Inorganica Chimica Acta 435 (2015) 103–108

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Diorganotin(IV) complexes of 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone: Synthesis, spectral characterization and crystal structure

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ARTICLE INFO

Article history:
Received 24 March 2015
Received in revised form 19 June 2015
Accepted 23 June 2015
Available online 29 June 2015

Keywords:
3,5-Dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone
Synthesis
Organotin(IV) complexes
Spectral characterization
Crystal structure

ABSTRACT

Three new diorganotin(IV) complexes of the formulae [Me_2Sn(cdet)] (**2**), [Bu_2Sn(cdet)] (**3**) and [Ph_2Sn(cdet)] (**4**) have been synthesized by the reaction of 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone [H_2cdet, (**1**)] and appropriate diorganotin(IV) chloride in the presence of KOH in absolute methanol. These compounds have been characterized by CHN analyses, UV–Vis, FT-IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic techniques. The molecular structures of the ligand (**1**) and its diphenyltin(IV) complex (**4**) have been determined by X-ray diffraction analysis. The ligand H_2cdet (**1**) remains as the thione form in the solid state. The crystal structure of [Ph_2Sn(cdet)] (**4**) revealed that the ligand is coordinated to central tin(IV) atom as a dinegatively tridentate chelating agent *via* the phenoxide oxygen atom, the azomethine nitrogen atom and the thiolate sulfur atom. The ^{119}Sn NMR chemical shift for the complexes (**2**–**4**) are found to be −177.08 to −169.22 ppm, confirming five coordinated tin(IV) centre. X-ray crystal structure showed that the coordination geometry of central tin(IV) atom is distorted trigonal bipyramid. The oxygen and sulfur atoms are in axial positions while two phenyl groups and the azomethine nitrogen atom of the ligand occupy the equatorial positions.

1. Introduction

Organotin(IV) compounds have been extensively studied for their industrial, agricultural and medical applications [1–4]. Thiosemicarbazones have received much attention recently due to the extensive application in the chemotherapeutic field [5,6]. Thiosemicarbazones and their metal complexes are important series of compounds due to their potential biological activity as antifungals, anti-virals, anti-malarials and anti-tumour agents [7–14]. In particular, transition metal complexes with substituted thiosemicarbazones have received much attention due to their coordination chemistry and potential biological activity [15–22]. The *N*(4)-substituted thiosemicarbazones and their metal complexes exhibit significant biological activities which vary from those of either metal atom or parent ligands [23–27]. Recently, Mouayed et al., have reported coordination chemistry of thiosemicarbazonato molybdenum (VI) complexes and their biological activity against various tumour cell lines [28,29]. Organotin complexes have been attracting the attention of researchers due to their considerable structural diversity. A series of diorganotin complexes were synthesized and investigated for their structural chemistry and various applications as PVC stabilizers, metal-based drugs and biocides [30–33]. Earlier reports, notably those of Sousa et al., and Tahereh et al., have reported the organotin(IV) complexes of substituted-*N*(4)-phenylthiosemicarbazones with potential biological properties [34,35]. Currently, the synthesis of organotin(IV) derivatives with thiosemicarbazones having two or more donor atoms has become a popular research area. Organotin(IV) complexes of ONS-tridentate *N*4-heterocyclic thiosemicarbazones were reported by Sousa et al., with the tin(IV) atoms exhibiting distorted trigonal bipyramidal (TBP) geometry [36]. To our best knowledge, there are still very little information available regarding the synthesis and structural studies of diorganotin(IV) complexes containing ONS-tridentate thiosemicarbazone ligand. Motivated by these promising studies, we find it desirable to investigate the synthesis and coordination mode of diorganotin(IV) complexes with 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone. This study also reported different spectroscopic characterizations of the diorganotin(IV) complexes and X-ray crystal structure of one representative complex.

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http://dx.doi.org/10.1016/j.ica.2015.06.015
0020-1693/

2. Experimental

2.1. Materials and methods

All reagents were purchased from Fluka, Aldrich and Sigma. All solvents were received as reagent grade and used without further purification. Melting point was measured on a Stuart Scientific SMP1 melting point apparatus. UV–Vis spectra were recorded in DMSO solution with a Perkin Elmer Lambda 25 UV–Vis spectrophotometer. Infrared (IR) spectra were measured on a Perkin Elmer System 2000 spectrophotometer using the KBr disc method in the range 4000–400 cm^{-1} at room temperature. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker 500 and 400 MHz NMR spectrophotometer relative to $SiMe_4$ and $SnMe_4$ in DMSO solvent. Elemental analysis was conducted using a Perkin Elmer 2400 Series-11 CHN analyzer. Molar conductivity measurements were carried out with a Jenway 4510 conductivity meter using DMSO as a solvent. X-ray crystallographic data were recorded on a Bruker SMART APEXII CCD area-detector diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. The data were collected and reduced using APEX2 and SAINT programs. The structure of compounds was solved by direct methods and was refined using the full-matrix least-squares method on F^2 using the SHELXTL program [37]. All nonhydrogen atoms were anisotropically refined. The molecular graphics were created using SHELXTL-97.

