Bull. Chem. Soc. Ethiop. **2012**, 26(1), 85-94.
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v26i1.9

ISSN 1011-3924

SYNTHESIS, CHARACTERIZATION AND THERMODYNAMIC STUDIES OF COMPLEXES OF DIMETHYL, DIETHYL, AND DIPHENYLTIN(IV) DICHLORIDES WITH (2H)-1,4-BENZOTHIAZINE-2,3-(4H)-DIONE DIOXIME

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(Received December 6, 2010; revised May 23, 2011)

ABSTRACT. The diorganotin(IV) compounds, [$Me_2SnCl_2(H_2L)$], [$Et_2SnCl_2(H_2L)$] and [$Ph_2SnCl_2(H_2L)$] (H_2L = (2H)-1,4-benzothiazine-2,3-(4H)-dione dioxime), were synthesized by treating the appropriate diorganotin(IV) dichloride with H_2L in anhydrous ethanol. These complexes were characterized by IR, MS, UV-Vis, and ^1H NMR. Thermodynamic studies of the reported complexes have been carried out and their stability were found in the order: [$Me_2SnCl_2(H_2L)$] > [$Et_2SnCl_2(H_2L)$] > [$Ph_2SnCl_2(H_2L)$]. Theoretical calculations at the HF/3-21G* level showed that structures with alkyl groups at axial positions are more stable than their counterparts having alkyl groups at equatorial.

KEY WORDS: Diorganotin(IV) dichloride, *vic*-Dioxime, (2H)-1,4-Benzothiazine-2,3-(4H)-dionedioxime, Thermodynamic studies

INTRODUCTION

Organotin(IV) complexes have a wide range of applications such as PVC stabilizers [1], for chemical vapor decomposition (CVD) [2], in non-linear optics [3] and in catalyses [4-6]. Organotin complexes present innumerous pharmacological applications as antitumorals [7], antimicrobials [8, 9] and biocides [10] and locking agent in the formation of dinuclear complexes [11]. The cytotoxic activity of a variety of organotin complexes against tumor cell lines has been demonstrated [12, 13]. A considerable number of metal-based compounds, including many organotin derivatives have been synthesized and characterized in the search for compounds with greater antitumour activity and lower toxicity than platinum complexes. In recent years, investigations have been carried out to test the antitumor activity of organotin compounds. It has been observed that several di- and triorganotin(IV) species are active against various types of cancer [14-15]. Biological activity of organotin complexes is believed to be independent on the structure of molecule and coordination number of metal [16]. For compounds [$SnR_2X_2(LL)$], where LL is an N,N-bidentate ligand, antitumour activity depends on the Sn-N distances (>2.39 and <2.39 Å for the active and inactive compounds, respectively [17]), which suggests that dissociation of the ligand is a significant step in their mechanism of action.

In this work we used the ligand (2H)-1,4-benzothiazine-2,3-(4H)-dione dioxime, a potentially N,N′-bidentate ligand [18, 19], for preparation of corresponding [$R_2SnCl_2(H_2L)$] (R = Me, Et, Ph) complexes. Thermodynamic parameters for these adducts have been determined and also theoretical calculations were use for determination of more stable geometry.

EXPERIMENTAL

All the diorganotin(IV) compounds were purchased from Merck and were used as received. Solvents were dried before use according to literature [20].

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IR spectra were obtained in the KBr using a Perkin Elmer FT IR–1605 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded in a multinuclear Brucker DRX-500 AVANCE instrument at 500 MHz and FT NMR 2.1 Materials 200 MHz of JEOL. The NMR spectra were carried out in DMSO-d_6. Mass data was obtained on a Shimadzu GC-MS model QP5050 instrument.

