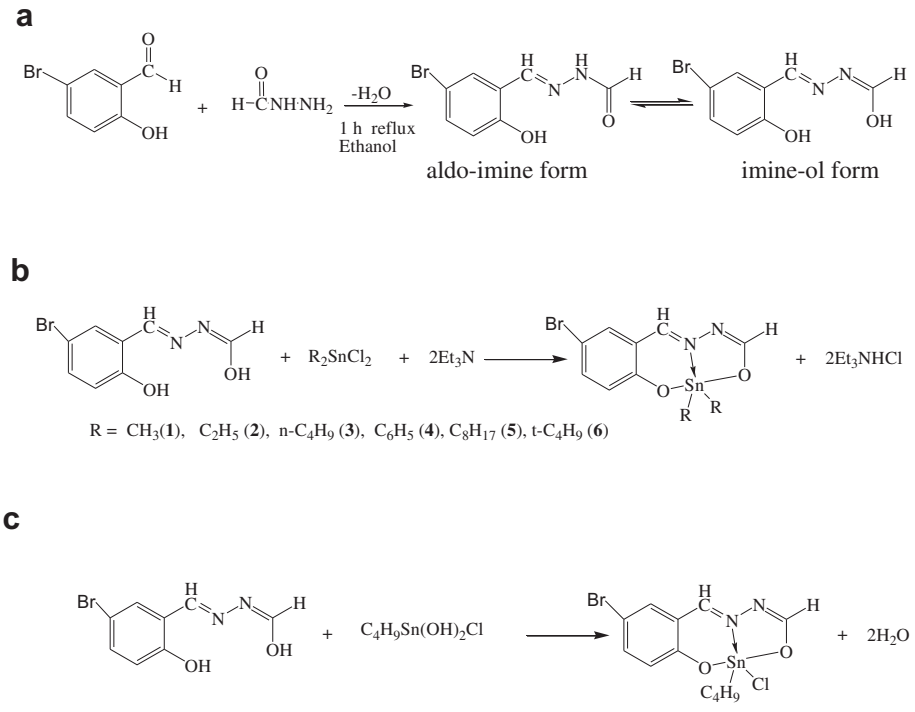
IR(cm^{-1}): 1609 ν(C=N), 1079 ν(N–N), 566 ν(Sn–O), 498 ν(Sn–N)

2.3.3. Diethyltin(IV) [N′-(5-bromo-2-oxidobenzylidene)-N-(oxidomethylene)hydrazine]; (**2**)

Compound 2 was prepared in the same way as **1**, using following quantities: N′-(5-bromo-2-hydroxybenzylidene)formohydrazide 0.73 g (3.0 mmol), diethyltin(IV) dichloride 0.74 g (3.0 mmol), triethylamine 0.84 mL (6.0 mmol) were reacted in 1:1:2 ratio. Solid product was recrystallized in chloroform and n-hexane (4:1) mixture. IR (cm^{-1}): 1605 ν(C=N), 1080 ν(N–N), 563 ν(Sn–O), 488 ν(Sn–N).

2.3.4. Dibutyltin(IV) [N′-(5-bromo-2-oxidobenzylidene)-N-(oxidomethylene)hydrazine]; (**3**)

Compound **3** was prepared in the same way as **1**, using following quantities: N′-(5-bromo-2-hydroxybenzylidene)formohydrazide 0.73 g (3.0 mmol), dibutyltin(IV) dichloride 0.91 g (3.0 mmol), triethylamine 0.84 mL (6.0 mmol) were reacted in 1:1:2 ratio. Viscous liquid product was obtained. IR (cm^{-1}): 1625 ν(C=N), 1088 ν(N–N), 548 ν(Sn–O), 472 ν(Sn–N).



Scheme 1. Synthesis of N′-(5-bromo-2-hydroxybenzylidene)formohydrazide (H_2L) *(a), diorganotin(IV) derivatives (b) and* butylchloridetin(IV) derivative (c).