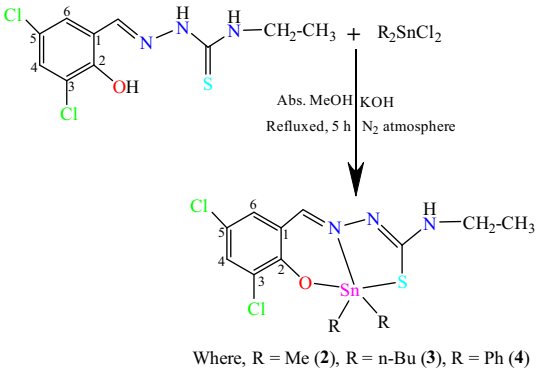
2.2. Synthesis of 3,5-dichloro-2-hydroxybenzaldehyde-N(4)-ethylthiosemicarbazone [H_2cdet, (**1**)]

A solution of 3,5-dichloro-2-hydroxybenzaldehyde (0.76 g, 4.0 mmol) in methanol (20 mL) was added to a solution of 4-ethyl-3-thiosemicarbazide (0.48 g, 4.0 mmol) in methanol (20 mL). The resulting yellow solution was refluxed with stirring for 2 h (Scheme 1) and then filtered, washed with cold methanol and dried in desiccators over anhydrous silica gel. Yield: 0.98 g, 79%: M.p: 185–187 °C: UV–Vis (DMSO) $\lambda_{max/nm}$: 267, 338, 376: FT-IR (KBr, cm^{-1}) ν_{max}: 3405 (s, OH), 3268, 3186 (s, NH), 1635 (m, C=N), 1549 (s, C_{aro}–O), 989 (m, N–N), 1367, 857 (w, C–S). ^{1}H NMR (DMSO-d_6, ppm): 11.40 (s, 1H, OH), 10.47 (s, 1H, N–NH), 8.83 (s, 1H, CS–NH), 8.28 (s, 1H, CH=N), 8.05 (s, 1H, PhC4–H), 7.73 (s, 1H, PhC6–H), 3.61 (m, 2H, CH_2), 1.13 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): 186.60 (C=S), 150.52 (C=N), 137.58–122.57 (Ph–C), 30.61 (CH_2), 18.46 (CH_3). *Anal.* Calc. for $C_{10}H_{11}Cl_2N_3OS$: C, 41.06; H, 3.76; N, 14.37. Found: C, 40.98; H, 3.56; N, 14.09%.

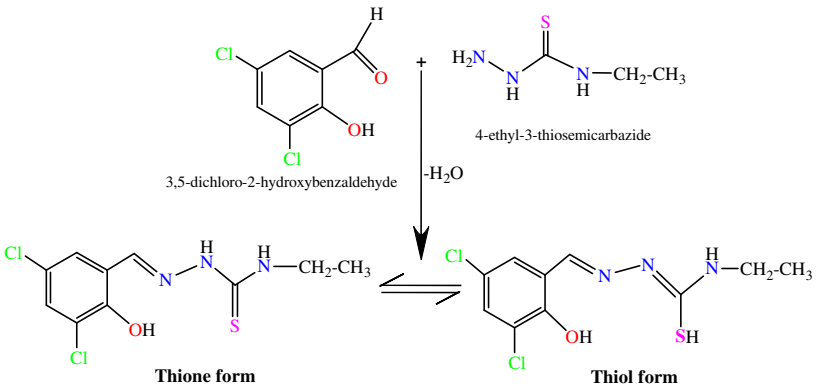
2.3. Synthesis of [Me_2Sn(cdet)] (**2**)