Synthesis of (2E,3E)-2H-1,4-benzothiazine-2,3(4H)-dionedioxime (H_2L)

To a stirring solution of 2-aminothiophenole (1.38 g, 11 mmol) in absolute ethanol 20 mL, a solution of dichloroglyoxime (0.156 g, 1 mmol) in aqueous THF (80%) 10 mL and $NaHCO_3$ 0.05 g was added at room temperature. The solution was stirred for 4 h, and then mixture was filtered. The filtrate was placed at room temperature for 24 h. The gray precipitate was removed by filtration and precipitate was washed with cold THF. Recrystallization from 2-propanol gave gray crystals of H_2L. Yield: 1.91 g, 91%, m.p. 219-221 ^{o}C. IR (KBr) cm^{-1}: 3400 (NH), 2800-3200 (OH), 1635 and 1600 (C=N). ^{1}H-NMR, ppm: 12.35 (1H, OH, exchangeable with D_2O), 10.76 (1H, OH, exchangeable with D_2O), 9.35 (bs, 1H, NH, exchangeable with D_2O), 6.82-7.37 (4H, CH_{Ar}). ^{13}C-NMR, ppm: 137.56, 137.24 (oximic carbons C2, C3), 133.64, 126.97, 125.89, 120.97, 116.62, and 112.81 (aromatic ring). MS: m/z; 418 (2M), 335, 209(M^+), 193 and 150. Elemental analysis for $C_8H_7N_3O_2S$ calculated: C, 45.93; H, 3.37; N, 20.08; S, 15.32; found: C, 45.91; H, 3.37; N, 20.12; S, 15.30.

Synthesis of [$R_2SnCl_2(H_2L)$] complex

To an ethanolic solution of H_2L 0.21 g (1 mmol, in EtOH 40 mL) diorganotin(IV) dichloride (1 mmol, in EtOH 20 mL) was added. The solution was stirred for 30 min. The pH of the solution was kept around 4.5-5 by addition a solution of NaOH (0.01 M). The mixture was refluxed for 5 h at 60 °C, volume of the solution reduced to 15 mL by reduced pressure distillation. The precipitate was filtered and washed with H_2O, Et_2O and hot EtOH.

[$Me_2SnCl_2(H_2L)$]. 0.23 g (54%), 246.5 °C (decomposed), ^{1}H NMR, IR (KBr, cm^{-1}) and EI-MS (m/z) data were given in Tables 2 and 3. Elemental analysis for $C_{10}H_{13}Cl_2N_3O_2SSn$ calculated: C, 28.00; H, 3.06; N, 9.80; found: C, 27.83; H, 3.01; N, 9.62. EI-MS (m/z): 429.

[$Et_2SnCl_2(H_2L)$]. 0.26 g (57%), m.p. 252 °C, ^{1}H NMR, IR (KBr, cm^{-1}) and EI-MS (m/z) data were given in Tables 2 and 3. Elemental analysis for $C_{12}H_{17}Cl_2N_3O_2SSn$ calculated: C, 31.54; H, 3.75; N, 9.20; found: C, 31.14; H, 3.64; N, 8.96. EI-MS (m/z): 457.

[$Ph_2SnCl_2(H_2L)$]. 0.30 g (57%), 294.5 °C (decomposed), ^{1}H NMR, IR (KBr, cm^{-1}) and EI-MS (m/z) data were given in Tables 2 and 3. Elemental analysis for $C_{20}H_{17}Cl_2N_3O_2SSn$ calculated: C, 43.44; H, 3.10; N, 7.60; found: C, 43.03; H, 3.01; N, 7.20. EI-MS (m/z): 553.

Solution studies

UV-Vis measurements were carried out by a titration method at 5, 10, 15, 20, and 25 ± 1 °C, in duplicate experiments. In a typical measurement, 2.0 mL solution of H_2L (1×10^{-4} M) in DMF was titrated by Me_2SnCl_2 (3.2×10^{-3} M). UV-Vis spectrum was recorded over a range of 260-510 nm and formation constant K (M^{-2}) of the complexes were calculated by the SQUAD program [21]. This program is designed to calculate the best values for the stability constants of the proposed equilibrium model by employing a non-linear least-squares approach.