H_2cdet (**1**) (0.292 g, 1.0 mmol) was dissolved in absolute methanol (10 mL) in a round-bottom reaction flask under nitrogen atmosphere. KOH (0.11 g, 2.0 mmol) dissolved in methanol was added dropwise to the ligand solution and the colour changed to orange. The resulting mixture was refluxed under nitrogen for 1 h. Then, a methanolic solution of dimethyltin(IV) dichloride (0.219 g, 1.0 mmol) was added dropwise and resulted in a yellow solution. The resulting reaction mixture was refluxed for 5 h (Scheme 2) and cooled to room temperature. Potassium chloride (KCl) was filtered off and the solution dried in desiccators over anhydrous silica gel. Yield: 0.39 g, 76%: M.p: 268–270 °C: Molar conductivity (1×10^{-3} mol L^{-1}; DMSO) Ω^{-1} cm^2 mol^{-1}: 11.30: UV–Vis (DMSO) $\lambda_{max/nm}$: 270, 341, 380, 458: FT-IR (KBr, cm^{-1}) ν_{max}: 3180 (s, NH), 1592 (m, C=N), 1526 (s, C_{aro}–O), 1023 (m, N–N), 1315, 822 (w, C–S), 608 (w, Sn–C), 557 (w, Sn–O), 482 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm, ^{2}J[119Sn,1H]): 8.85 (s, 1H, CS–NH), 8.20 (s, 1H, CH=N), 8.10 (s, 1H, PhC4–H), 7.70 (s, 1H, PhC6–H), 3.67 (m, 2H, CH_2), 1.10 (t, 3H, CH_3) 1.04 (s, 6H, Sn–$(CH_3)_2$ [86.31 Hz]). ^{13}C NMR (DMSO-d_6, ppm, ^{1}J[(^{13}C–^{119}Sn]): 170.13 (C=S), 168.24 (C=N), 144.88–130.55 (Ph–C), 30.82 (CH_2), 18.52 (CH_3), 14.85 (Sn–CH_3), [562.33 Hz]. ^{119}Sn NMR (DMSO-d_6, ppm): −169.22. *Anal.* Calc. for $C_{12}H_{15}Cl_2N_3OSSn$: C, 32.84; H, 3.44; N, 9.57%. Found: C, 32.93; H, 3.55; N, 9.68%.

The other diorganotin(IV) complexes (**3**–**4**) were synthesised following the same procedure by using the appropriate diorganotin(IV) chloride(s) (Scheme 2).



Scheme 2. Reaction scheme for the synthesis of diorganotin(IV) complexes (**2**–**4**).



Scheme 1. Synthesis of 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone [H_2cdet, (**1**)].

*2.4. Synthesis of [Bu_2Sn(cdet)] (**3**)*

Yield: 0.47 g, 78%: M.p: 254–256 °C: Molar conductivity (1×10^{-3} mol L^{-1}; DMSO) Ω^{-1} cm^2 mol^{-1}: 13.23: UV–Vis (DMSO) $\lambda_{max/nm}$: 269, 340, 379, 448: FT-IR (KBr, cm^{-1}) ν_{max}: 3193 (s, NH), 1587 (m, C=N), 1518 (s, C_{aro}–O), 1019 (m, N–N), 1318, 821 (w, C–S), 612 (w, Sn–C), 555 (w, Sn–O), 473 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm): 8.88 (s, 1H, CS-NH), 8.25 (s, 1H, CH=N), 8.12 (s, 1H, PhC4–H), 7.62 (s, 1H, PhC6–H), 3.64 (m, 2H, CH_2), 1.14 (t, 3H, CH_3), 1.43–1.35 (m, 2H Sn–$\underline{CH_2}$–CH_2–CH_2–CH_3), 1.28–1.20 (m, 2H, Sn–CH_2–$\underline{CH_2}$–CH_2–CH_3), 1.16–1.11 (m, 2H, Sn–CH_2–CH_2–$\underline{CH_2}$–CH_3), 1.06–0.91 (t, 3H, Sn–CH_2–CH_2–CH_2–$\underline{CH_3}$). ^{13}C NMR (DMSO-d_6, ppm, ^1J(^{13}C–^{119}Sn]): 169.41 (C=S), 162.11 (C=N), 148.31–132.25 (Ph–C), 30.60 (CH_2), 18.38 (CH_3), 31.23, 28.31, 24.26, 20.75 (Sn–Bu) [548.45 Hz]. ^{119}Sn NMR (DMSO-d_6, ppm): −171.52. *Anal.* Calc. for $C_{18}H_{27}Cl_2N_3OSSn$: C, 41.33; H, 5.20; N, 8.03. Found: C, 41.26; H, 5.12; N, 8.12%.

*2.5. Synthesis of [Ph_2Sn(cdet)] (**4**)*

Yield: 0.48 g, 75%: M.p: 243–245 °C: Molar conductivity (1×10^{-3} mol L^{-1}; DMSO) Ω^{-1} cm^2 mol^{-1}: 9.58: UV–Vis (DMSO) $\lambda_{max/nm}$: 272, 342, 381, 437: FT-IR (KBr, cm^{-1}) ν_{max}: 3198 (s, NH), 1581 (m, C=N), 1520 (s, C_{aro}–O), 1027 (m, N–N), 1331, 814 (w, C–S), 609 (w, Sn–C), 564 (w, Sn–O), 449 (w, Sn–N). ^{1}H NMR (DMSO-d_6, ppm): 8.84 (s, 1H, CS–NH), 8.19 (s, 1H, CH=N), 8.14–7.64 (m, 12H, Ph–H), 3.65 (m, 2H, CH_2), 1.16 (t, 3H, CH_3). ^{13}C NMR (DMSO-d_6, ppm, ^1J(^{13}C–^{119}Sn]): 168.74 (C=S), 164.53 (C=N), 149.05–129.61 (Ph–C), 30.75 (CH_2), 18.48 (CH_3) [552.34 Hz]. ^{119}Sn NMR (DMSO-d_6, ppm): −177.08. *Anal.* Calc. for $C_{22}H_{19}Cl_2N_3OSSn$: C, 46.93; H, 3.40; N, 7.46. Found: C, 46.98; H, 3.47; N, 7.54%.