X-ray structure analysis of H_2L

The structure of compound (H_2L) was established by X-ray crystallography (see Figure 1, Table 1 and also experimental section for details). There are some unusual structural features for H_2L.

Table 1. Crystal and structure refinement for (2*E*,3*E*)-2*H*-1,4-dibenzothiazine–2,3 (4*H*)-dione dioxime.

Formula	$C_8H_{11}N_3O_4S$
Formula weight	209
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 9.1636(18) Å α = 90° b = 9.8195(18) Å β = 90° c = 24.165(4) Å γ = 90°
V	2174.4(7) Å^3
Z, Calculated density	8, 1.498 mg/m^3
Absorption coefficient	0.302 mm^{-1}
F(000)	1024
Crystal size	0.5 x 0.5 x 0.1 mm^3
Theta range for data collection	1.69 to 27.04°
Index ranges	-11<=h<=11, -12<=k<=12, -30<=l<=28
Reflections collected	15018
Independent reflections	2337[R (int) = 0.0823]
Completeness to theta	27.04°, 97.8%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2337/ 0 /145
Goodness-of-fit on F^2	1.018
Final R indices for 1482 refl. with [I>2Sigma(I)]	R1 = 0.0458, wR2 = 0.0962
R indices (all data)	R1 = 0.0850, wR2 = 0.1072
Largest diff. peak and hole	0.433 and -0.251 eÅ^{-3}

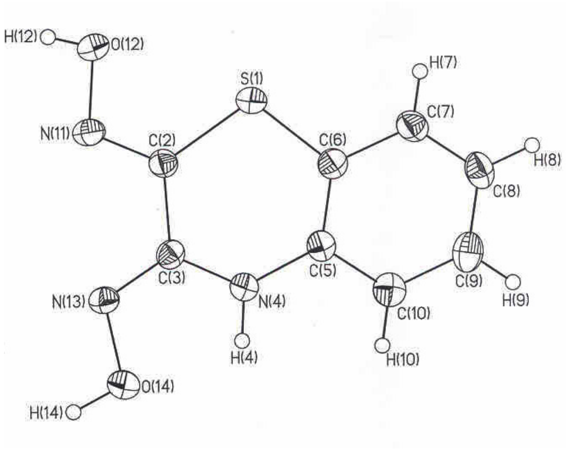


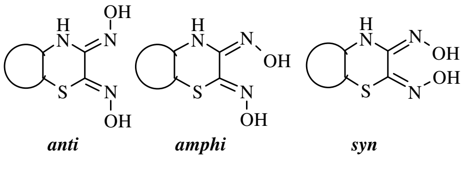
Figure 1. ORTEP drawing of H_2L.

The clear colorless crystal with the dimensions 0.5 × 0.5 × 0.1 mm^3 was used for data collection on a Bruker SMART 1000 CCD diffractommeter with graphite monochromated MoKα (λ = 0.71073 Å). $C_8H_{11}N_3O_4S$, FW = 245.26. Orthorhombic crystals in a Pbca Space group, a = 9.1636(18) Å, b = 9.8195(18) Å, c = 24.165(4) Å, β = 93.08(1)°, V = 1284.07(16) $Å^{-3}$. Z = 8, D (X-ray, calcd) = 1.498 Mg/m^3. μ = 0.302 mm^{-1}, F (000) = 1024, T = 120(2)° K. Of the 15018 total reflections, 2337 were unique. R_{int} = 0.0823. The structure was dissolved by direct methods (SHELEXTL PC) [22] and refined by full-matrix leaste-squares (isotropic refinement of the molecule and location of remaining non-hydrogen atoms from a difference Fourrier and subsequent anisotropic refinement on all atoms; H atoms were found after high-angle refinement in a difference Fourrier and their positions included in the final stages of refinement), factors of R1 = 0.0458, Rw2 = 0.0962 for 1482 unique observed reflections (another reflections, with I > 2σ (I), were considered unobserved). No significant features, only ripples from –0.251 to 0.433 e $Å^{-3}$, were observed in the final difference map. The nonhydrogen atoms were refined anisotropically.

Torsion angles for N_4-C_5-C_6-S_1, C_5-C_6-N_4-C_3 and C_5-C_6-S_1-C_2 are –2.1°, 3.4° and –7.6°, respectively, which they show that the thiazine ring is slightly moved from planarity with respect to the fused aromatic ring. Results show a resonance between aromatic ring and C=N bonds of oxime, in which N and S atoms of the H_2L have been included in this resonance. This can be attributed to the influence of bond lengths, bond angles, pyramid and planarity of thiazine ring. The torsion angles of N_{13}-C_3-C_2-N_{11}, N_4-C_3-C_2-S_1, and C_6-C_5-C_2-C_3 are -16.8(3)°, –19.9° and 9.93 (18)°, respectively. These data show that C_2 and C_3 are not coplanar and the C_2-C_3 bond shows a single bond characteristic.

Furthermore, the X-ray data showed that molecule H_2L could be existed as a dimmer through intermolecular hydrogen bond formation. The unit cell of the resulting crystal clearly revealed that a three dimensional network is formed owing to the presence of intermolecular hydrogen bond interaction. The hydrogen bonding in H_2L leads to a face-to-edge [23] configuration which is supported by two lattice water molecules.

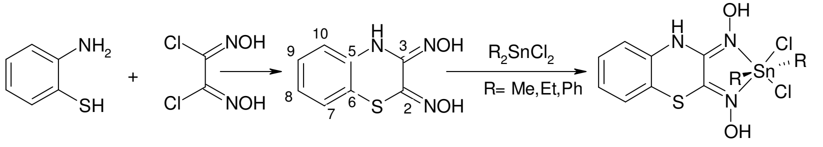
The experimental data and structural models show the existence of three possible cyclic configurations for *vic*-dioximes (anti, amphi and syn), Scheme 1. The isomer distribution depends on steric effects of substitutions and the possibility of hydrogen bond formation between the oxime groups. The torsion angles of molecule H_2L, N_{11}-C_2-C_3-N_{13}, C_2-C_3-N_{13}-O_{14}, N_4-C_3-C_2-S_1 and C_3-C_2-N_{11}-O_{12} confirm an anti configuration and the oxime groups will not be coplanar unless they are linked by a hydrogen bond. Also mass spectrum of H_2L shows a molecular ion peak at 418 m/z which confirm its dimmer structure that arise hydrogen bonding. Atomic coordinate, temperature factors, bond distances, bond angles and torsion have been deposited at the Cambridge Crystallographic Data Center. Number CCDC 299488. These data can be obtained free of charge *via* WWW.ccdc.cam.ac.uk/conts/retrieving; html (or from Cambridge Crystallographic Data Center; deposit@ccdc.cam.ac.uk).



Scheme 1. Possible isomer of cyclic *vic*-dioximes [24].

RESULTS AND DISCUSSION

Reaction of diorganotin(IV) dichlorides with H_2L led to formation of $[R_2SnCl_2(H_2L)]$ complexes in yields of 54-57% (Scheme 2). Products were characterized by means of FT-IR, ^1H NMR, EI-MS, and mole ratio determination using UV-Vis electronic absorption methods, (Figure 2). The results obtained through these techniques are in agreement with the proposed 1:1 stoichometry between the organotin moieties and the *vic*-dioxime ligand. Due to the low solubility of these complexes, our attempts were failed to get single crystals suitable for X-ray crystallographic.