3. Results and discussion

3.1. Synthesis

The 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone (H_2cdet) was prepared by the condensation reaction of 3,5-dichloro-2-hydroxybenzaldehyde and 4-ethyl-3-thiosemicarbazide. This ligand may exist in two tautomeric forms, either thiol or thione tautomer (Scheme 1). Three new diorganotin(IV) complexes (**2**–**4**) were prepared by the direct reaction of H_2cdet (**1**) with appropriate diorganotin(IV) chloride(s) under nitrogen atmosphere in the presence of KOH in 1:2:1 M ratio (Scheme 2). All the diorganotin(IV) complexes are yellow solids, air stable and soluble in $CHCl_3$, CH_2Cl_2, DMSO, DMF and THF at room temperature. The molar conductivities of the complexes were 13.23–9.58 Ω^{-1} cm^2 mol^{-1} in DMSO, which indicates the neutral behaviour of the diorganotin(IV) complexes [38]. All the complexes have been characterized by various spectroscopic techniques and analytical methods. The analytical data and physical properties of the compounds **1**–**4** are presented in the Section 2. The molecular structures of the H_2cdet (**1**) and its diphenyltin(IV) complex **4** have been confirmed with the help of X-ray diffraction studies. Investigations exhibited that H_2cdet (**1**) coordinate in ONS-tridentate as dinegative deprotonated in all complexes.

3.2. UV–Vis spectra

The electronic spectra of the H_2cdet (**1**) and its complexes (**2**–**4**) were measured in DMSO at room temperature. Three absorption bands were observed at 262, 328 and 361 nm in the UV–Vis spectra of ligand (**1**), which are assigned to π–π^* transition of the aromatic ring and n–π^* transitions of the azomethine and thiolate function. These bands are shifted a little upon complexation due to intra ligand transition. An additional absorption band in the 458–437 nm range for complexes (**2**–**4**) can be assigned to the ligand to metal charge transfer (LMCT) transitions [39]. This band indicates that coordination takes place between the ligand and Sn(IV) atom.

3.3. Infrared spectra

The strong bands of ν(OH) and ν(N–NH) groups at 3405 and 3268 cm^{-1} of the free ligand (**1**) disappeared in the complexes (**2**–**4**) suggesting coordination *via* the phenolic oxygen and thiolate sulfur to the tin(IV) ion, respectively. The ligand (**1**) showed ν(C=N) stretching vibration at 1635 cm^{-1} which is shifted to lower frequencies in the spectra of the complexes (**2**–**4**) indicating coordination *via* azomethine nitrogen to tin(IV) ion [40]. The medium ν(C_{aro}–O) band at 1549 cm^{-1} for free ligand (**1**) is shifted to lower frequencies in the spectra of the complexes suggesting coordination *via* phenolic oxygen atom to tin(IV) ion. The frequency of ν(N–N) band was found to shift to higher frequencies in the complexes compared to the free ligand further confirming the coordination *via* the azomethine nitrogen [41]. The free ligand (**1**) displayed two bands at 1367 and 857 cm^{-1} due to stretching and bending vibration of ν(C=S), which is shifted to lower frequencies at 1331–1315 and 822–814 cm^{-1} range in the complexes (**2**–**4**), indicating the coordination *via* thiolate sulfur atom [42]. Moreover, the two new band ranges at 564–555 and 482–449 cm^{-1} provide a strong confirmation for the existence of ν(Sn–O) and ν(Sn–N), respectively, in the complexes [43]. According to the above spectral results, it is established that H_2cdet (**1**) is tridentate coordinating to the Sn(IV) centre *via* the phenolic oxygen, the azomethine nitrogen and thiolate sulfur atoms.

3.4. ^{1}H, ^{13}C and ^{119}Sn NMR spectra

The NMR spectral studies of the compounds **1**–**4** were accomplished and interpreted based on the atom labeling in Scheme 2. The sharp singlet that appeared for the OH proton of the free ligand at 11.40 ppm disappears in the complexes, indicating deprotonation of oxygen atom and coordination of the phenolic oxygen to the Sn(IV) atom. The singlet attributed to the N-NH proton at 10.47 ppm for the free ligand (**1**) is absent in the complexes (**2**–**4**), providing evidence for coordination of the thiolate sulfur to the Sn(IV) atom. The resonance signal due to the CH=N (8.28 ppm) in the free ligand is slightly shifted to a downfield region at 8.25–8.19 ppm in the complexes suggesting deshielding after coordination to Sn(IV) atom. The aromatic protons of the ligand and its complexes were observed in the region of 8.12–7.62 ppm. For complex **2**, the resonance signal of the two methyl groups attached to tin(IV) centre appears at 1.02 ppm with ^2J [^{119}Sn, ^{1}H] of 86.31 Hz confirming five coordinated tin(IV) atom and similar to those previously reported [44,45]. The signals observed in the region at 3.67–3.61 and 1.16–1.10 ppm have been assigned to the (–CH_2) and (–CH_3) protons of the ligand and its complexes, respectively. The butyl groups bonded to the Sn(IV) centre appear as a multiplet at 1.43–1.11 ppm and as a triplet at 1.06–0.91 ppm.