Scheme 2

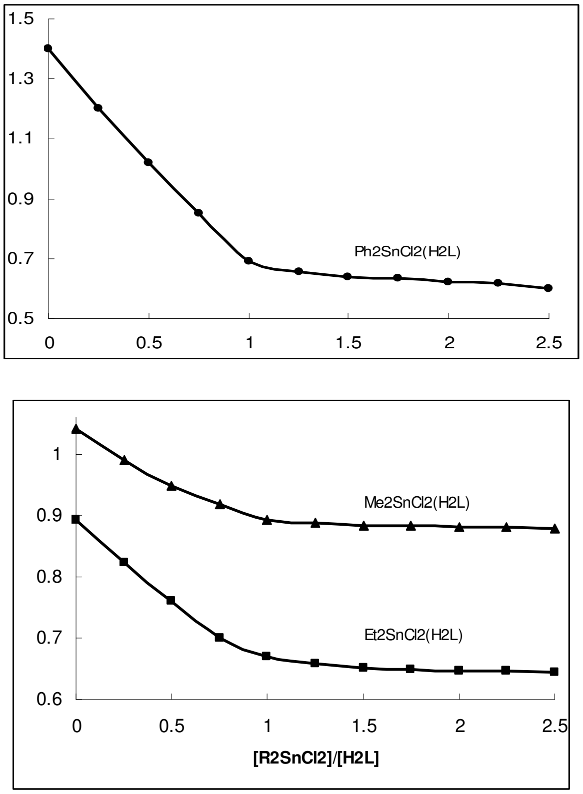


Figure 2. Absorbance versus mole ratio plots for titration of H_2L with R_2SnCl_2 ($[Me_2SnCl_2(H_2L)]$ at 277, $[Et_2SnCl_2(H_2L)]$ at 310 and $[Ph_2SnCl_2(H_2L)]$ at 308 nm).

^{1}H NMR spectral analysis

The ^{1}H NMR data for the H_2L and its complexes with diorganotin(IV) dichlorides are given in Table 2. The ^{1}H NMR spectrum of H_2L is characterized by four signals at 12.34, 10.76, 9.36 and 6.83-7.38 ppm, which are assigned to the protons associated with -OH, -OH, -NH and aromatic ring protons, respectively. The OH protons of the ligand are magnetically nonequivalent thus they give two single resonances at δ 12.34 and 10.76 ppm. In ^{1}H NMR spectra of $[R_2SnCl_2(H_2L)]$ complexes the signals of OH protons are seen at 12.39 and 10.79 ppm for $Me_2SnCl_2(H_2L)$, 12.38 and 10.80 ppm for $Et_2SnCl_2(H_2L)$ and $Ph_2SnCl_2(H_2L)$ complexes. Also, the NH proton of H_2L is appeared at 9.36 that shifted downfield to 9.44 ppm in $Me_2SnCl_2(H_2L)$, and 9.40 ppm for $Et_2SnCl_2(H_2L)$ and $Ph_2SnCl_2(H_2L)$ complexes. The aromatic protons of the H_2L (6.83-738 ppm) shifted slightly downfield (6.90-7.45 ppm) upon complex formation. The magnitude of $^2J(^{119}Sn\text{-}H)$ for five to six or seven coordinated dimethyltin(IV) complex has been reported in the range of 71-116 Hz depending on the stereochemistry of tin and the nature of the ligand [25]. Various kinds of protons in $[R_2SnCl_2(H_2L)]$ complexes have been identified and total numbers of protons estimated from the integration curves of ^{1}H NMR spectra are in agreement with the proposed molecular formula. The sharp signal attributed to the methyl group of $(CH_3)_2SnCl_2(H_2L)$ appeared as a singlet at 1.06 ppm and the $^2J(^{119}Sn\text{-}H)$ and $^2J(^{117}Sn\text{-}H)$ coupling constant values are 77 Hz and 73 Hz, which are almost similar with the coupling constant previously reported for six coordinated tin complexes. In the complex $(CH_3CH_2)_2SnCl_2(H_2L)$ a triplet at 1.27-1.30 ppm for CH_3 and a quartet at 1.53-1.58 ppm for CH_2 are assigned to ethyl group of complex. $(C_6H_5)_2SnCl_2(H_2L)$ showed a multiplet in the region 6.86-7.44 ppm, which may be assigned to aromatic ring protons of H_2L and Sn-Ph protons. The signals could not properly assign due to overlap of corresponding signals of Ph-Sn and aromatic ring protons.

Table 2. ^{1}H NMR chemical shift (δ/ppm) of H_2L and its complexes with R_2SnCl_2.

Compound				Proton
$Ph_2SnCl_2(H_2L)$	$Et_2SnCl_2(H_2L)$	$Me_2SnCl_2(H_2L)$	H_2L	
12.38 (s)	12.38 (s)	12.39 (s)	12.34(s)	H21 (OH)
10.80 (s)	10.80 (s)	10.79 (s)	10.76(s)	H20 (OH)
9.40 (s)	9.40 (s)	9.44 (s)	9.36(s)	H18 (NH)
6.86-7.44 (m)	7.39-7.41 (d)	7.43-7.45 (d)	7.37-7.38 (d, J = 8.11)	H7
6.86-7.44 (m)	7.21-7.22 (d)	7.24-7.25 (d)	7.18-7.19 (d, J = 7.84)	H10
6.86-7.44 (m)	7.10-7.13 (t)	7.12-7.15 (t)	7.07-7.10 (t, J = 7.5)	H8
6.86-7.44 (m)	6.86-6.89 (t)	6.90-6.92 (t)	6.83-6.86 (t, J = 7.44)	H9
6.86-7.44 (m)	1.27-1.30 (t), 1.53-1.58 (q)	1.06 (t)	-	Me-, Et-, Ph-

Infrared spectral analysis

The IR data for the ligand H_2L and its complexes are given in Table 3. The free ligand exhibiting characteristic $\nu_{(N\text{-}O)}$, $\nu_{(C=N)}$, $\nu_{(OH)}$, and $\nu_{(NH)}$ bands at 920, 1635, 2800-3200 and 3400 cm^{-1}, respectively. All these band absorptions were seen in the complexes but some of them shifted with respect to free H_2L. The stretching vibration of N-O observed at 920 cm^{-1} in H_2L is shifted to the higher region at 922-945 cm^{-1} in the complexes supporting that oxime N atoms are coordinated to Sn(IV). In the 440-480 cm^{-1} region of infrared spectra of complexes some bands appeared for Sn-N stretching vibration [26]. The intense band observed at 1635 cm^{-1} in the H_2L attributed due to imine C=N appears at 1645-1649 cm^{-1} in the IR spectra of complexes. Also band characteristic of the NH and the OH stretching frequencies are remained and appeared at 3120-3400 cm^{-1} in the complexes.

Table 3. Vibrational sterching frequencies (cm^{-1}) of H_2L and its complexes with R_2SnCl_2.

Compound	$\nu_{(N-O)}$	$\nu_{(C-C)}$ Oxime	$\nu_{(C=N)}$	$\nu_{(C-H)}$ Aliph	$\nu_{(C-H)}$ Arom	$\nu_{(OH)}$	$\nu_{(NH)}$
H_2L	920	1600,1420	1635	-	3100	2800-3200	3400
$Me_2SnCl_2(H_2L)$	934	1593,1437	1649	2800-2930	3095	3120-3330	3331
$Et_2SnCl_2(H_2L)$	945	1592,1432	1646	2800-2950	3110	3240-3390	3391
$Ph_2SnCl_2(H_2L)$	922	1590,1428	1645	-	3116	3125-3341	3338

EI-MS spectral analysis

In the EI-MS spectrum a molecular ion peak appeared at 429 for $Me_2SnCl_2(H_2L)$. By fragmentation some peaks have been appeared at 404, 392, 374, 374, 362, 352, 331, 322, 298, 276, and 268. The parent molecular ion peak and its related fragments are in a good agreement with our proposed structure.