The ^{13}C NMR spectra of all complexes showed significant information to support the proposed structures. The signal of the (C=S) group for ligand (**1**) appeared at 186.60 ppm which is shifted to an upfield region at 170.13–168.74 ppm in the complexes (**2**–**4**), authenticated coordination of (C–S) group to Sn(IV) atom. For all complexes, the downfield chemical shifts of (C=N) carbon were found in comparison with the free ligand, indicating bonding of azomethine nitrogen to Sn(IV) atom. The chemical shifts for the

aromatic carbons were found to be slightly more downfield for the complexes than the free ligand. The chemical shift values for the (–CH_2CH_3) carbons was found at 30.82–30.60 and 18.52–18.38 ppm region, respectively. The coupling constant $^1J(^{13}C–^{119}Sn)$ values indicate the possible coordination arrangement of diorganotin(IV) compounds in solution. The coupling constant $^1J(^{13}C–^{119}Sn)$ values for dimethyltin(IV) complex (**2**), dibutyltin(IV) complex (**3**) and diphenltin(IV) complex (**4**) were observed to be 562.33, 548.45 and 552.34 Hz, respectively. Therefore, the *J* values confirmed the penta-coordinate geometry about the tin(IV) atom [46]. Likewise, the C–Sn–C angle of the diorganotin complexes can also be determined using the Lockhart–Manders equation $\theta(C–Sn–C) = [|^1J(^{13}C–^{119}Sn)| + 875]/11.4$ and affords C–Sn–C angles of 126.08°, 124.86° and 125.20° for complexes **2**, **3**, **4**, respectively. The calculated C–Sn–C angle values obtained from the NMR spectra show a slight deviation from the $C_{phenyl}–Sn–C_{phenyl}$ angle obtained from X-ray diffraction studies of complex **4**. The observed C–Sn–C angles lies in the range 124.86–126.08°, which correspond to five-coordination of the tin atom in the complexes [47].

^{119}Sn NMR spectra provide valuable information to confirm the coordination number around the tin. ^{119}Sn NMR spectra of all complexes displayed one sharp single peak supporting the formation of a single species. ^{119}Sn NMR chemical shifts of diorganotin(IV) complexes (**2**–**4**) ranging from −177.08 to −169.22 ppm demonstrated the five coordinated Sn atom [48,49].

3.5. X-ray crystallography diffraction analyses of H_2cdet (**1**)

The molecular structure of the free ligand H_2cdet (**1**), together with the atom numbering scheme and its packing in the crystal lattice are shown in Figs. 1 and 2, respectively. Summary of crystal data and structure refinement results, and selected bond lengths (Å) and angles (°) are given in Tables 1 and 2, respectively. Based on the molecular structure, the H_2cdet (**1**) remains in its tautomeric thione form with S1 and N1 in the E configuration with respect to the N2–C8 bond. The H_2cdet (**1**) exhibits the *trans* geometries of the S1 in relation to N1 atom. Furthermore, shows the *syn* geometries of N1 in relation to N3 atom. This is confirmed by the torsion angle of 176.97(12)° (N1–N2–C8–S1) [50]. The observed bond lengths confirmed that the free ligand (**1**) exist in thione form in the solid state. The bond distances of C8–S1 and C8–N2 are 1.6945(16) Å and 1.362(2) Å, respectively. These bond distances are closer to that expected of a C=S double bond (1.60 Å) [51] than to C–S bond length (1.81 Å), and the C=N double bond (1.28 Å) [52]. Similarly, the N1–N2 bond distance is 1.3743(18) Å indicating the value is closer to the N–N single bond distance (1.45 Å) than the N=N double bond distance (1.25 Å) [51].

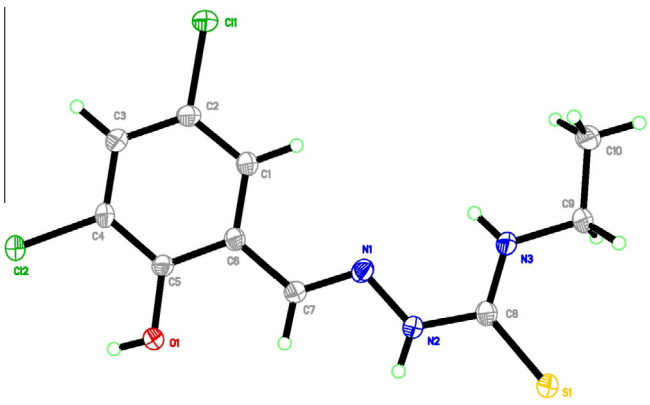


Fig. 1. Molecular structure of 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone [H_2cdet, (**1**)].

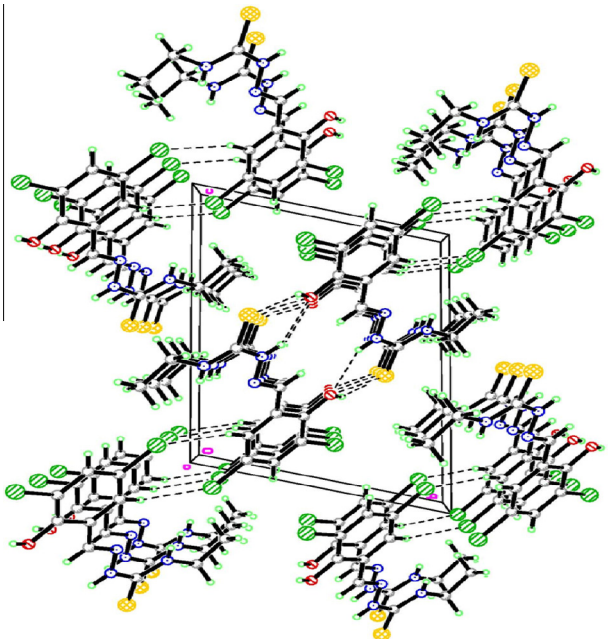


Fig. 2. The packing diagram of H_2cdet (**1**) in the crystal lattice. Intermolecular hydrogen bonds are shown as dotted lines.

Table 1
Crystal data and structure refinement parameters for H_2cdet (**1**) and [Ph_2Sn(cdet)] (**4**).

Compound	H_2cdet (**1**)	[Ph_2Sn(cdet)] (**4**)
Empirical formula	$C_{10}H_{11}Cl_2N_3OS$	$C_{22}H_{19}Cl_2N_3OSSn$
Formula weight	292.18	563.05
T (K)	100	100
λ (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	*P*–1	$P2_1/n$
Unit cell dimensions		
a (Å)	5.3023(2)	14.1937(7)
b (Å)	9.3655(3)	9.0137(5)
c (Å)	12.9787(5)	17.2872(9)
α (°)	104.444(2)	90.00
β (°)	95.345(2)	92.6314(9)
γ (°)	91.663(2)	90.00
V (Å^3)	620.51(4)	2209.4(2)
Z	2	4
Calculated density (mg/m^3)	1.564	1.693
Radiation type *λ* (Å)	Mo K/α	Mo K/α
F(000)	300	1120
Crystal size (mm)	0.12 × 0.23 × 0.44	0.081 × 0.303 × 0.463
Crystal colour	colorless	yellow
Scan range *θ* (°)	2.3–30.0	2.87–30.22
Absorption coefficient (*μ*) (mm^{-1})	0.677	1.513
Max. and min. transm	0.9238 and 0.7544	0.887 and 0.541
Goodness-of-fit (GOF) on F^2	1.099	1.048
Data/restrains/parameters	3581/0/167	6522/0/276
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0335, wR_2 = 0.0800	R_1 = 0.0176, wR_2 = 0.0447
R indices (all data)	R_1 = 0.0429, wR_2 = 0.0869	R_1 = 0.0190, wR_2 = 0.0455

The length, longer than usual of C=S and C=N points out the extended conjugation in the molecule similar to other thiosemicarbazones. The above bond lengths indicate the 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone (H_2cdet) exists in the thione form in the solid state. The packing of the molecules is stabilized by inter and intra-molecular hydrogen bonding interactions in the crystal lattice. In the crystal packing, centrosymmetrically related molecules associate into dimers *via*

Table 2
Selected bond lengths (Å) and angles (°) of H_2cdet (**1**) and [Ph_2Sn(cdet)] (**4**).