The EI-MS spectrum of $Et_2SnCl_2(H_2L)$ showed a molecular ion peak at 457 and some fragments at 442, 427, 411, 396, 384, 365, 344, 322, 304, and 290. These fragments confirm our proposed structure for this complex. Similarly, The presence of a molecular ion peak at 553 and some other peaks at 507, 486, 449, 430, 395, 373, 298, 282, 266, 248, and 191 in the mass spectrum of $Ph_2SnCl_2(H_2L)$, confirms our considered structure for this complex.

Thermodynamic studies

Interactions of diorganotin(IV) dichlorides with H_2L were studied by means of UV-Vis titration. By addition of diorganotin(IV) dichlorides to a solution of H_2L, the original band of H_2L (260-370, λ_{max} 278 nm) was weakened. In contrast, a new weak band was appeared at (380-430, λ_{max} 417 nm) for the complex.

The occurrence of isosbestic points during a reaction is very informative. Isosbestic points are wavelengths at which the absorbance remains constant as the reactant and product composition changes. Isobesdic point suggests that the molecule exists as Zwitter ion, in the case of complex it is indicative of the formation of only one product. The occurrence of isosbestic points implies the absence of appreciable amount of reaction intermediates. Also it has been mentioned in the literature that the presence of isosbestic points means that the complex forms through equilibrium reactions [14]. Therefore, a clear isosbestic point at 357 nm for this interaction (Figure 3) represents a reversible complex formation in solution. The molar ratio plots are indicating 1:1 stoichimetry for these complexes (Figure 2).

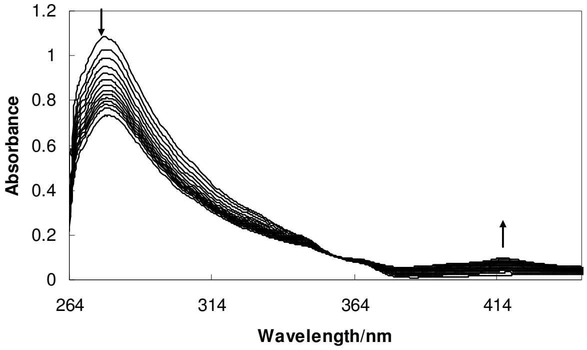


Figure 3. Titration spectrum of H_2L with Me_2SnCl_2 in DMF, $[Me_2SnCl_2(H_2L)]$, isosbestic point at 357 nm.

The thermodynamic parameters are useful tools for studying these reactions and understanding the charactristic of corresponding complexes. The formation constant K (M^{-1}) of complexes was determined at several temperatures by analyzing the concentration and temperature dependence of the UV-Vis absorbtion by a SQUAD program (Table 4). Van't Hoff plots of these formation constants, K (M^{-1}), lead to other thermodynamic parameters, ΔH°, ΔS°, and ΔG° (Table 4).

Table 4. The formation constants (log K) for $[R_2SnCl_2(H_2L)]$ complexes.

Complex	Temp. (°C)				
	10	15	20	25	30
$Me_2SnCl_2(H_2L)$	4.25 ± 0.02	3.93 ± 0.04	3.46 ± 0.02	3.18 ± 0.01	2.85 ± 0.02
$Et_2SnCl_2(H_2L)$	3.67 ± 0.01	3.23 ± 0.03	2.91 ± 0.06	2.67 ± 0.02	2.32 ± 0.03
$Ph_2SnCl_2(H_2L)$	3.19 ± 0.02	2.94 ± 0.01	2.64 ± 0.02	2.21 ± 0.04	1.96 ± 0.02

Table 5. The thermodynamic parameters for $[R_2SnCl_2(H_2L)]$ complexes.