Bond lengths (Å)			
[Ph_2Sn(cdet)] (**4**)		H_2cdet (**1**)	
Sn1–S1	2.4955(4)	S1–C8	1.6945(16)
Sn1–N1	2.2269(11)	O1–C5	1.3487(19)
Sn1–C17	2.1325(12)	N1–C7	1.287(2)
O1–C1	1.3166(15)	N1–N2	1.3743(18)
N1–C7	1.3021(16)	N2–C8	1.362(2)
N3–C8	1.3535(15)	N3–C8	1.324(2)
C1–C2	1.4121(17)	N3–C9	1.467(2)
Sn1–O1	2.0798(9)	Cl1–C2	1.7406(16)
S1–C8	1.7510(13)	Cl2–C4	1.7370(16)
N1–N2	1.3854(14)	C1–C2	1.381(2)
N2 –C8	1.3070(16)	C1–C6	1.394(2)
Bond angles (°)			
[Ph_2Sn(cdet)] (**4**)		H_2cdet (**1**)	
S1–Sn1–O1	153.04(3)	C7–N1–N2	114.44(13)
S1–Sn1–C11	105.16(4)	C8–N2–N1	121.24(14)
O1–Sn1–N1	82.18(4)	C8–N3–C9	123.47(14)
O1–Sn1–C17	88.75(4)	C2–C1–C6	119.76(15)
N1–Sn1–C17	144.70(5)	C1–C2–C3	121.82(15)
Sn1–S1–C8	96.18(4)	C1–C2–Cl1	119.16(13)
Sn1–N1–N2	121.12(8)	C3–C2–Cl1	119.00(12)
S1–Sn1–N1	78.22(3)	C4–C3–C2	118.13(14)
S1–Sn1–C17	96.62(4)	N1–C7–C6	121.47(14)
O1–Sn1–C11	97.29(4)	N3–C8–N2	117.25(14)
N1–Sn1–C11	103.62(4)	N3–C8–S1	123.43(12)
C11–Sn1–C17	111.36(5)	N2–C8–S1	119.32(12)

C-H…O interactions and stack in columns along the *b* axis *via* π–π interactions. There are two significant intermolecular H-bonding contact involving the N3–H···S1 and N2–H···S1. On the other hand, the one hydrogen atom of N3 and imine-N1 atoms are directed to the same side of the molecule enabling the formation of an intramolecular N–H···N hydrogen bond. Additionally, stabilization is afforded by the C–H…π and π…π [ring centroid(hydroxybenzene)] interactions.

3.6. X-ray crystallography diffraction analyses of [Ph_2Sn(cdet)] (**4**)

The molecular structure of [Ph_2Sn(cdet)] (**4**) along with the atomic numbering scheme is given in Fig. 3. Table 1 summarizes crystal data and structure refinement results of compound **4**. Selected bond lengths (Å) and angles (°) are shown in Table 2. Compound **4** crystallizes into a monoclinic lattice with space group $P2_1/n$. The crystal structure of the title complex **4** displayed that the dianionic ligand is coordinated to the tin(IV) centre *via* the phenolic-O, azomethine-N and thiolate-S atoms. Thus, molecular structure of diphenyltin(IV) complex **4** confirmed that the central tin(V) has a penta-coordinated geometry in distorted trigonal bipyramidal arrangement. The meridional plane consists of the azomethine nitrogen (N1) and two phenyl groups (C11, C17) from the tin(IV) centre. The sum of the bond angles (N1–Sn1–C17) (144.69(4)°), (C17–Sn1–C11) (111.36(5)°) and (C11–Sn1–N1) (103.62(4)°) is 359.61° showing that thiosemicarbazone portion is in the same plane of tin(IV) centre. The axial positions are occupied by the phenolic oxygen (O1) and thilate sulfur (S1) of the ligand. The distorted trigonal bipyramidal geometry of complex **4** is evidenced from the largest bond angle containing the tin(IV) atom O1–Sn1–S1 of (153.04(4)°), which deviated from the ideal value of 180°. The bond angles of O1–Sn1–N1 is 82.18(4)° whereas N1–Sn1–S1 is 78.22(3)° thus the sum of these two bond angles is 160.38° demonstrating deviation from the ideal value of 180°. Most probably distortion is due to the involvement of the N1 atom in the five member chelate rings, besides the large covalent radius of tin(IV). The distortion from the ideal trigonal bipyramidal

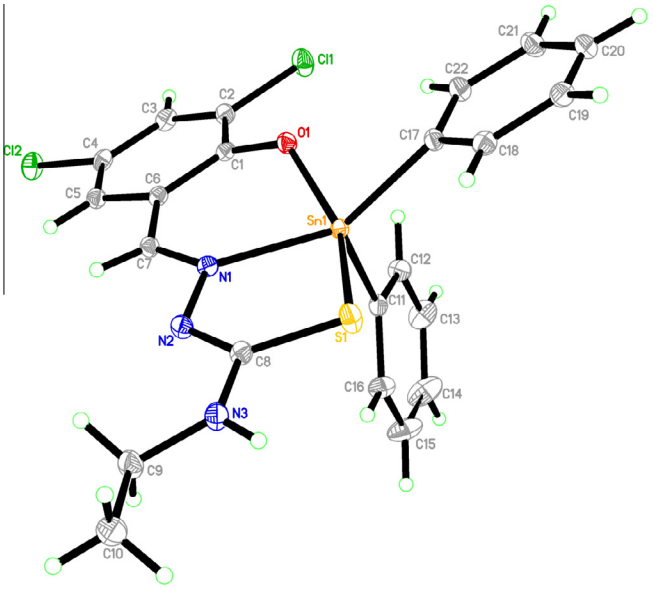


Fig. 3. Molecular structure of [Ph_2Sn(cdet)] (**4**) showing displacement ellipsoids at the 50% probability level.

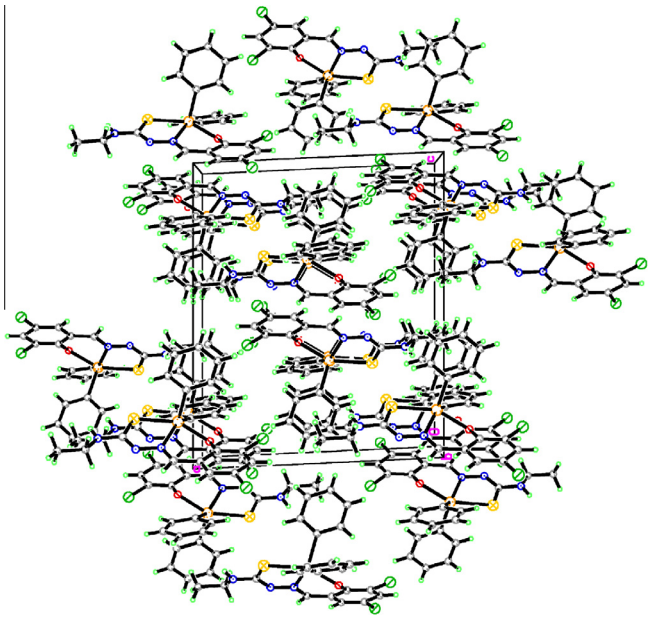


Fig. 4. The packing diagram of [Ph_2Sn(cdet)] (**4**) in the crystal lattice, viewed along the *a* axis.

geometry is affected by strain force by the non-planar five and six membered chelate rings, Sn1–S1–C8–N2–N1 and Sn1–O1–C1–C6– C7–N1. The bond angles of C11–Sn1–C17 (111.36(5)°), C11–Sn1–N1 (103.62(4)°) and C17–Sn1–N1 (144.69(4)°) for C11, C17 and N1 are situated at the three edges of the trigonal plane. So bond angles C11–Sn1–C17 and C17–Sn1–N1 are rather smaller than 120° though C17–Sn1–N1 is little larger. This is most possibly due to the repulsion induced by the two phenyls at tin(IV) centre. Therefore, the geometric results indicate a strongly distorted trigonal bipyramidal arrangement around tin(IV) atom. The Sn1–N1 bond distance (2.22 Å) found to be close to the sum of the covalent radii of Sn–N (2.15 Å) [53], is evidence that the azomethine nitrogen (N1) is bonded to the tin (Sn1) atom very tightly. The Sn1–O1

bond distance (2.08 Å) is almost close to the covalent radii of Sn–O (2.10 Å) and comparable with those reported in articles [54,55]. The Sn1–S1 bond length (2.495 Å) was found close to the sum of the covalent radii of Sn–S (2.42 Å) [56], indicating thiolate sulfur bonded to the Sn moiety after deprotonation and is comparable with the reported values for Sn–S (2.50 Å) in [Ph_2Sn(dact)] [57]. The two phenyl groups are bonded to the tin(IV) atom [Sn1–C11 = 2.1269(12) Å, Sn1–C17 = 2.1326(12) Å which are slightly shorter than the non-polar covalent radii of Sn–C (2.17 Å) [53], but are comparable with other reported diorganotin(IV) complexes [43,58]. The packing of the [Ph_2Sn(cdet)] (**4**) in the crystal lattice is shown in Fig. 4. The dimeric aggregates of the crystal structure are made up of alternating layers that stack along the *a* direction and are connected by C–H$\cdots\pi$ interactions.

4. Conclusion

In conclusion, different analytical and spectral methods were used for the characterization of three new diorganotin(IV) complexes of 3,5-dichloro-2-hydroxybenzaldehyde-*N*(4)-ethylthiosemicarbazone (H_2cdet). X-ray diffraction analysis of complex **4** reveals ONS coordination mode of the ligand (**1**) and displays the existence of a distorted trigonal bipyramidal geometry around the Sn(IV) atom. The NMR chemical shifts and X-ray crystallographic studies revealed that the diorganotin(IV) complexes are five coordinated.

Acknowledgment

R.A.H. thanks Universiti Sains Malaysia (USM) for the Research University (RU) Grant 1001/PKIMIA/811217. M.A.S. thanks USM and World Academy of Sciences (TWAS) for a post-doctoral research fellowship. We also thank the Bangladesh Petroleum Exploration and Production Co. Ltd. (BAPEX), Bangladesh, for the study leave to M.A. Salam.

Appendix A. Supplementary material

CCDC 885660 and 1050802 contains the supplementary crystallographic data for [H_2cdet)] (**1**) and [Ph_2Sn(cdet)] (**4**). 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 http://dx.doi.org/10.1016/j.ica.2015.06.015.

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