Complex	$-\Delta H^\circ$ (kcal mol^{-1})	$-\Delta S^\circ$ (cal $mol^{-1}K^{-1}$)	$-\Delta G^\circ$ (kcal mol^{-1})
$Me_2SnCl_2(H_2L)$	117.1 ± 4.8	331.8 ± 16.3	18.2 ± 4.8
$Et_2SnCl_2(H_2L)$	107.6 ± 5.4	335.4 ± 18.2	15.1 ± 5.3
$Ph_2SnCl_2(H_2L)$	104.7 ± 5.8	308.7 ± 19.9	13.1 ± 5.8

Table 4 shows that the formation constant of complexes undergo a regular decrease from $Me_2SnCl_2(H_2L)$, $Et_2SnCl_2(H_2L)$ to $Ph_2SnCl_2(H_2L)$. This order might return to the importance of steric parameters on stability of complexes. For example, at 20 °C we have the following order of the formation constants: $Me_2SnCl_2(H_2L) > Et_2SnCl_2(H_2L) > Ph_2SnCl_2(H_2L)$, $3.46 > 2.91 > 2.64$. The log K values decreased with rising temperature, it shows that reactions under investigations have exothermic characteristics.

The values of ΔH°, ΔG°, and ΔS°, are negative for these complexes. Generally, negative values of ΔH° are assigned to the exothermic reactions and the $\Delta S^\circ < 0$ refers to association between donor and acceptor molecules (Table 4). A greater contribution of the ΔH° relative to the ΔS° leads to a negative value of the ΔG° in the Equation (2):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{1}$$

Negative values for ΔG° show that these complex formations are energetically favorable.

Computational studies

Calculations were performed using the Gaussian 98 system of codes [27]. For geometry optimization, starting structures of reactants H_2L and R_2SnCl_2 as well as products $[R_2SnCl_2(H_2L)]$ were fully optimized at HF/3-21G*. Considering size of under investigation complexes and our calculation tools this level seems suitable for our purpose. Harmonic vibrational frequency calculations at HF/3-21G* level confirmed the structures as minima and enabled the evaluation of zero point energies (ZPE). The stabilization energy of products was defined as total energy corrected for ZPE of products minus reactants: $SE = E\,[R_2SnCl_2(H_2L)] - (E\,H_2L + E\,R_2SnCl_2)$.

For each complex two structures were considered. In the first structure the R groups occupied equatorial positions, while in the second one R groups were axial. According to our theoretical calculations predicted stabilization energies of axial and equatorial structures of

$Me_2SnCl_2(H_2L)$ are −25.79 and −20.12 kcal.mol^{-1}, respectively. Similarly, predicted stabilization energies for axial and equatorial structures of $Et_2SnCl_2(H_2L)$ adducts are −26.27 and −19.51 kcal.mol^{-1}. These results show that presence of R groups at axial positions leads to more stability of complexes. Less steric crowding in structures with R groups at axial positions probably lead to their greater stability. Another parameter that may help to greater stability of axial structure is possibility of hydrogen bonding interaction between NOH group of oxime with Cl atoms of organotin. However the HF/3-21G* is not a sophisticated level for study of hydrogen bonding but optimized structures showed that axial isomers with H…Cl distances smaller than 2.4 Å have better conditions for formation of such hydrogen bond interactions.

CONCLUSIONS

The synthesis and physical properties of a series of diorganotin(IV) dichloride complexes with (2H)-1,4-benzothiazine-2,3-(4H)-dione dioxime are described. The ligand behave as a bidentate fashion towards to tin(IV). The X-ray crystalographic data of ligand is given. The $[R_2SnCl_2(H_2L)]$ compounds were characterized using IR, MS, UV-Vis, and ^{1}H NMR methods. Theoretical calculations at the HF/3-21G* level was used to determine more stable structure. Thermodynamic stability of $[R_2SnCl_2(H_2L)]$ complexes are in the order: $[Me_2SnCl_2(H_2L)] > [Et_2SnCl_2(H_2L)] > [Ph_2SnCl_2(H_2L)]$.

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